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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Table of contents

List of tables

List of figures

List of symbols

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

1. Introduction

1.1 The purpose of the study

Copper compounds and chelates like ethylene diamine tetraacetic acid (EDTA) are widely used in industry and agriculture, and are persistent chemicals in the environment. Copper is used in orchards in fungicidal sprays, it is applied to soil with sewage sludge, plus it is used, along with chromium and arsenic, as a timber preservative. These practices have led to some soils being contaminated with copper. The copper concentration in contaminated soils in New Zealand ranges from 100-1800 mg kg^{-1}, whereas the average total concentration in non-polluted soils is only 20 mg kg^{-1} (Roberts *et al.,* 1996). EDTA is widely used in the photographic industry, in textile and paper manufacturing, and for industrial cleaning (Ghestem and Bermond, 1998). It is also used in agriculture and horticulture to increase the solubility and plant availability of micronutrients. Further, as outlined below, it has been suggested that EDTA be added to copper-contaminated soils to facilitate remediation. The possibility thus exists for human interaction to bring copper and EDTA together in the soil either inadvertently, or intentionally.

Metals, like copper, are usually strongly adsorbed onto soil and aquifer materials such as organic matter, clays and oxides. However, this adsorption does not guarantee long-term immobilisation of the metals in the subsurface environment, as they can form strong anionic complexes with organic ligands. Enhanced transport of metal ions in the presence of chelates, or ligands, has been observed because of the difference in sorption behaviour between the anionic complex and the free metal (Szecsody *et al.,* 1994). An understanding of the behaviour of the copper-EDTA complex in soil and earth materials is necessary for predicting its persistence and mobility in natural systems.

In contaminated soils where heavy metals are very strongly bound to the soil matrix, the use of chelates, especially EDTA, to bring these metals into solution has been suggested as a step towards soil remediation. Remediation could be achieved by removing the soil and leaching it off site with an EDTA solution (Tuin and Tels, 1990; Yu and Klarup, 1994), or perhaps by applying EDTA to soil *in situ* to enhance the uptake of metal by plants (Cunningham *et al.*, 1996; Blaylock *et al.,* 1997; Huang *et al.,* 1997; Brooks, 1998; Wu *et al.*, 1999; Kirkham, 2000).

While EDTA could be used to induce metal desorption from the soil matrix into solution, the success of metal extraction using this chemical, either *ex situ* or *in situ*, depends on several factors that govern EDTA- metal interactions in soil. These include the soil type, the binding strength between the metal and the soil constituents, the metal concentration in the soil, the presence of other metals, the pH, the concentration of EDTA used (Ghestem and Bermond, 1998), the age of the contamination, and the transport processes involved. Once the metal combines with the EDTA to a form a complex (Me-EDTA), its mobility in soils and aquifers depends on the interactions between the hydrological processes, and a series of rate-limited reactions (Davis *et al.,* 2000). Copper is one of the metals that has limited mobility in the soil. So it is a candidate for EDTA-enhanced phytoremediation. The effective use of EDTA-enhanced remediation techniques at copper-contaminated sites will require a good understanding of the processes involved and their interactions. Contributing to this understanding was one aim of this work.

In situ application of EDTA for phytoremediation of copper-contaminated soil however involves the risk of the copper polluting the ground water. Although some of the studies of chelate-enhanced phytoremediation, referred to above, have mentioned this risk of the target metal being leached below the root zone to the ground water, little attention has been to the measurement of such leaching. Clearly, the potential mobility of chelated metals needs to be evaluated before commercialisation of this technology is attempted. So the relative importance of plant uptake and leaching of copper following the addition of EDTA needs to be investigated. Carrying out such an investigation was a second aim of this work.

The use of mechanistic models for simulating the fate and transport of heavy metals as Me-EDTA complexes is a key tool for an environmental impact assessment, and for planning the rates and timing of EDTA applications for remediation purposes. An understanding of the reactive transport of the copper-EDTA complex (CuEDTA) involves quantifying the kinetics of the interacting geochemical processes under flow conditions. So a third aim of this work was to develop a model describing the dominant physico-chemical interactions occurring when EDTA is applied to copper-contaminated soils.

In summary, the overall aim of this study was to study the physical and chemical processes that influence the interactions between soil copper and EDTA in contaminated soils, and from this understanding to develop models of EDTA-enhanced copper transport through the root zone.

1.2 Theory of water and solute transport

Since chemical transport in the soil is coupled with the transport of water, the theory of water flow in the soil is discussed first. Then the theory of chemical transport using the convective-dispersive approach, will be outlined.

1.2.1 Theory of water flow in soil

Consider the case of a steady-state situation of one-dimensional vertical flow where the water flux is constant with depth. That is, the water flux into a given soil volume is equal to the water flux leaving this volume. As a consequence, the local water and air contents are constant with time. Water will only flow if (i) there is a driving force (i.e. a water potential gradient) and (ii) there is hydraulic connection throughout the soil volume (i.e. non-zero hydraulic conductivity).

In saturated porous materials, Darcy's law describes the water flow as,

$$q_w = -K_s \frac{dH}{dz} \tag{1-1}$$

where q_w is the volumetric water flux density [m s^{-1}], K_s is the saturated hydraulic conductivity [m s^{-1}], dH/dz [m m^{-1}] is the driving force, H is the hydraulic potential [m] and z is the depth [m]. Here H is the sum of two component potentials, the pressure potential (P) [m] and the gravitational potential (Z) [m]. In equation (1-1), K_s is determined by the geometry of the pore space and by the physical properties of the water phase. The flux density q_w is also the velocity of the water entering, or exiting a soil column. Within the column, water only flows through the water-filled pore space with volumetric water content of θ [m^3 m^{-3}] and thus has the higher average vertical velocity,

$$v = \frac{q_w}{\theta} \tag{1-2}$$

where v is the pore water velocity [m s^{-1}]. In saturated soil, θ equals the porosity less the entrapped air.

The geometry of the water phase does not change in a rigid, saturated porous medium. However, the soil is usually unsaturated, with part of the pore volume occupied by the gas phase. As the pressure potential P becomes more negative, air replaces water first in the coarse parts of the pore space, and at successively lower values also in the finer pore structures. As a consequence, the geometry of the water phase changes with the pressure potential. So, in an unsaturated porous medium the hydraulic conductivity (K) is a not a constant, but is a function of the water content. This function is called the unsaturated hydraulic conductivity to distinguish it from the saturated hydraulic conductivity, which is a constant. In 1910, Buckingham extended Darcy's law to describe the flow in an unsaturated soil. The Darcy-Buckingham equation is

$$q_w = -K(\theta)\frac{dH}{dz}. \qquad (1\text{-}3)$$

As $H = Z + P$, and defining z as positive downwards and assuming $z = 0$ at the surface, Z equals $-z$. So equation (1-3) can be written as

$$q_w = -K(\theta)\left(\frac{dP}{dz} - 1\right). \qquad (1\text{-}4)$$

Soil water flow is rarely, if ever, at a steady state in the root zone. Intermittent rainfall and surface evaporation, combined with the variable plant uptake of water, cause the water content (θ) to fluctuate with time at any particular point in the soil, and q_w to vary with both depth and time. Flow can then only be described by combining the Darcy-Buckingham equation with the equation for the conservation of water. This combined equation relates the rate of change of θ in an infinitesimally small soil volume to the change in water flux into and out of that volume, allowing for any water removed by plant uptake. Again assuming that flow is only vertical, and that there are no sources or sinks for water in the soil apart from plant uptake, the continuity equation is,

$$\frac{\partial \theta}{\partial t} = -\frac{\partial q_w}{\partial z} - U_w \qquad (1\text{-}5)$$

where t is time [s] and U_w [s^{-1}] is a sink term accounting for root uptake.

Substituting for q_w from the Darcy-Buckingham equation gives one form of Richards' equation, which describes the transient water flow through unsaturated soil. But the resulting equation has four variables θ, P, t and z and so in this form it is not very useful. However, the soil water retentivity curve provides a link between P and θ. Using the chain rule to change variables in equation (1-4) it can be written as,

$$q_w = -K(\theta)\left(\frac{dP}{d\theta}\frac{d\theta}{dz} - 1\right) = -D(\theta)\frac{d\theta}{dz} + K(\theta) \qquad (1\text{-}6)$$

where D is defined as the product of K and $dP/d\theta$, and is called the soil water diffusivity [$m^2\ s^{-1}$]. As the soil-water retentivity relationship is hysteretic, it only makes sense to define D for soil that is either monotonically wetting, or drying. As already mentioned, the hydraulic conductivity K is a strong function of soil water content. Here, $dP/d\theta$ is just the slope of the soil water retentivity curve, and is also dependent on θ. Thus D, which is the product of K and $dP/d\theta$, is also a function of θ. On substitution of equation (1.6) into equation (1-5), a simpler form of Richards' equation is obtained.

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left[D(\theta)\frac{\partial\theta}{\partial z} - K(\theta)\right] - U_w . \qquad (1\text{-}7)$$

This equation can readily be solved numerically, provided the initial and boundary conditions are specified and the parameters appropriately defined.

The theory of water flow described above implies soil that is homogenous. However, natural field soils are quite variable in both the vertical and horizontal planes. A common index used to express the variability of a property is the sample coefficient of variation (CV). Warrick and Nielsen (1980) reviewed soil physical data from various sources and found that bulk density and porosity had a relatively small CV of about 8 % at the paddock scale. In contrast, saturated hydraulic conductivity had a CV above 100%.

Rather than just the CV, the variation of soil properties is more completely described by a probability density function (pdf). For many soil properties, such as the soil water content and bulk density, the pdf is a bell-shaped or Gaussian curve with a normal distribution. For normally distributed data, the mean, median and mode are identical and occur at the centre of the bell-shaped curve. However pdfs of saturated hydraulic conductivity data are commonly skewed (Campbell, 1985), and so non-Gaussian. But an approximately Gaussian pdf is found when the natural logarithms of the values are plotted. In this case the data are called log-normally distributed. For a log-normal distribution a relatively few large values lead to a mean value larger than that of the majority of the observations. Hence not recognising that the observed values of saturated conductivity were log-normally distributed can cause an underestimation of the mean.

There are other features of soil properties of which the researcher needs to be aware. One is that they are usually spatially correlated. In classical statistics, using tools such as analysis of variance and regression analysis, it is implicitly assumed that individual observations or measurements are randomly distributed spatially, and thus uncorrelated. But more careful measurement and analysis often shows that there is less variation between samples taken in closer proximity to each other than between more widely spaced samples. Sampling schemes need to take this into account, and more detailed experiments can use geostatistics and regionalised variable analysis (Campbell, 1985) to investigate the different spatial structures within and between data sets. Another feature of the saturated hydraulic conductivity is that it is a highly dependent on soil structure. It thus is subject to temporal variation, sometimes by orders of magnitude. Pugging by grazing animals or cultivation can cause such variations in the short term, while net additions or losses of organic matter can cause large variation over the longer term.

1.2.2 Solute transport in soil

Two main groups of processes; namely surface and subsurface transport, are responsible for chemical transport in and over soils. However, only the subsurface transport process is described in this chapter, as it is the process relevant to this study. Solute transport in soil has been studied intensively during the last 40 years, especially since Nielsen and Biggar (1961) described a laboratory apparatus and protocol for conducting miscible displacement experiments in soils.

Although there are different approaches to describe solute transport through soils, the traditional convective-dispersive approach is used in this study, and so it is outlined in this section. This approach is the most widely used, and has been verified for a wide range of conditions (Vogeler *et al.,* 1998). In its simplest form the interaction between the soil-solid phase and the solute is assumed to be negligible, and the solute is considered to be conservative with no decay, or production. Conservative and non-reactive chemicals are of interest because they trace the flow of the water, which is the carrier of all solutes. So the transport of such tracers is described first. However copper, and many other pollutants, interact strongly with the soil. Therefore the theory for the transport of reactive chemicals is also discussed. Lastly, the applicability of the convection-dispersion equation (CDE) is discussed in well-structured or aggregated soil.

1.2.2.1 Non-reactive solute transport

Before describing solute transport through the soil, it is important to distinguish between solute flux-concentrations and solute resident-concentrations. The resident concentration (C_r) is the volume-averaged concentration, defined as the mass, or number of moles, of solute present in unit volume of soil solution [kg or mol m^{-3}]. It represents solute concentration in both the more mobile, and the less-mobile regions of the soil solution at a certain time. In contrast, the flux concentration (C_f) is a flux averaged concentration [kg or mol m^{-3}], so it represents only the concentration in the mobile water, weighted to its relative velocity. Thus C_f is defined as the ratio of solute flux density q_s [kg or mol m^{-2} s^{-1}] to the water flux density q_w [m s^{-1}].

At the microscopic scale, two fundamental and interacting processes are operating during solute transport, molecular diffusion and convection. Molecular diffusion occurs in any liquid in response to a concentration gradient. Convection occurs whenever there is mass flow of water containing a solute. When convection is the only significant transport processes and all the water is moving at the same velocity, the solute flux density q_s is given by,

$$q_s = q_w C_r \, . \tag{1-8}$$

However, molecular diffusion does inevitably occur, and its effects are usually significant. Diffusion of solutes occurs longitudinally in the direction of flow when there is a longitudinal concentration gradient. This reduces the steepness of the solute concentration gradient. But this is only significant at low velocities. Molecular diffusion also occurs in any direction where the resident concentration at any depth is not locally uniform. Fick's first law, modified for soils, describes molecular diffusion when the soil solution is stationary as,

$$q_s = -D_i\theta \frac{\partial C_r}{\partial z}, \tag{1-9}$$

where D_i is the effective diffusion coefficient in the soil [$m^2\ s^{-1}$]. The tortuosity effect that accounts for the increased diffusive path length in the soil compared to water is included in D_i.

If the water flux and resident concentration were locally uniform, solute movement would be due to the non-interacting additive effects of convective mass flow of water and molecular diffusion. So combining equations (1-8) and (1-9),

$$q_s = q_w C_r - \theta D_i \frac{\partial C_r}{\partial z}. \tag{1-10}$$

However, in real soil at the microscopic scale, q_w is not uniform locally and the equation above does not apply. Water, and therefore solute, move much faster in some pores than others. Also, as mentioned above, molecular diffusion does not just occur in the direction the water is flowing. It occurs in all directions, tending to smooth out any local differences in solute concentration induced by different water velocities. This complicated interaction between convection and molecular diffusion at the pore scale is responsible for a phenomenon called hydrodynamic dispersion. Mathematically, hydrodynamic dispersion can usually be described as a diffusion-like processes, so the total solute flux is given by

$$q_s = q_w C_r - \theta D_h \frac{\partial C_r}{\partial z} \tag{1-11}$$

where D_h is the hydrodynamic dispersion coefficient [$m^2\ s^{-1}$].

To obtain the convection-dispersion equation (CDE), the mass conservation law for solute is considered in combination with the above flux law, equation (1-11). The general form of the mass conservation law is given by,

$$\frac{\partial M}{\partial t} = -\frac{\partial q_s}{\partial z} + S \tag{1-12}$$

where M is the total amount of solute per a unit volume of soil [kg or mol m^{-3}] at the depth and time of interest, and S is a source/sink term [kg or mol m^{-3} s^{-1}]. Combining the solute flux equation (1-11) with the mass conservation equation (1-12) yields the CDE. For conservative non-reactive solutes, $M = \theta C_\mathrm{r}$ so,

$$\frac{\partial(\theta C_\mathrm{r})}{\partial t} = \frac{\partial}{\partial z}\left(\theta D_\mathrm{h} \frac{\partial C_\mathrm{r}}{\partial z}\right) - \frac{\partial}{\partial z}(q_w C_r) + S\,. \tag{1-13}$$

Under steady-state water flow conditions, and with no sink/source terms, this equation reduces to (van Genuchten, 1981; Kutilek and Nielsen, 1994)

$$\frac{\partial C_\mathrm{r}}{\partial t} = D_\mathrm{h}\frac{\partial^2 C_\mathrm{r}}{\partial z^2} - v\frac{\partial C_\mathrm{r}}{\partial z} \tag{1-14}$$

where equation (1-2) is used to relate θ, q_w and v.

Unless the solute is moving very slowly, D_h is much greater than D_i, and has often been found to be approximately linearly related to v. Thus

$$D_\mathrm{h} \approx \lambda v \tag{1-15}$$

where the proportionality constant λ [mm] is called the dispersivity, and it usually has values between 1 to 100 mm.

By incorporating equation (1-15), equation (1-14) can be rewritten in dimensionless form as

$$\frac{\partial(C_\mathrm{r}/C_\mathrm{c})}{\partial T} = \frac{\partial^2(C_\mathrm{r}/C_\mathrm{c})}{\partial Z^2} - \frac{\partial(C_\mathrm{r}/C_\mathrm{c})}{\partial Z}, \tag{1-16}$$

where following Kirkham and Powers (1972) $T = v\ t/z_c$, $\tau = \lambda/z_c$, $Z = z/z_c$, z_c is a characteristic length and C_c is a characteristic concentration. Commonly z_c is taken as the column length for laboratory studies, or the depth of interest in field studies. Here, T then equals the number of liquid filled pore volumes to have exited the column, or passed depth z_c at a time t. Further, C_c is usually taken as the concentration applied (C_0) in laboratory miscible displacement experiments.

The analytical solutions of the dimensionless form of the CDE, for a range of boundary conditions, have shed light on the basic phenomena characterising solute movement in soil. The effects of these phenomena can be illustrated by drawing an elution, or breakthrough curve. When a solution containing a solute of concentration C_o is applied at a steady rate to a column of solute-free soil, and the effluent collected and analysed, the fraction of this solute in the effluent at time t can be calculated as C_f/C_o. Plots of C_f/C_o vs. T, are commonly called breakthrough curves (BTC). If piston displacement had occurred, no mixing would have taken place between the displacing and displaced solutions, resulting in a step function for the BTC. A sigmoidal-shaped BTC indicates some mixing. A shift of the curve to the left indicates exclusion of the solute, or bypass flow excluding a significant portion of the soil solution. A shift of the curve to the right indicates adsorption or solute retention by the soil. Figure 1.1 illustrates these behaviours.

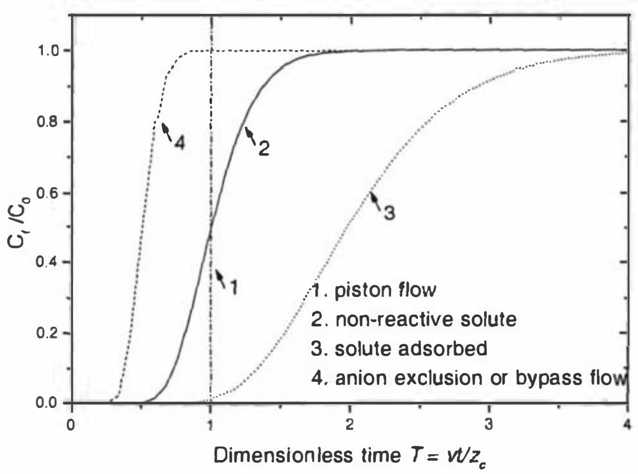

Figure 1-1 Breakthrough curves for piston flow, non-reactive solutes, adsorbed solutes, and with anion exclusion. The characteristic length z_c, is the length of the column L.

1.2.2.2 Reactive solute transport in soil

So far, the theory described has centred on solutes which do not react with the soil solids. Solutes usually considered non-reactive with soil are nitrate, chloride and bromide, though adsorption or exclusion of all these solutes in soil has been observed to some extent, depending on the chemical properties of the soil (Biggar and Nielsen, 1962; Krupp *et al.*, 1972). Duwig *et al.* (2000) showed that nitrate could be retained by the positively charged surface of aluminium and ferric oxides in a New Caledonian soil. Most chemicals of environmental interest, including copper, are subject to chemical or biological reactions during transport through the soil. Both anions and cations are subject to reactions with the soil solid phase. These reactions include cation exchange, adsorption-desorption, and chemical precipitation-dissolution reactions. The basic CDE presented in equation (1-14), can however be modified to include the processes involved. Microbial transformation reactions of these solutes will not be discussed here, as they are not relevant to the study.

A reactive chemical is present in two phases, on the adsorbate (soil) where there is say S_s [mol kg^{-1}], and in the soil solution where the concentration is C_r. Thus,

$$M = \rho_b S_s + \theta C_r \tag{1-17}$$

where, ρ_b is the bulk density of the soil [kg m^{-3}]. The CDE, with an additional term to account for this adsorption reaction, then becomes

$$\frac{\partial C_r}{\partial t} = D_\mathrm{h} \frac{\partial^2 C_r}{\partial z^2} - v \frac{\partial C_r}{\partial z} - \frac{\rho_b}{\theta} \frac{\partial S_s}{\partial t}. \tag{1-18}$$

The expression $\partial S_s / \partial t$ represents the rate of adsorption or desorption by the soil, which can be described in a number of ways.

Often adsorption is assumed to be instantaneous, as equilibrium is assumed between the solute in soil solution and the adsorbate. A curve relating the amount of solute adsorbed per unit mass of dry solids to the solute concentration in the soil solution is called an adsorption isotherm. If the isotherm is linear, its slope is called the distribution constant, K_d [m^3 kg^{-1}]. The simplest, equilibrium adsorption isotherm is a straight line through the origin. This implies adsorption is instantaneous, reversible, and proportional to the solution concentration. For such an adsorption isotherm,

$$S_s = K_d C_r \,. \tag{1-19}$$

But realistically, there is a limit to the amount of solute any soil can adsorb so the concentration range over which it is approximately linear is limited. The most commonly-used non-linear isotherms are the Freundlich and Langmuir equations. The Freundlich equation is,

$$S_s = aC_r^n \tag{1-20}$$

where, *a* and *n* are specific constants for the soil and solute. The Langmuir equation is given by

$$S_s = \frac{abC_r}{1+aC_r} \tag{1-21}$$

where *a* is a constant relating to the bonding energy and *b* the adsorption maximum when the adsorbent is completely saturated.

The CDE is often written with a retardation factor for the adsorption occuring in it,

$$R\frac{\partial C_r}{\partial t} = D_{\mathrm{h}}\frac{\partial^2 C_r}{\partial z^2} - v\frac{\partial C_r}{\partial z} \tag{1-22}$$

where dimensionless retardation factor *R* is given by

$$R = 1 + \frac{\rho_b K_d}{\theta} \tag{1-23}$$

given equation (1-19) applies. In dimensionless form equation (1-22) becomes

$$R\frac{\partial C_r}{\partial T} = \frac{\partial^2 C_r}{\partial Z^2} - \frac{\partial C_r}{\partial Z}\,. \tag{1-24}$$

The effect of adsorption is to retard or delay the rate of solute movement by the factor *R*. Dispersion is also effectively reduced by the same factor *R*. This means that an adsorbed solute will take *R* times longer than a non-adsorbed solute to travel a given distance. In Figure 1-1, for the non-reactive solute $R = 1$, for the adsorbed solute $R = 2$ was assumed, and for the curve showing anion exclusion $R = 0.5$.

Although the simplistic concept of reversible equilibrium sorption has successfully described some experimental data, there is increasing evidence that this assumption is not always valid (Wagenet and Chen, 1998). For several heavy metals, including copper, retention and release reactions in the soil solution have been observed to be strongly time-dependent. As a result, kinetic adsorption models, where the amount of solute adsorption is a function of contact time have been introduced.

One of the earliest chemical non-equilibrium models is the kinetic one-adsorption site model (van Genuchten *et al.,* 1974). Later Selim *et al.* (1976) and Cameron and Klute (1977) developed two-adsorption site models. The two sites are those which appear to adsorb, or react, with solutes rapidly or effectively instantaneously. Those, which appear to react more slowly, result in a kinetic reaction. However, real soils contain many different sorptive components that may react with solute at a wide range of rates. Amacher *et al.* (1988) and Selim *et al.* (1989) showed that multi-reaction retention models could better describe the slow and tailed release profile of heavy metals. More recently, a chemical non-equilibrium model with a maximum adsorption capacity (a second-order reaction model) has been proposed by Selim and Amacher (1988). This was later modified by Ma and Selim (1994). This multi-reaction approach is more comprehensive than the ones described earlier. However, it is difficult to determine independently the appropriate kinetic parameters, hence they are usually estimated by curve fitting to the experimental results.

Past researches have shown discrepancies between sorption isotherms obtained from batch and column leaching experiments. Bajracharya *et al.* (1996) compared Cd sorption measured in batch and flow experiments and they found that the batch-determined partition coefficients were 60-80% higher than those determined by column experiments conducted at various flow rates. Plassard *et al.* (2000) also reported a lower retention of Cd, Pb and Zn in column leaching studies compared to batch studies. The differences in the results obtained using the two methods are apparently due to the different soil-to-solution ratios, the amount of agitation and so the soil disruption involved, as well as in the removal of the desorbed species in one case, but not the other (Kookana *et al.*, 1999; Szecsody *et al.,* 1998a).

In aggregated soils, the chemical sorption kinetics may be complicated by the simultaneous occurrence of physical non-equilibrium processes resulting from the soil aggregate structure. This is discussed later in this chapter. Copper-adsorption models are discussed in Section 1.3.1.2.

In general, if non-linear and/or kinetic adsorption reactions are assumed, solutions of the CDE must be found numerically.

1.2.2.3 Some initial and boundary conditions and solutions for them

Solution of the CDE can be attempted either analytically or numerically, depending on the complexity of the boundary and initial conditions involved. In either case, the initial and boundary conditions need to be specified. For generality, dimensionless variables are used here.

A common initial condition is that the initial concentration of the solute of interest in a soil is zero, that is

$$C_r = 0 \qquad \text{for } T < 0 \text{ and } Z \geq 0. \tag{1-25}$$

However, in some situations the solute of interest can be present in the soil initially, and in that case, C_i replaces zero in equation (1-25) where, C_i refers to a constant initial concentration. In most of the experiments in this study, copper was present in the soil initially. Also, in some cases, the initial concentration of copper varied with depth.

The lower-boundary condition assumed by Parker and van Genuchten (1984) for their analytical solutions is that applicable for semi-infinite domains. This is given by,

$$\frac{\partial C_r}{\partial Z} = 0 \qquad \text{as } Z \to \infty. \tag{1-26}$$

Under steady-state water flow conditions, three different input functions are commonly used to describe what happens at the inlet, often referred to as a first, a second or a third-type boundary condition. Only the third inlet-type boundary condition is discussed, as it is the one relevant to this study. The third- or flux type of boundary condition defines the solute flux density at the upper surface. For a constant flux concentration at the surface of C_o,

$$C_r / C_o - \tau \frac{\partial (C_r / C_o)}{\partial Z} = 1 \qquad \text{for } Z = 0, T \geq 0, \tag{1-27}$$

This third-type of condition assumes that molecular diffusion and dispersion above the soil surface are negligible. This can lead to differences between C_r and C_f at $Z = 0$. This difference in the flux and resident concentration at the inlet end increases with the dispersivity (Parlange *et al.*, 1985). The solute introduction at the inlet end is often for a finite time t_p, after which water flow continues. But no more solute is introduced. This boundary condition is

$$C_{\mathrm{r}} - \tau \frac{\partial C_{\mathrm{r}}}{\partial Z} = C_{\mathrm{o}} \qquad \text{for } Z = 0, \quad 0 < T \le v t_{\mathrm{p}} / z_{\mathrm{c}}$$

$$C_{\mathrm{r}} - \tau \frac{\partial C_{\mathrm{r}}}{\partial Z} = 0 \qquad \textit{for } Z = 0, \quad T > v t_{\mathrm{p}} / z_{\mathrm{c}}. \tag{1-28}$$

Analytical solutions of equation (1-14) for a number of boundary conditions are given by van Genuchten and Alves (1982). The solution for equation (1-16) with the above initial and boundary conditions (equations 1-25, 1-26 and 1-28) is,

$$C_r(Z,T) = C_{\mathrm{o}} A(Z,T) \qquad 0 < T \le v t_{\mathrm{p}} / z_{\mathrm{c}}$$

$$C_r(Z,T) = C_{\mathrm{o}} A(Z,T) - C_{\mathrm{o}} A(Z, T - v t_{\mathrm{p}} / z_{\mathrm{c}}) \qquad T > v t_{\mathrm{p}} / z_{\mathrm{c}} \tag{1-29}$$

where

$$A(Z,T) = \frac{1}{2}\mathrm{erfc}\left[\frac{Z-T}{2(T\tau)^{\frac{1}{2}}}\right] + \left[\frac{T}{\pi\tau}\right]\exp\left[\frac{(Z-T)^2}{4T\tau}\right] - \frac{1}{2}\left[1 + \frac{Z}{\tau} + \frac{T}{\tau}\right]\exp\left[\frac{Z}{\tau}\right]\mathrm{erfc}\left[\frac{Z+T}{2(T\tau)^{\frac{1}{2}}}\right]. \tag{1-30}$$

In many cases, solute flux distributions as well as resident concentrations are of interest. That was the case in this study, when effluent concentration was measured to find the BTC. Thus it is useful to express the initial and boundary conditions in terms of the flux concentration. The initial boundary condition is

$$C_{\mathrm{f}} = 0 \qquad \text{for } T < 0 \text{ and } Z \ge 0, \tag{1-31}$$

the lower boundary condition is

$$\frac{\partial C_{\mathrm{f}}}{\partial Z} = 0 \qquad \text{as} \quad Z \to \infty \quad , \tag{1-32}$$

and the third-type boundary condition is

$$C_{\mathrm{f}} = C_{\mathrm{o}} \qquad \text{for } Z = 0, \quad 0 < T \le v t_{\mathrm{p}} / z_{\mathrm{c}}$$

$$C_{\mathrm{f}} = 0 \qquad \text{for } Z = 0, \quad T > v t_{\mathrm{p}} / z_{\mathrm{c}}. \tag{1-33}$$

It is also useful to have an equation relating C_{f} to C_{r}. It follows from equations (1-8) and (1-11) in dimensionless form that

$$C_f / C_o = C_r / C_o - \tau \frac{\partial (C_r / C_o)}{\partial Z} \tag{1-34}$$

From the above equation, it can be seen that the discrepancy between C_f and C_r increases with the dispersivity (Kreft and Zuber, 1978), and where the concentration gradient is steep.

The CDE written in terms of the flux concentration (Parker and van Genuchten, 1984) is

$$\frac{\partial C_f}{\partial T} = \frac{\partial^2 C_f}{\partial Z^2} - \frac{\partial C_f}{\partial Z}. \tag{1-35}$$

The analytical solution of equation (1-35) with the initial and boundary conditions given in equation (1-31), (1-32) and (1-33) is

$$\begin{aligned} C_f(Z,T) &= C_o B(Z,T) && 0 < T \le vt_p / z_c \\ C_f(Z,T) &= C_o B(Z,T) - C_o B(Z, T - vt_p / z_c) && T > vt_p / z_c \end{aligned} \tag{1-36}$$

where,

$$B(Z,T) = \frac{1}{2}\operatorname{erfc}\left[\frac{Z - T}{2(T\tau)^{\frac{1}{2}}}\right] + \frac{1}{2}\exp\left[\frac{Z}{\tau}\right]\operatorname{erfc}\left[\frac{Z + T}{2(T\tau)^{\frac{1}{2}}}\right]. \tag{1-37}$$

In this study, this flux analytical solution was used to verify that the numerical solution developed was sound.

1.2.2.4 Comparing the flux and the resident concentrations

Whether a flux or resident concentration is appropriate depends on what is of interest. Flux concentrations are obtained from measurements of effluent from a soil column. Resident concentrations are obtained by sectioning soil columns and extracting the solute from the soil samples. The importance, or otherwise of differentiating between the flux and resident concentrations is shown in Figures 1-2 and 1-3 (from Parker and van Genuchten, 1984). Figure 1-2 shows the flux and resident concentrations as a function of dimensionless depth for different values of $\tau = \lambda / z_c$, where as Figure 1-3 shows the flux and resident concentrations as a function of dimensionless time, for

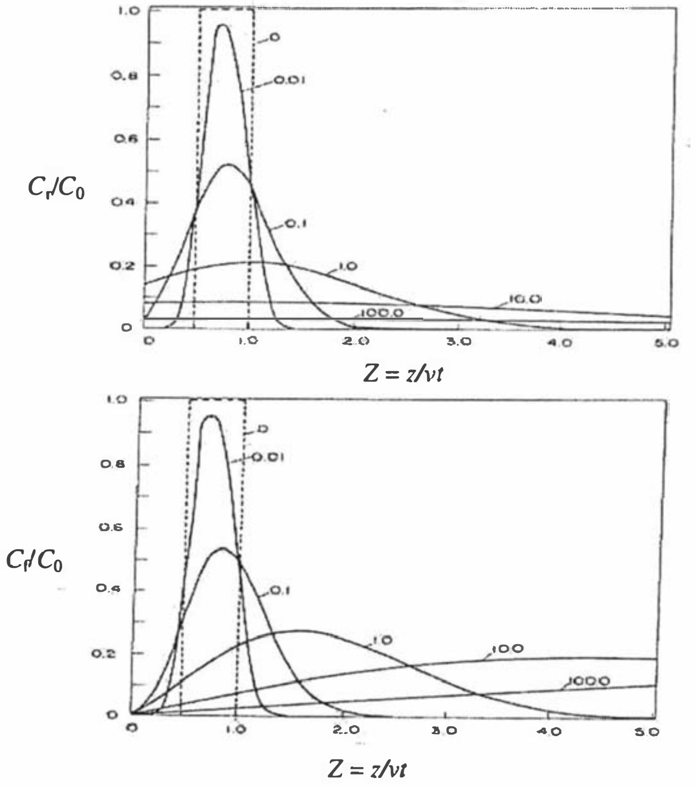

Figure 1-2 (a) Resident concentrations and (b) flux concentrations as functions of dimensionless distance for a pulse of duration 0.5 T and a final time of T for various values of τ (values indicated on curves) after Parker and van Genuchten (1984).

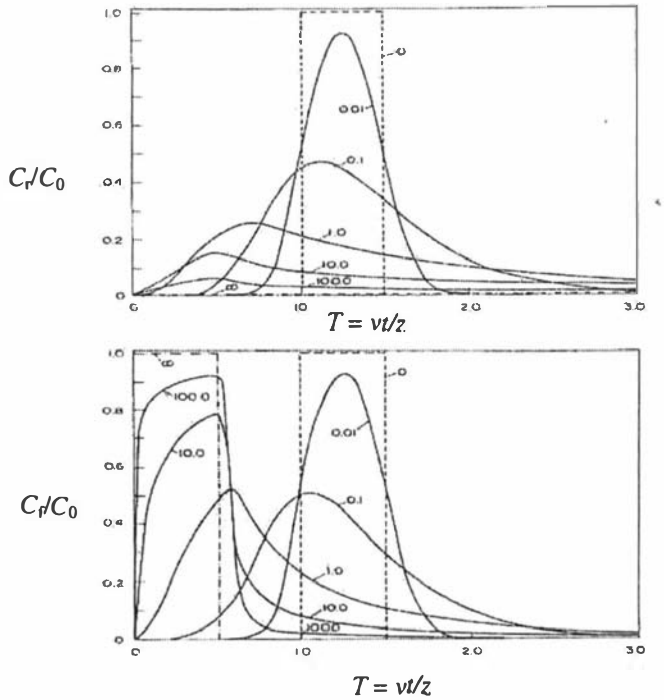

Figure 1-3 (a) Resident concentrations and (b) flux concentrations as functions of dimensionless time at $Z = 1$ for a pulse of duration of 0.5 T and for various values of τ (values indicated on curves) after Parker and van Genuchten (1984).

different $\tau = \lambda/z_c$. From the figures it can be seen clearly that the flux and resident concentrations are virtually same, provided the $\tau \leq 0.1$. Therefore there is no need to differentiate between the flux concentration and resident concentration when τ, or λ/vt_c is less than 0.1.

In this study, flux concentration was measured in the collected aliquots to build the BTC. At the end of each experiment the soil was sectioned to measure the resident concentration.

1.2.2.5 Non-equilibrium solute transport

Large pores, termed macropores, often occur in soils as shrinkage cracks, earthworm channels, or old root holes. The local flow-velocities in soils with macropores can vary widely from point to point in both magnitude and direction. The velocity in a water-filled pore is at a maximum at the centre of the pore, whereas the water adjacent to the pore wall does not move. Also the average velocity in larger pores exceeds that through smaller pores. Biggar and Nielsen (1962) have shown that in aggregated soil, when the aggregate size is increased, the range of microscopic flow velocities increases, and most of the flow occurs through macropores between aggregates. Also, as the distances between macropores increase, molecular diffusion is much less effective in dissipating local concentration gradients between the soil solution in the macropores and within the aggregates. Thus mixing in the columns becomes less complete and this affects the shape of the BTC. Solute moving through macropores is responsible for an early breakthrough, while slow solute movement in or out of micropores within aggregates is responsible for a long tail on the BTC. Whether or not such preferential flow occurs depends on the soil structure, the pore size distribution, the Darcy flux density and importantly the soil water content. Macropores that are air-filled do not induce preferential flow.

Many authors have stressed the importance of preferential flow in soil and aquifers, and many strategies have been used for modelling the preferential transport of solute by the more-rapidly moving water. These approaches range from the use of convective-stochastic transfer functions, pore network schemes, and cellular-automation fluids, through to the traditional CDE (Clothier *et al.,* 1998). The main non-equilibrium model used is the mobile-immobile model (MIM) of Coats and Smith (1964), and van Genuchten and Wierenga (1976). In this approach the liquid-filled pore space is somewhat arbitrarily divided into two different domains. This separation includes a dynamic domain which contains mobile water (θ_m), and a stagnant domain which contains immobile water (θ_{im}). Convective-dispersive transport occurs in the mobile water fraction only. Solute transfer between the mobile and immobile domains is by diffusion, and described by a first order equation (van Genuchten and Wierenga, 1976). The transfer coefficient between the mobile and immobile regions is a fitted parameter, affected by aggregate size and the water content in the aggregate, the molecular diffusion coefficient, the tortuosity, and the fraction of water in the mobile region. For reactive solutes, it also depends on the flow velocity (van Genuchten and Wierenga, 1977). Although the MIM can simulate the early breakthrough, and late tailing of the BTC for structured soils, its interacting parameters cannot be obtained directly.

Physical non-equilibrium is the result of a heterogenous water flow regime, while chemical or sorption non-equilibrium is caused by kinetic adsorption (Selim *et al.,* 1976). The two processes affect the BTC in a similar way. So when the two processes occur simultaneously it is difficult to separate out the effect of either. In a medium with a complex pore geometry and a reactive solute-matrix combination, tailing of the reactive solute breakthrough could be due to both slow diffusion of solutes into or out of the micro-pores (physical non-equilibrium), or to kinetic adsorption processes (chemical non-equilibrium).

Flow interruption has been one approach used to discriminate between the physical and chemical processes responsible for non-equilibrium (Murali and Aylmore, 1980; Brusseau *et al.*, 1989; Brusseau *et al.*, 1997; Jardine *et al.,* 1998). The approach involves applying the solute of interest at a steady flow-rate to a soil column, then stopping the flow for a period of time, and then later reinitiating the flow. The temporal changes in the effluent concentration in the BTC, are monitored. Flow interruption will have an impact only for systems in a state of non-equilibrium. Hence, imposition of flow interruption should not significantly influence the breakthrough curve obtained for transport of a nonreactive solute in a homogenous porous medium.

To separate the processes responsible for non-equilibrium, both a reactive and a non-reactive solute can be used in the same leaching experiment and the BTC measured. If a flow-interruption causes a sudden effluent concentration drop when the flow is resumed, then physical non-equilibrium is presumed to have occurred. The occurrence of a sudden drop in the concentration of a sorbing solute, in conjunction with the absence of a concentration drop for of the nonreactive solute, signifies sorption-related non-equilibrium (Brusseau *et al.*, 1989).

1.3 Copper in soil and EDTA as a chelator

Together with knowledge of solute transport theory, successful chelation of copper leading to efficient soil remediation requires good understanding of the soil-metal-chelate interactions. This section summarises present knowledge in terms of the following:

- the nature of copper in soil and its availability in the soil-liquid phase
- chelation process in soil and EDTA as a chelator
- metal extraction from contaminated soils using EDTA
- the stability of Me-EDTA in soils

1.3.1 The nature of copper in soil

In general copper levels are low in soils, commonly ranging from 2.5 to 60 mg kg^{-1}. Even deficiencies have been reported in some cases. However, human activities such as treating soil with municipal sludge, the use of fungicidal sprays, and timber treatment practices are important sources of copper to the soil. These practices have led to elevated concentrations in the soil, with values of 100-1800 mg kg^{-1} copper in New Zealand (Roberts *et al.,* 1996). Copper at low concentrations is tightly bound to soil. Also most of the added copper remains in the top 15 cm of the soil, bound to various soil constituents (Merry *et al.,* 1983, Velez *et al.,* 1996; Brun *et al.,* 1998; Epstein and Bassein, 2001). Right at the surface, the elevated concentration of copper might be toxic to plants, earthworms and microbes (Epstein and Bassein, 2001). In some circumstances, as discussed later in this section, copper can also leach to ground water.

The insufficiency, adequacy, or toxicity of heavy metals to plants, and the likelihood of their leaching into the ground water is largely determined by their retention in soils (Lehmann and Harter, 1984), and the prevailing hydrological processes.

Copper can occur in many different forms in soils (McLaren and Crawford, 1973a & 1973b):

- in the soil solution, both as a cation and in a complex,
- as a cation on the exchange sites,

- on specific sorption sites of clay, organic matter and oxides,
- occluded in iron, aluminium and manganese oxides,
- in biological residues and living organisms, and
- in the lattice structure of primary and secondary minerals.

Only a very small amount of the solution-plus-exchangeable copper (representing the available copper) is present in the soil solution. It has been suggested that these available forms of copper are in equilibrium with the specifically adsorbed forms (McLaren and Crawford, 1973b). The key processes that regulate the retention of copper in these soil constituents, and the fate of copper in the soil profile, are sorption-desorption, precipitation-dissolution and complexation.

1.3.1.1 Sorption-desorption processes governing the fate of copper in the soil profile

Of the processes mentioned above, it is now generally accepted that the soil solution concentration of copper, and hence its availability, is mainly controlled by sorption-desorption reactions (Wu *et al.*, 1999). Therefore these two processes are discussed below.

Copper is mainly adsorbed by sites other than 'normal cation exchange' ones. At such sites, copper is adsorbed by soil colloids in amounts in excess of their conventional exchange capacities. Adsorption of copper by colloids that takes place when the normal cation exchange sites are saturated with major nutrients cations, has been termed specific adsorption (McLaren and Crawford, 1973b). If a relatively small amount of copper is added to soil, it is specifically adsorbed and tightly bound to high-energy sites. When more copper than this is added, these sites may be expected to fill preferentially, with the excess copper being retained by lower energy sites, and thus is more readily available for other reactions (Lehmann and Harter, 1984).

Organic matter (humic and fulvic acids), silicate clay minerals (montmorillonite, kaolinite, illite, etc.), and the amorphous oxides of Fe and Mn, are the constituents responsible for the sorption of copper in soils (Wu *et al.,* 1999). The relative contribution of these soil fractions to sorb copper varies, depending on the amount of these constituents, the soil type and its solution composition. McLaren and Crawford (1973b) reported the copper adsorption hierachy in soil as manganese oxides > organic matter > iron oxides > clay minerals. However, in Spodosols, Bibak (1997) have shown the order as Al oxides > crystalline Fe oxides > organic matter > clay silicates. McLaren and Crawford (1973b) also indicated that the gross contribution of soil constituents that show a weak adsorption, but are abundant, can override those of others constituents that adsorb strongly but are present in smaller amounts. In a heterogeneous soil the constituents may interact, and hence change the level of adsorption that would occur if they were present alone. For example, Wu *et al.* (1999) showed that Fe oxides may coat the lateral surfaces of layer silicates, blocking the access of copper to potential sorption sites. Sequi and Aringhieri (1977) reported that removal of organic matter released new sorption sites on soil. Cavallaro and McBride (1984) also found that the treatment of the soil clays to remove of organics tended to enhance the sorption of copper. They attributed this behaviour to the dominance of oxides compared to organic component as copper sorbing constituents.

In a heterogenous and dynamic system such as soil, several interacting factors determine the nature and extent of retention reactions for copper. Not only the amount and nature of the sorbent affect the retention processes, but also a range of other factors such as pH, dissolved organic carbon (DOC), the ionic strength of soil solution, the presence of inorganic ligands, the effect of competing ions, and the age of contamination.

1.3.1.2 Factors affecting sorption

Soil solution composition and characteristics such as pH, DOC, and the presence of ligands and other cations influence the interactions of copper with soil constituents. As Römkens *et al.* (1999) indicated, no single relation exists between parameters like pH, total copper content, DOC and the copper availability in the soil solution as these factors interact. While it is difficult to isolate the individual effects of various factors influencing copper sorption, some workers have been able to develop relations which can describe the influence of the individual factors.

A decreasing pH leads to an increase of trace metals in solution according to the reaction;

$$Me^{2+}_{soil} + 2H^{+} \leftrightarrow 2H^{+}_{soil} + Me^{2+}$$

where $Me^{2+}{}_{\text{soil}}$ is the metal ion adsorbed to soil, and Me^{2+} is metal ion in solution. A large body of literature has established that soil solution pH has the most critical influence on the sorption-desorption of metals. Several studies have indicated that the proportion of the total labile copper in the soil that could be desorbed readily, was strongly influenced by pH. Padmanabham (1983a) and Hogg *et al.* (1993) showed that below pH 6.5 desorption increased with decreasing pH. Similarly, Cavallaro and McBride (1984), McGrath *et al.* (1988) and Reddy *et al.* (1995) reported that the proportion of copper present in the soil solution as Cu^{2+} increased as pH decreased. Therefore toxicity of copper occurs most commonly in acid soils, and is most likely to occur in unbuffered soils exhibiting a small CEC (Gupta and Aten, 1993). In some studies copper availability has been shown to increase at both low and high pH values (Swift and McLaren, 1991; Hogg *et al.*, 1993). Apart from the direct effect of pH, by competitive proton sorption, on the copper availability, pH also affects processes like precipitation-dissolution reactions and metal complexation by humic materials that lead to changes in copper availability.

One of the major pathways by which copper can be solubilised and mobilised in soils is through organic complexation with dissolved organic matter, or DOC. When DOC is present in the soil solution, copper makes stable complexes with DOC through organo-mineral complexation reactions at near neutral pH (Römkens *et al.*, 1999) and in alkaline sodic soils (Fotovat and Naidu, 1998). Over a pH range from 4.5 to 6.0, 95% of the dissolved copper was found to be bound to DOC (Breault *et al.*, 1996). Changes in the DOC concentration, therefore, have a strong impact on the solubility of copper in soils with copper being more soluble at high DOC levels. Heavy metal-cation complexation with a variety of inorganic ligands has also been recognised. But for copper, organic complexation is likely to be more significant in soils.

Competition with other cations in the soil solution can have a marked effect on ion sorption by soils. However, copper has been found to be selectively sorbed by soil. Kuo and Baker (1980) showed that copper preferentially sorbs over Zn and Cd. Similarly, Harter (1992) reported that copper was sorbed selectively by soil constituents from a 0.5 mol m^{-3} solution containing Co and Ni at a near-neutral pH. Gomes *et al.* (2001) reported the selectivity sequence of metals in a competitive system as Cr> Pb> Cu > Cd> Zn> Ni, and they indicated that Cr, Pb and Cu were the heavy-metal cations most strongly adsorbed by soils with different chemical and minerological characteristics. Cations such as Ca^{2+} in the soil solution can also compete with heavy metals for sorption sites. But for copper, a selective sorption with respect to Ca^{2+} was found by Cavallaro and McBride (1978), Petruzzelli *et al.* (1985) and Harter (1992). These findings suggest that Cu^{2+} is bonded more specifically, than non-specifically, to exchange sites.

Desorption of sorbed copper from soil is probably more relevant than adsorption for assessment of its mobility and its potential adverse impact on the environment. However, the desorption kinetics of copper in soils are not understood well (Hogg *et al.*, 1993). Of the few desorption studies reported in the literature, most have examined desorption from individual soil components (McLaren *et al.*, 1983), except the study reported by Lehmann and Harter (1984) who examined the desorption kinetics of copper applied to intact soil.

As with adsorption, desorption is also affected by several soil and soil solution factors. However the amount of copper that can be readily desorbed from soil is usually very small, as sorption of copper by a range of soil components has been shown to be largely kinetic with a slow release and /or to be irreversible (McLaren *et al.*, 1983; Padmanabham, 1983a,b; Ghestem and Bermond, 1998). Adsorption-desorption isotherms indicate that the amount of irreversibility (hysteresis) increases with longer sorption incubation times. Hogg *et al.* (1993) reported < 8.5% of added copper desorbed after an initial contact period between the copper, and the soil of 24 hours. However there was a further substantial decrease in the proportion of copper desorbed when the contact period increased to 12 weeks. The same authors suggested that, with increased time of sorption, there is a slow redistribution of copper ions to more strongly bound or less accessible sites. This possibly involved diffusion into extremely small pores and interparticle spaces.

Scientists have quantified the retention of copper in soils using two contrasting approaches. One represents equilibrium reactions using Langmuir or Freundlich models (McLaren *et al.*, 1983; Amacher *et al.*, 1986; Atanassova, 1995), while the second approach assumes kinetic or time-dependent type reactions (Aringhieri *et al.*, 1985). Hogg *et al.* (1993) provided more evidence for the existence of slow reactions between added copper and soil. These reactions gradually reduce the ability of the copper to desorb back into the soil solution. The failure of equilibrium models to describe copper adsorption-desorption paved the way for approaches such as the two-site equilibrium-kinetic model (Selim *et al.*, 1976), multireaction models, and more recently the second-order two-site model (Selim and Ma, 2001). The basis of the multisite approach is that the soil's solid phase is made up of different constituents (soil minerals, organic matter, iron and aluminium oxides), and that a solute species is likely to react with the various constituents via different mechanisms (Amacher *et al.*, 1988), and at different rates (Hinz *et al.*, 1994). Specifically, all these studies assume that a fraction of the total adsorption sites is kinetically controlled, whereas the remaining fraction interacts instantaneously with the solute in the soil solution. However, some assume the irreversible reactions are concurrent, while others assume a consecutive sequence of reactions. The second-order, two-site model by Selim and Ma (2001) accounts for both concurrent and consecutive type of irreversible reactions. They also consider that the rate coefficients are not concentration dependent, rather only one *overall* set of parameters is needed to describe the reactions.

In field soils, both kinetics of chemical adsorption-desorption reactions and transport processes occur simultaneously. Therefore both the soil solid and solution phase composition, and the hydrological process, affect the transport of copper.

1.3.2 Chelation processes in soil, and EDTA as a chelator

Chelation is a process by which heavy metals and cations bond to ligands, or functional chelate groups to form inner-sphere complexes (Sparks, 1995). Chelating agents in soil have a large effect on the behaviour of pollutant metals in the environment. There are two possible outcomes of chelate-metal binding, with different environmental implications for the mobility and migration of the metal. This includes: (i) metal ions forming soluble organic complexes with the potential to retain the metal in the soil solution and to contaminate groundwater; and (ii) insoluble complexes forming and result in a reduction in bioavailability with a consequent reduction in eco-toxicity. The capability of a chelate to form a soluble complex with heavy metals offers a great opportunity for facilitated transport of the metals, despite the metals' strong binding capacities with the soil colloids. While NTA, EDTA, CDTA, DTPA, EGTA are some of anthropogenically added organic chelates to soils, fulvic and humic acids are naturally occurring chelates, appearing in the rhizosphere as exudates of plants and microbes.

EDTA, because of its wide usage in industry and agriculture, and its strong affinity towards metals, was used in this study as the chelator.

1.3.2.1 Sources of ethylene diamine tetra acetic acid (EDTA) in soil

EDTA is present in the effluents from wastewater treatment plants with concentrations up to 18 μM (Kari and Giger, 1996). It is also found in many aquatic environments such as rivers (where 0.6 μM has been measured), lakes and groundwater, due its wide use in industry (Nowack *et al.,* 1997). The paper manufacturing, photographic and electroplating industries use EDTA as a powerful complexing agent for metals like Ca, Zn and Fe(III). In agriculture, EDTA has been in use for 30 years to extract elements from soil samples in order to predict bioavailability or extractability (Lindsay and Norvell, 1978; Shuman, 1985). It is also used as a commercial soil amendment to improve micronutrient availability (Li and Shuman, 1996). In the past few years it has also been used for contaminated-soil remediation purposes, both for *ex situ* washings (Norvell and Lindsay, 1969, Yu and Klarup, 1994), and for facilitated phytoremediation of lead and cadmium (Huang and Cunningham, 1996; Blaylock *et al.,* 1997; Kirkham, 2000). There are both advantages and disadvantages associated with the use of this chelating agent for remediation purposes, as will become apparent later in this thesis.

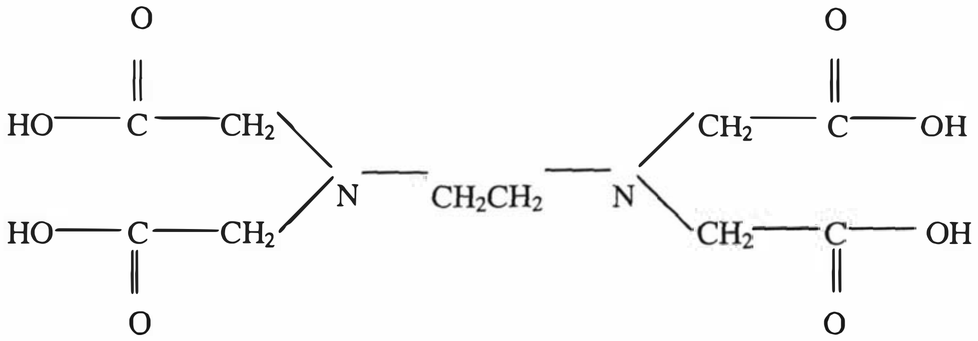

Figure 1-4 Structure of EDTA

1.3.2.2 EDTA-metal complex formation

EDTA's weak acid property makes it available in four different anionic forms through dissociation. The relative amounts of each anionic species vary with pH as shown in Figure 1-5, where α denotes the mole fraction of the species present in solution at any given pH.

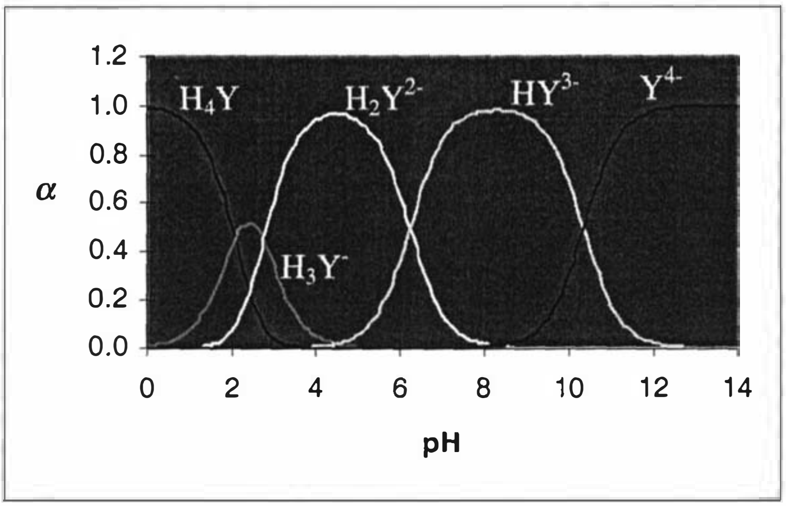

Figure 1-5 The relative amount of each EDTA anionic species with pH (after Skoog and West, 1976)

In a pure system of metals and EDTA solution, reaction between these two chemicals occurs very rapidly. Depending on the solution pH, the anionic form of the EDTA that reacts with the metal varies. The major reaction between copper and EDTA at a pH between 4 and 7 (GEOCHEM database) is,

$$Cu^{2+} + H_2Y^{2-} \leftrightarrow CuY^{2-} + 2H^+$$

The chelated metal-complex exhibits anionic characteristics and shows quite different adsorption and retardation behaviour to the un-complexed metal. The EDTA-metal formation constant indicates how stable the complex is. The EDTA (Y)–metal (M) formation constant is defined by;

$$K_{M-Y} = \frac{(MY)}{(M)(Y)}$$

where $K_{M\text{-}Y}$ is the EDTA-metal formation constant. Formation constants for different metal-chelates have been defined and are available, but these constants have been determined in a system where there is only one metal and one chelate under equilibrium conditions. For EDTA, the order (log $K_{M\text{-}Y}$) is Fe^{3+} (25.1) followed by Cu^{2+}(18.8), Zn^{2+}(17.5), Mn^{2+}(14.04), Fe^{2+}(14.2), Ca^{2+}(10.59) and Mg^{2+}(8.69) (GEOCHEM database). This is the reason why Fe(III)EDTA is found to be a major EDTA species in wastewater treatment plants and rivers, contributing 20-90% of the total EDTA (Nowack *et al.*, 2001).

1.3.2.3 EDTA as a metal carrier in soil

A chelator used as a metal carrier in soils should be able to keep the metal in a soluble and stable form, and be reusable. To accomplish this, the chelator should have a high affinity towards the target metal, and remain in soils without much degradation. EDTA is a hexadentate chelate providing six points of chemical bonding, and forms stable complexes in aqueous solution with metals (Tuin and Tels, 1990; Li and Shuman, 1996), as reflected by the high equilibrium formation constants given above (Norvell, 1991; Hong and Pintauro, 1996a). It is persistent in the environment because it is relatively resistant to decomposition by radiation (Kari and Giger, 1996), thermally stable and rather slowly biodegradable in the natural environment (Tiedje, 1977, Li and Shuman, 1996; Wasay *et al.*, 1998). Bolton *et al.* (1993) showed that only 15% of EDTA added to soil was degraded after 5 months, indicating that it could be effective for a significant period of time. EDTA is less destructive to soil than other synthetic chelates and acid washing (Yu and Klarup, 1994). These special characteristics of EDTA make it a candidate for use in the field for remediation purposes.

However there are some negative aspects of EDTA that need to be taken into account. EDTA is not selective in extracting metals. Not only does it form very stable complexes with heavy and trace metals, but it also chelates strongly with the alkaline earth metals of Ca and Mg, plus Fe. In natural systems, the reactions of un-complexed EDTA in soil involve its adsorption to Fe (and Al) oxides (Nowack and Sigg, 1997), and the subsequent dissolution of the iron oxide (Jardine *et al.*, 1993; Szecsody *et al.*, 1994). Hence Fe and Al can be competitors for chelation of EDTA with heavy metal pollutants (Ghestem and Bermond, 1998). But in a polluted soil with elevated metal concentrations, leaching of Ca and Mg is very unlikely provided the pH is kept to below 6.0.

Also the cost of EDTA (about US$4/kg of commercial EDTA – Camford Chemical Price Report, Camford Information Services Inc, August 1999) limits its use for the remediation of metal-contaminated sites.

1.3.3 Metal extraction from contaminated soil using EDTA

While EDTA is theoretically capable of solubilising many heavy metals, the extraction efficiency is highly variable, and depends on several other soil factors and the metal of target. Many laboratory studies, using either batch extraction (Elliot and

Brown, 1989; Brown and Elliot, 1992; Hong and Pintauro, 1996a,b; Ghestem and Bermond, 1998), or leaching-column methodology (Heil *et al.,* 1999; Papassiopi *et al.*, 1999) have shown that EDTA is effective in removing Pb, Zn, Cu and Cd from contaminated soils. EDTA-metal interaction in soil is governed by the pH, the EDTA concentration, the thermodynamic stability constants, the concentration of the metals, the method of metal retention in soil, (Ghestem and Bermond, 1998) and the ageing of the contaminating metal.

In principle, the relative metal extraction recovery is greater for metal-EDTA complexes with higher formation constants. However, comparison of complex formation constants only indicates which solution reactions are thermodynamically favoured. They provide little insight into the rate at which detachment and solubilisation may occur in soil, because of its heterogeneous nature.

In several studies, the influence of pH on the solubilisation of metals has been reported, and the lower the pH, the greater the extractability of metals (Elliot and Brown, 1989; Yu and Klarup, 1994). However, Ghestem and Bermond (1998) found that an excess of chelating agent has a buffering effect and reduces the pH influence. When EDTA is added in excess, the quantities of certain metals that can be extracted have been found to be pH-independent, whatever the type of soil or cation. In contrast, when there is a lack of EDTA, complexation is pH dependent, and depends on the degree of pollution by the metal, and on the other competing cations (Fe^{3+} in acidic media and Ca^{2+} in neutral media).

A maximum of 60% extractability of the trace metals Cd, Pb, Zn and Cu was obtained in a batch study from polluted sandy-loamy soils using 0.05 *M* EDTA at a pH of 6.5 (Ghestem and Bermond, 1998). Using 1 m*M* EDTA, 85% of the total Cd on kaolin de-sorbed under weakly acidic conditions (Hong and Pintauro, 1996a,b). Increased metal extraction can be achieved however by regulating both pH and the concentration of EDTA. For example Yu and Klarup (1994) found high metal recovery with a low pH and increased EDTA concentration. Whatever the concentration and amount of EDTA used, most of the metal extraction studies reported the EDTA:metal ratio in the extracted complex as 1:1 (Brown and Elliott, 1992; Hong and Pintauro, 1996b; Kedziorek *et al.,* 1998).

The release of metals from contaminated soils depends not only on the extraction conditions of the pH and EDTA concentration, but also on the modes of metal retention within the soil and the origin of the contaminant. Using 0.05 *M* EDTA at a neutral pH, only 37% of Pb, 11% of Ni and 19% of Zn were extracted from a contaminated soil (Barona *et al.,* 2001). They claimed the low recovery was due to the retention mode, and the distribution of the metals in the different solid phases of soils. Wasay *et al.* (1998) reported that soils with relatively low concentrations of heavy metals are the hardest to remediate, because the heavy metals are preferentially adsorbed by the sites with the highest binding energies. These require higher concentrations of EDTA for extraction to occur.

Together with the mode of metal retention in the soil, the origin of contamination also plays an important role. For instance, soils which have been artificially polluted in the laboratory yield higher recoveries of metals compared to soils obtained from orchards or soils treated with sewage sludge (Barona *et al.,* 2001). Mineral-bound metals may be more labile than organically bound metals.

The rate of extraction is an important parameter when considering the length of time needed for soil clean-up. In many of the studies above, a period of 24 hours was used as the extraction time, though the reaction between metal and EDTA has been found time-dependent. Yu and Klarup (1994) showed that the extraction processes consisted of a rapid phase for the first few minutes, followed by a slower extraction phase, which lasted up to several hours. Thus the metal extraction is fully effective only if the EDTA is accessible to the metals and enough contact time is given for the chelate-metal complexation to occur (Kedziorek *et al.*, 1998). The partitioning of metal sorption sites between the mobile and the immobile regions of the pore space (Schulin *et al.,* 1989) further influences the extraction of metals by the EDTA moving with the soil water. So the hydraulic properties of the soil need to be considered as they largely determine the residence time of EDTA in the soil.

In summary, chelation and de-sorption are governed by the properties of both the heavy metal ions and the chelator, with the soil playing an important intermediary role. Therefore, the physical, hydrological and chemical characteristics of a soil all play important roles in the process of extracting a metal from a polluted soil using EDTA.

1.3.4 The stability of Metal-EDTA complexes in natural systems

In soil, and subsurface sediments, the chemical stability and distribution of Me-EDTA complexes is controlled by interactions with Fe, Al and Mn-oxides. Me-EDTA reactions with sediments include adsorption, oxidation and Fe and Al oxide dissolution (forming Fe(III)EDTA, Al(III)EDTA). Like un-complexed EDTA, EDTA when present in strong aqueous metal complexes (Me-EDTA) can be adsorbed by Fe and Al oxides in a ligand-like fashion (Szecsody *et al.,*1994; Zachara *et al.,* 1995; Nowack and Sigg, 1997). Me-EDTA or EDTA adsorption to oxides is a pH dependent, rate-limited reaction that depends on the abundance, distribution and type of exposed reactive oxides (Mayes *et al.,* 2000).

Investigations of Me-EDTA complexes have shown that upon adsorption to Fe oxides, the complexes become unstable and dissociate into an aqueous metal cation and Fe(III)EDTA$^-$, due to the high aqueous stability of the product Fe(III)EDTA$^-$ (Norvell and Lindsay, 1969; Jardine *et al.,* 1993; Szecsody *et al.,* 1994; Jardine and Taylor, 1995; Brooks *et al.,* 1996; Nowack and Sigg, 1997; Davis *et al.,* 2000). However, the dissolution rate of Fe oxides and the release of Fe(III)EDTA$^-$ is reduced if EDTA is complexed by metals in comparison to un-complexed EDTA (Nowack and Sigg, 1997). The adsorption, dissolution and dissociation reactions have been observed to occur at different time scales. While adsorption occurred in hours, dissolution took 10-1500 hours, and oxidation in 10-100 hours, all at pH 6.5 when Co(II)EDTA was used as the Me-EDTA complex (Szecsody *et al.,* 1998a). During transport, such reactions coupled with the hydrological processes result in complex changes in the mobility of the metal and spreading due to the different migration velocities of reactions products (i.e., Me^{2+}, $MeEDTA^{2-}$, $MeEDTA^-$).

The extent of dissociation is a function of the stability constants of the Me-EDTA complex, and the resultant chelated soil-metal complex (Jardine *et al.,* 1993; Szecsody *et al.,* 1998a) of the Me-EDTA residence time (Szecsody, 1998b, Mayes *et al.,* 2000), of the easily available Fe in the soil, and of the affinity of the metal cation to the soil (Davis *et al.,* 2000). Each metal ion has a unique pH-dependent adsorption affinity with the soil (Szecsody *et al.,* 1994; Davis *et al.,* 2000), which is also affected by the initial metal concentration in the soil. Metal re-adsorption by soil is an important reaction affecting the transport of the metal and its distribution when EDTA is used for enhanced copper transport.

Many of the geochemical reactions between Me-EDTA and Fe and, Al oxides have studied the transport behaviour of $Co^{II/III}$EDTA, while few have studied CdEDTA and PbEDTA. In one of these, Davis *et al.* (2000) describe a field investigation of an aquifer involving multi-species (PbEDTA, ZnEDTA, CuEDTA and NiEDTA) reactive transport. Many of the studies mentioned above, have used synthetic oxides or subsurface sediments, or were performed in ground water. Only a few Me-EDTA transport studies have been carried out in topsoil containing a mixture of oxides, namely those of Jardine *et al.* (1993), Jardine and Taylor (1995) and Mayes *et al.* (2000).

1.4 The structure of the study

The experiments described in this study were all carried out in the laboratory, or a glass house. Experiments described in the thesis were not replicated and hence statistical analyses were not performed in the usual way. But the controlled conditions imposed reduced the need for replication. For example, flow rates were imposed, so variations on hydraulic conductivity did not affect the flow rate. Also, and more importantly, modelling of the data allowed the coherence of the data to be verified, with differences in variables such as the bulk density specifically taken into account.

In Chapter 2, EDTA enhanced transport of copper through homogenous repacked columns of Manawatu soil, and the stability of CuEDTA as a function of time are discussed. Differences in the transport of copper in soil with "native" copper, and the same soil that had been artificially contaminated to higher concentrations in the laboratory, are described.

In Chapter 3, CuEDTA transport through repacked Opotiki soil that had been subjected to fungicidal spray for 10 years is described. Also considered is the transport of copper from contaminated topsoil into essentially copper-free subsoil following EDTA application.

Chapter 4 deals with the transport of CuEDTA, and its temporal stability, in undisturbed Opotiki soil, as the effects of soil structure are important in that they influence both transport related properties and the copper distribution. Using undisturbed soil takes the experiments a step closer to the field environment.

Chapter 5 deals with the relative importance of plant uptake and leaching of copper, following the addition of EDTA for remediating contaminated soil growing a grass.

Water movement and root growth in repacked soil may not be the same as in soil with its structure intact, and quite different pore geometry. So, plant uptake and leaching experiments using intact cores are also described.

In Chapter 6, the results of the experiments described in Chapter 2, 3, 4 and 5 are modelled and discussed using the convection-dispersion equation.

Finally, Chapter 7 summarises the results and the insight gained from the study, and considers some practical implications of the work.

The Appendix, lists the main computer programs used to model solute movement in the study.

2. EDTA-enhanced copper transport in Manawatu fine sandy loam soil: Repacked column experiments

2.1 Introduction

As discussed in Chapter 1, batch studies have shown that EDTA enhances the solubility of the copper in soil (Yu and Klarup, 1994; Ghestem and Bermond, 1998; Wasay *et al.*, 1998). However at contaminated sites, copper solubilisation and mobilisation occur simultaneously with the transport of water. While the reaction network controlling the solute transport in the soil is the same whether evaluated in a batch or column experimental system, information obtained from batch studies are often different to the column leaching studies because of the different experimental conditions involved in these two systems, as discussed in Chapter 1. Also past research indicates reaction parameters based upon batch experiment results often poorly describes reactive transport in columns (Szecsody *et al.*, 1998a). These findings suggest a need for controlled soil column experiments to describe the transport of reactive solutes. As a first step for better understanding EDTA-enhanced copper transport in contaminated soils, leaching experiments were carried out using repacked soil columns.

This chapter describes the EDTA-enhanced transport of copper through repacked Manawatu fine sandy loam. Experiments were conducted in the laboratory using soil containing native copper, and using the soil that had been artificially contaminated to higher copper concentrations. The aims of this study were;

- to investigate the effect of EDTA at different concentrations on the leaching of copper from the Manawatu fine sandy loam contaminated with various levels of copper.
- to investigate the effect of leaving EDTA in the soil for varying periods of time before leaching with a weak $CaCl_2$ solution.

2.2 Materials and methods

2.2.1 Soil description and preparation of copper contaminated soil

The soil used was a Manawatu fine sandy loam, a Dystric Fluventric Eutrochrept in Soil Taxonomy, and a Weathered Fluvial Recent soil in the NZ classification system. The soil was collected in two batches from the A horizon of Massey University's Fruit Crops Unit. First batch was dug from an area of 4 m^2 and 0.1 m depth and used for the experiments described in Sections 2.2.2.1 and 2.2.2.2, while the soil in the second batch was collected from a slightly different spot and deeper depth and used for the experiments described in Section 2.2.2.3. In all cases the soil was passed through a 2 mm nylon sieve and homogenised before packing into columns. The acid-extractable copper content of the soil in the first batch was 60mg kg^{-1}, while the concentration in the second batch of soil was 20 mg kg^{-1}. The likely reason for this wide variation in copper content was due to the different collection depths as indicated above and discussed further in Chapter 6. New Zealand pasture soils typically contain about 30 mg kg^{-1} of copper (Roberts *et al.,* 1996) and therefore the concentration range from 20-60 mg kg^{-1} will be referred to as low-Cu soil.

Some soil was artificially contaminated by spraying on $CuSO_4.5H_2O$ solution. After sprayed on the $CuSO_4$ solution, the soil was mixed, and stored in double plastic bags at room temperature and re-mixed regularly for 10 d prior to further experimentation. About six samples were taken from each bag for the analysis of the total copper concentration in the soil. The copper concentrations measured were 201-219 mg kg^{-1}, referred to as medium-Cu soil, and 380-490 mg kg^{-1}, referred to as high-Cu soil. This range of total soil copper concentration was chosen, as 500 mg kg^{-1} was the average concentration found in a heavily copper fungicide sprayed orchard in New Zealand. The acid-extraction method used to measure the copper concentrations given is described in Section 2.2.3. Some physical and chemical properties of the Manawatu fine sandy loam top soil are given in Table 2-1. The organic matter content ranged from 5 to 9%.

Table 2-1 Physical, chemical and mineralogical properties of Manawatu fine sandy loam (A.S. Palmer, personal communication).

Particle size %			CEC Meq %	% C	Acid oxalate extractable (%)			Pyrophosphate-extractable (%)		Dithionite-citrate extractable (%)	
sand	silt	clay			Fe	Al	Si	Fe	Al	Fe	Al
63	21	16	15.5	3.4	0.37	0.16	0.03	0.26	0.10	0.68	0.16

Minerology Clay fraction	Minerology sand fraction
M_{65} C_{12} V_{15}	Q_{40} F_{20} M_4 C_4 A_{30}

Q = quartz, M = mica, C = chlorite, V = vermiculite, F = feldspar, A = aggregates

2.2.2 Leaching experiments

The acrylic leaching columns into which the soil was packed had nylon mesh at the base, and were 45 mm in internal diameter. Soil was packed to a depth of 100 mm at a bulk density of about 0.85 Mg m^{-3} for the experiments described in Section 2.2.2.1 and 2.2.2.2, while for experiments described in Section 2.2.2.3 it was packed at a bulk density of 1.0 Mg m^{-3}. A peristaltic pump was used to apply the leaching solutions to the columns at about 44.5 ml h^{-1}, corresponding to a Darcy flux density of 28 mm h^{-1}. The leachate dripped from the bottom of the columns at atmospheric pressure and was collected in aliquots.

The influent $EDTA_0$ solutions used in these experiments were prepared by mixing equal molarities of EDTA as Na_2H_2EDTA and either Cl as $CaCl_2$ or Br as $CaBr_2$. The Cl or Br were used as inert tracers. In all experiments, the inert tracer concentration was the same as the EDTA concentration. The solutions were then brought to pH 6.4 by the addition of KOH.

Although separate controls were not included in the experimental design, each of the experiments involved pre-leaching of the soil using $CaCl_2$ provided a quasi-control in that it gave the amount of copper leached by $CaCl_2$ solution. Pre-leaching was carried out in order to wet the soil, to induce steady-state flow conditions, to leach freely available and exchangeable metals including copper and also to leach any DOC present in soil.

At the conclusion of each experiment the soil was extruded from each column, cut into sections and weighed. A sub-sample was used for gravimetric water content determination and another sub-sample was analysed for copper as described in Section 2.2.3.

2.2.2.1 Application of EDTA pulses of three different concentrations

This experiment involved continuously leaching a soil column with a 0.0025 *M* $CaSO_4$ solution, interspersed with three short pulses of $EDTA_0$, each of 45 ml (corresponding to 28 mm of infiltration). The column was packed with soil containing 425 mg kg^{-1} of Cu (high-Cu soil). The first pulse contained 0.001 *M* EDTA with 0.001 *M* Br, the second 0.01 *M* EDTA with 0.01 *M* Br and the third 0.1 *M* EDTA with 0.1 *M* Br. Ninety-five ml (60 mm) of the $CaSO_4$ solution was applied before the first EDTA pulse. Each pulse was followed by about 900 mm of $CaSO_4$ solution of the same strength used for pre-leaching.

2.2.2.2 Continuously leaching the contaminated soil with EDTA

In this study four leaching experiments were conducted on low-Cu and high-Cu soils. These experiments involved continuously leaching soil columns with about 300 ml (186 mm) of either 0.001 *M* or 0.01 *M* $EDTA_0$ solution. Prior to the application of the $EDTA_0$, 0.0025 *M* $CaCl_2$, was applied to preleach the soil. The low-Cu and the high-Cu soils used in the experiments initially contained 60 and 430 mg kg^{-1} of acid extractable copper respectively.

2.2.2.3 CuEDTA stability with varying residence time

This study involved leaving pulses of $EDTA_0$ in the soil for periods of up to a month before leaching the EDTA from the soil columns. After the initial application of about 100 ml (62 mm) of 0.0025 *M* $CaCl_2$ solution, 50 ml (31 mm) of 0.001 *M* $EDTA_0$ was added to four soil columns. The first of these was leached immediately with about 200 ml (120 mm) of 0.0025 *M* $CaCl_2$ solution. The second was leached with the same amount of $CaCl_2$ solution after a one-day delay, the third after a one-week delay and the fourth after a one-month delay. During the delay periods the columns were wrapped in polythene bags to minimise evaporation. This four-column experiment was carried out using soil initially containing 25 mg kg^{-1} (low), 212 mg kg^{-1} (medium) and 480 mg kg^{-1} (high) of copper, giving 12 columns in total. A summary of the experiments conducted is given in Table 2-2 below.

Table 2-2 Experimental procedures on Manawatu soil

Section 2.2.2.1 study (high-Cu soil) 1 column	Section 2.2.2.2 study (low or high Cu soils) 4 columns	Section 2.2.2.3 study (low or medium or high Cu soils) 12 columns
Pre-leaching with 0.0025M $CaSO_4$	Pre-leaching with 0.0025M $CaCl_2$	Pre-leaching with 0.0025M $CaCl_2$
↓		↓
Application of 0.001M EDTA+0.001M Br (45 ml)	↓	Application of 0.001M EDTA+0.001M Cl (50ml)
↓		↓
Leaching with 0.0025M $CaSO_4$ over night	Leaching with either 0.001M EDTA+0.001M Br or 0.01M EDTA+0.01M Br	Wrapped with polythene bags and kept for 0, 1, 7 or 30 days
↓		↓
Application of 0.01M EDTA+0.01M Br (45ml)	↓	Leaching with 0.0025M $CaCl_2$
↓		↓
Leaching with 0.0025M $CaSO_4$ over night	Destructive sampling	Destructive sampling
↓		
Application of 0.1M EDTA+0.1M Br (45ml)		
↓		
Leaching with 0.0025M $CaSO_4$ over night		
↓		
Destructive sampling		

2.2.3 Chemical analyses

Leachate from the columns was collected in aliquots, acidified to avoid copper adsorbing to the polypropylene container walls and analysed for copper and iron using a GBC 904 atomic absorption spectrophotometer. Bromide (Br) and chloride (Cl) concentrations were measured using a Dionex HPLC. Dissolved organic carbon (DOC) was analysed using a Shimadzu TC-5000 analyzer to determine EDTA (Mayes *et al., 2000*). It was assumed that all DOC present was EDTA after subtracting background DOC (DOC concentration measured in the last leachate collected during pre-leaching).

The pH was also measured. Some leachate samples were passed through Maxi-Clean IC-Chelate Cartridges (capacity of 0.5 milliequivalents) to remove free metal cations from the leachates and leave only the complexed metal ions. These samples were analysed for metal concentration before and after passing through the IC-Chelate Cartridges using the atomic absorption spectrophotometer.

To measure the copper content in the soil, about 0.2 g of sieved soil was weighed into boiling tubes. Ten ml of concentrated HNO_3 was then added and the mixture boiled until a final volume of 3 ml was reached. A further 10 ml of concentrated HCl was then added and the mixture again evaporated to 3 ml. After filtration, the solutions were analysed for copper as described above.

2.3 Results and discussion

2.3.1 Application of EDTA pulses of three different concentrations

There have been a number of reports in the literature of EDTA having a deleterious effect on soil structure, resulting in a significant decrease in hydraulic conductivity (Sun *et al*., 2001; Kedziorek *et al*., 1998). However, there was no ponding observed in this experiment. Therefore the saturated hydraulic conductivity remained higher than 28 mm h^{-1}.

Figure 2.1a shows the effluent concentrations of EDTA (assuming all DOC was present as EDTA) and Br after the first two $EDTA_0$ (0.001*M* and 0.01*M*) pulses were applied to the high-Cu soil column sequentially. The BTCs of the Br and EDTA for the third 0.1 *M* $EDTA_0$ pulse are not shown in the figure as the effluent DOC was not measured. The breakthrough of EDTA coincided with Br, a non-reactive tracer, with regard to the time of the peak concentration. This shows that EDTA was not subject to any retardation due to adsorption at the flow rate and the pH measured. The pH in the leachate ranged from 5.8 to 6.4 during the leaching of the first two pulses of $EDTA_0$. Similarly, Kedziorek *et al.* (1998) found no evidence of EDTA adsorption in their Cd and Pb leaching experiments. They suggest that because the effluent pH was well above the point of zero charge (PZC) there was no reason to expect adsorption. However many other studies have reported adsorption of EDTA and/or metal-EDTA complexes in soils and several oxides of Fe or Al (Jardine *et al.*, 1993; Szecsody *et al.*, 1994, 1998a,b; Jardine and Taylor, 1995; Brooks *et al.,* 1996; Nowack and Sigg, 1997; Davis *et al.*, 2000). The reason for this non-adsorbing behaviour of EDTA in this study could be the pH that prevailed during the experiment. The effect of pH on the EDTA adsorption will be discussed more in the Chapter 3. Mass recovery of EDTA for this experiment is not given as the DOC analysis was done only for selected leachate aliquots.

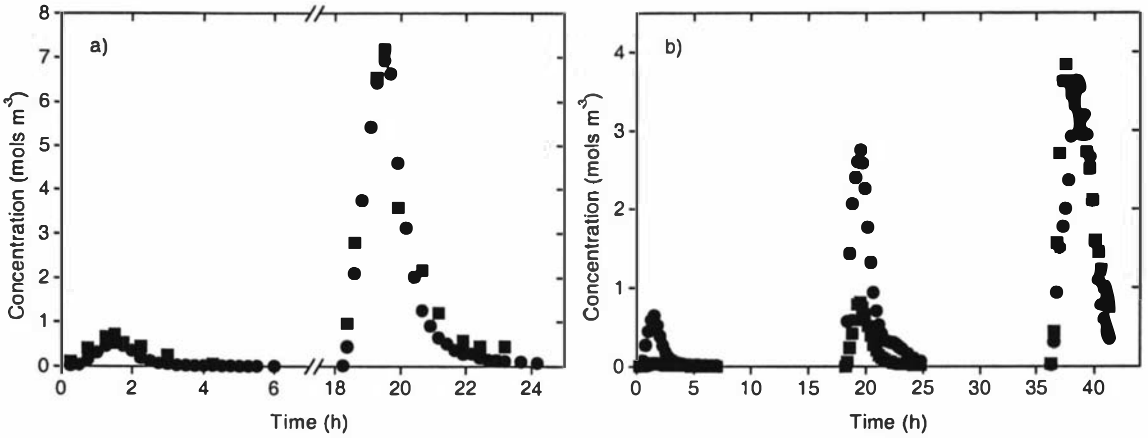

Figure 2-1 Measured effluent concentrations of (a) Br and EDTA (b) copper and iron. The circles are for Br and copper; the squares are for EDTA and iron.

Figure 2.1b shows the effluent copper and iron concentration during the experiment. The EDTA applied to enhance the copper solubility also mobilised significant pulses of iron during its passage. Only small amounts of iron and copper were found in the leachate during pre-leaching with 0.0025 *M* $CaSO_4$. Thus the copper and iron present in the leachate after the addition of $EDTA_0$ were nearly all brought into solution by the EDTA. This was also confirmed by passing the samples through IC-Chelate cartridges. The metal (copper and iron) concentrations measured in the leachate before and after passing through the IC-Chelate cartridges were identical, confirming that the leached copper or iron were in complex with EDTA rather than in cationic forms.

As a result of the first $EDTA_0$ application of $4.5x10^{-5}$ mol, the combined molar amount of copper ($4x10^{-5}$ mol) and iron ($0.3x10^{-5}$ mol) in the leachate almost added up to the amount of EDTA applied. This confirmed that each mole of EDTA was combining with one mole of metal. Although there have been studies reporting the formation of more than one species of copper-EDTA and iron-EDTA complexes at different stoichiometric ratios, $CuEDTA^{2-}$ is the most probable species formed at the pH studied here (GEOCHEM-PC version 2-database, Parker *et al.*, 1995). During the second and third leaching pulses, the amount of copper plus iron leached was lower than the amount of bromide and EDTA. This is probably due to the remaining soil copper and also iron being less readily available for complexation. There were negligible amounts of zinc, aluminium and manganese in the effluent. So the rest of the EDTA in the leachate was probably complexed with calcium. This was confirmed by speciating cationic and anionic components of the column effluent using GEOCHEM-PC version 2 (Parker *et al.*, 1995).

The ten-fold increase in the EDTA concentration in the second pulse resulted in a seven-fold increase in the amount of copper leached, together with a twenty-fold increase in the amount of iron. However, the hundred-fold increase in the EDTA concentration in the third pulse leached only 3.9 x 10^{-4} mol of copper and 4.7 x 10^{-4} mol of iron. This shows only 19% of the applied EDTA during the third pulse was complexed with copper or iron, due to the limited availability of both the copper and iron for complexation.

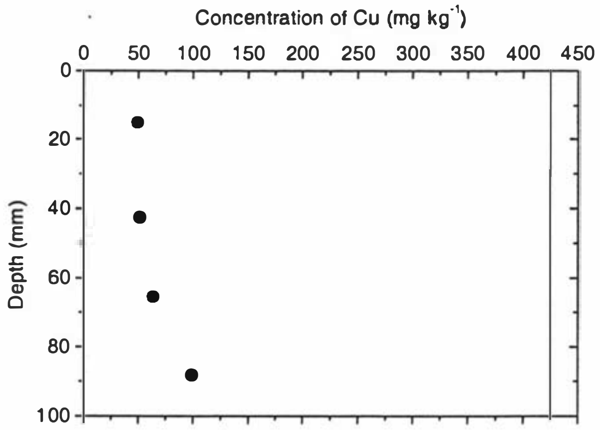

Figure 2-2 Resident soil copper concentration (●) and initial soil copper concentration (—) as a function of depth. In this figure and elsewhere the data point depths represent the mid points depths of the sectioned soil was extruded from the columns.

Figure 2.2 shows the final soil copper as a function of depth. EDTA leaching reduced the copper concentration in the soil from 425 to 50 mg kg^{-1} in the top 55 mm. The concentration measured in the soil below the 55 mm depth is higher, presumably because the leaching was stopped before the copper solubilised by the third pulse of EDTA was completely removed. The copper concentration of 0.35 mol m^{-3} measured in the last leachate aliquot supports this explanation (Figure 2.1b). EDTA applied in excess leached about 85% of the soil copper with some copper being non-extractable by EDTA at the prevailing experimental conditions. The reason for this will be discussed below in Section 2.3.2.

2.3.2 Continuously leaching with EDTA of different concentrations

No observable ponding occured in any of the four columns despite the continuous application of EDTA both at 0.001*M* and 0.01*M* concentrations to the soil hence, the K_S was not affected.

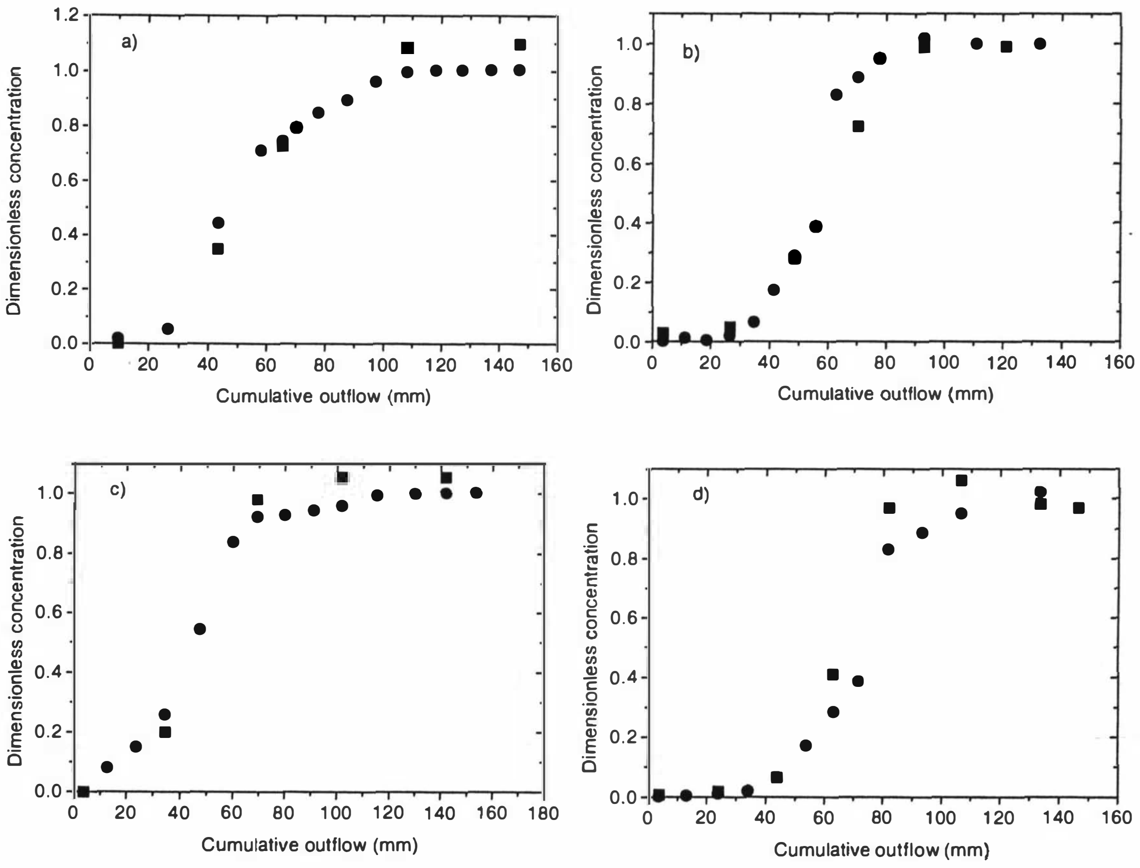

Figure 2-3 Normalised breakthrough data of Br (●) and EDTA (■). Figures (a) and (c) are for 0.001 *M* leaching and Figures (b) and (d) are for 0.01 *M* leaching. Figures (a) and (b) are for low-Cu soil while (c) and (d) are for high-Cu soil.

Figure 2.3 shows the Br and EDTA effluent concentrations when low and high-Cu soils were continuously leached with two different concentrations (0.001 *M* and 0.01 *M*) of $EDTA_0$. Figures 2.3a and 2.3b shows the results for the leaching using 0.001 *M* and 0.01 *M* $EDTA_0$ respectively on low-Cu soil. Similarly Figures 2.3c and 2.3d are for the high-Cu soil. The dimensionless concentrations shown were found as $(C - C_1)/(C_2 - C_1)$, where C is the measured effluent concentration, C_1 is the concentration of bromide or chloride or EDTA in the pre-leaching solution (zero in this case), and C_2 is the applied concentration of Br or EDTA. In all experiments, breakthrough of EDTA closely followed the non-reactive tracer Br, and hence there was again no evidence of adsorption of EDTA. This is consistent with the results found in the experiment discussed in Section 2.3.1.

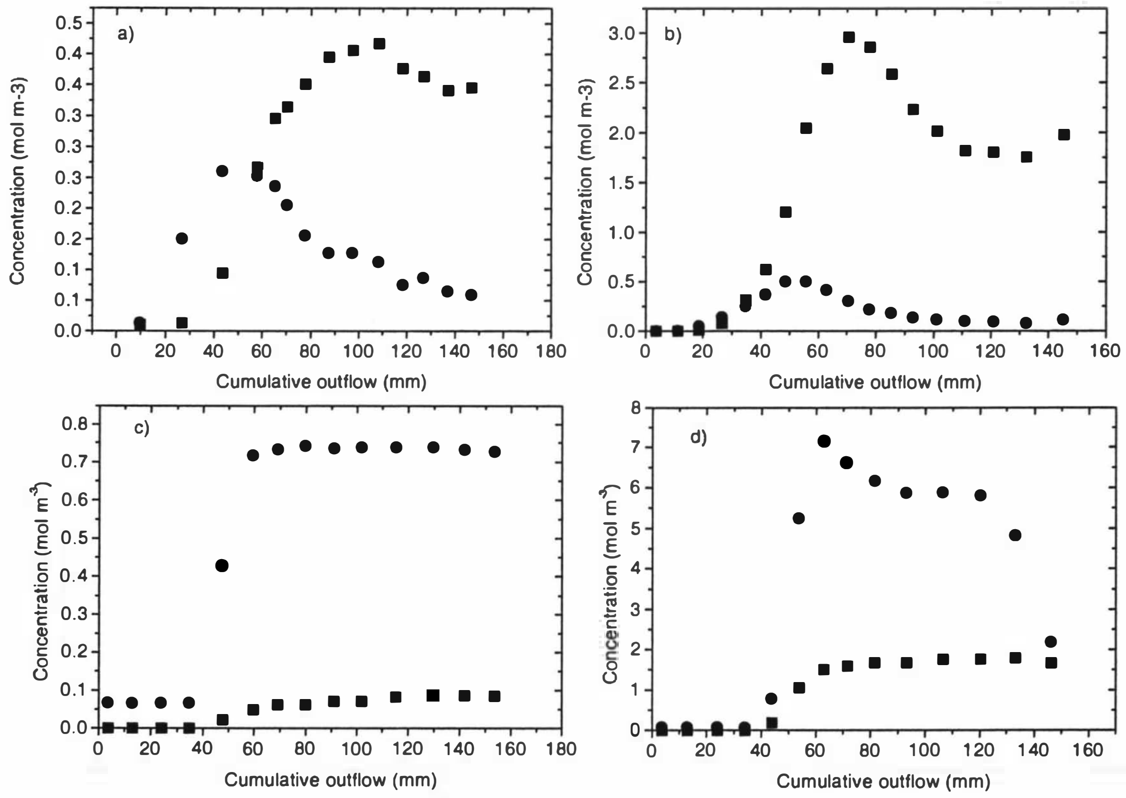

Figure 2-4 Measured effluent concentrations of copper (●) and iron (■). (a) 0.001 *M* leaching on low-Cu soil (b) 0.01 *M* leaching on low-Cu soil (c) 0.001 *M* leaching on high-Cu soil (d) 0.01 *M* leaching on high-Cu soil.

Figure 2.4 shows the effluent concentrations of copper and iron. Figures 2.4a and 2.4b are the results for the 0.001 *M* and 0.01 *M* $EDTA_0$ leaching of the low-Cu soil while Figures 2.4c and 2.4d shows the results for the 0.001*M* and 0.01*M* $EDTA_0$ leaching of the high-Cu soil. The leachate copper concentration increased steadily to a peak and then declined to a low value when the leaching was done with EDTA in excess of that needed to complex all the copper initially present in the soil (Figures 2.4 a,b and d). This reflects the fact that copper is adsorbed to the different soil materials such as organic matter, iron and aluminium oxides and clay fractions with varying strengths, and each fraction differs in its ease of extraction (McLaren and Crawford, 1973a,b; Hong *et al.,* 1999; Barona *et al.*, 2001). Iron leaching also showed a similar trend. In this case, it could be due to the different forms of iron oxides (amorphous and crystalline) having different dissolution kinetics, or due to the iron oxides having limited adsorption sites for EDTA. Elliott and Shastri (1999) showed that the amount of iron extractable from soils varies widely, depending on the ease and speed with which it can be extracted by agents such as EDTA.

Table 2.3 Summary of experiment results described in Section 2.2.2.2

	Low Cu soil		High-Cu soil	
	0.001 M EDTA leaching	0.01 M EDTA leaching	0.001 M EDTA leaching	0.01 M EDTA leaching
Amount of EDTA added (μmol)	224	2240	224	2240
Amount of leached Cu (μmol)	30	44	120	867
Amount of leached Fe (μmol)	60	369	11	39

As shown in Table 2.3, in the low-Cu soil, 30 μmol of copper and 60 μmol of iron were leached by 2.5 liquid-filled pore volumes (PV) of 0.001 *M* $EDTA_0$ (224 μmol). An equal amount of 0.001*M* $EDTA_0$ leached 120 μmol of copper and 11 μmol of iron from the high-Cu soil. Similarly, more copper and less iron were leached from the high-Cu soil compared to the low-Cu soil by 0.01 *M* $EDTA_0$. In both leaching experiments an excess of EDTA was available after complexation with copper, even in the high-Cu soil. It seems that the extra copper in the soil reduced the dissolution of iron by EDTA. This could be due to the extra added copper in the high-Cu soil being more readily available than the soil iron. Or it could have been due to the additional copper masking some of the iron oxide from the percolating EDTA. Therefore the copper or iron complexation and extraction by EDTA depends on the copper concentration in the soil and /or the ease with which the metals are available. This is likely to be affected by ageing, that is the contact time of copper with the soil. It is also noteworthy that the lower iron extraction in the high-Cu soil was not due to a higher pH, as the effluent pH was always lower in the high-Cu soil than in the low-Cu soil.

At the end of the 0.01 *M* EDTA leaching experiments where the EDTA was applied in excess, 35 % and 86 % of the copper that was initially present was leached from the low- and high-Cu soils respectively. The residual concentrations of copper in the soil after leaching are shown in Figure 2.5. The average residual-Cu concentration in the low-Cu soil after leaching with both 0.001 *M* and 0.01 *M* EDTA was about 40 mg kg^{-1}, down 20 mg kg^{-1} from the initial copper content of 60 mg kg^{-1} (Figure 2.5a). Leaching the high-Cu soil with 0.01 *M* EDTA also brought down the concentration in most of the soil in the column to about 40 mg kg^{-1} from 420 mg kg^{-1} (Figure 2.5b). However the bottom layer contained 68 mg kg^{-1}, presumably because the experiment was concluded before the extractable copper from this layer was completely depleted. It appears that EDTA could not extract about 40 mg kg^{-1}of copper from the soil during the leaching with up to 4 PV, due to the strong binding of some copper to the soil organic matter and clay as discussed above.

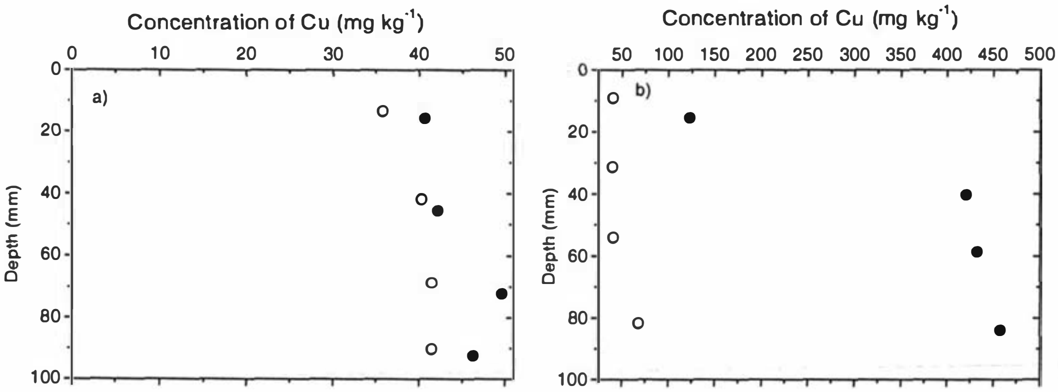

Figure 2-5 Final measured copper concentrations in the soil as a function of depth. (a) Low-Cu soil (b) high-Cu soil. Closed circles for 0.001 *M* EDTA$_0$ and open circles are for 0.01 *M* EDTA$_0$ leaching experiments

2.3.3 CuEDTA stability with varying residence time in soil

In this study some ponding was noticed during the final leaching phase of the columns when leaching was delayed for one month. However similar columns kept for a month after applying water or $CaCl_2$ solution, but with no EDTA application, also showed ponding. Therefore the probable cause of the ponding was clogging of macropores by gums produced by localised anaerobic microbial activity in the poorly aerated soil, rather than dispersion or dissolution due to EDTA or sodium. The air-filled porosity (calculated from the gravimetric water content and bulk density, assuming a particle density of 2.5 Mg m^{-3}) was between 0.07 and 0.09 m^3 m^{-3} indicating aeration in the soil was marginal.

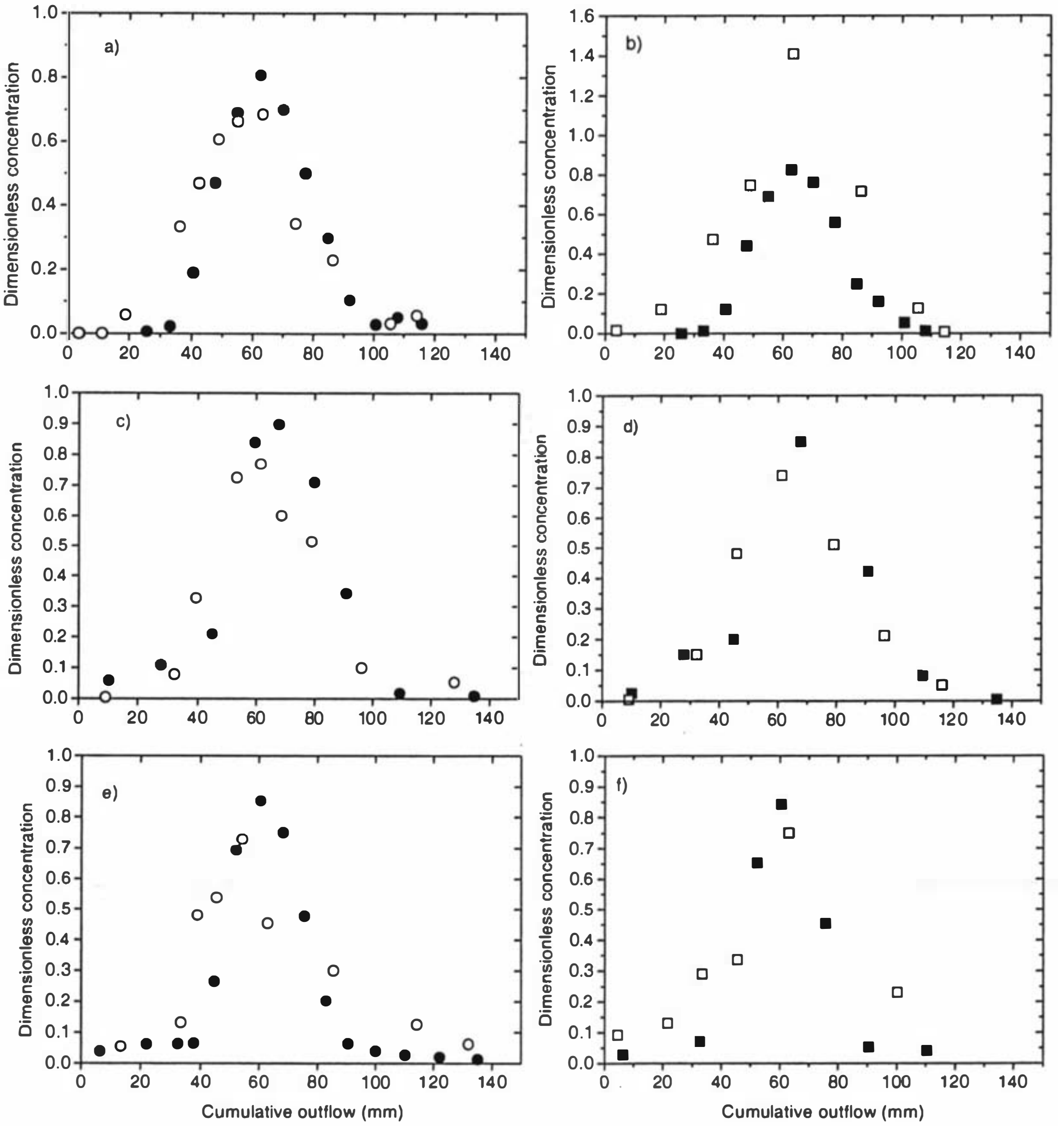

Figure 2-6 Normalised breakthrough data of chloride (circles) and EDTA (squares). Figures (a) and (b) are for the low-Cu soil; (c) and (d) for the medium-Cu soil; (e) and (f) for the high-Cu soil. Figures (a), (c) and (e) show the measured chloride for immediate (●) and a month delayed (○) leaching. Figures (b), (d) and (f) show the measured EDTA for immediate (■) and a month delayed (□) leaching.

Figure 2.6 shows that the EDTA was not adsorbed, as the breakthrough curves for EDTA show no retardation relative to the non-reactive tracer, which is consistent with the experimental results discussed earlier in Sections 2.3.1 and 2.3.2.

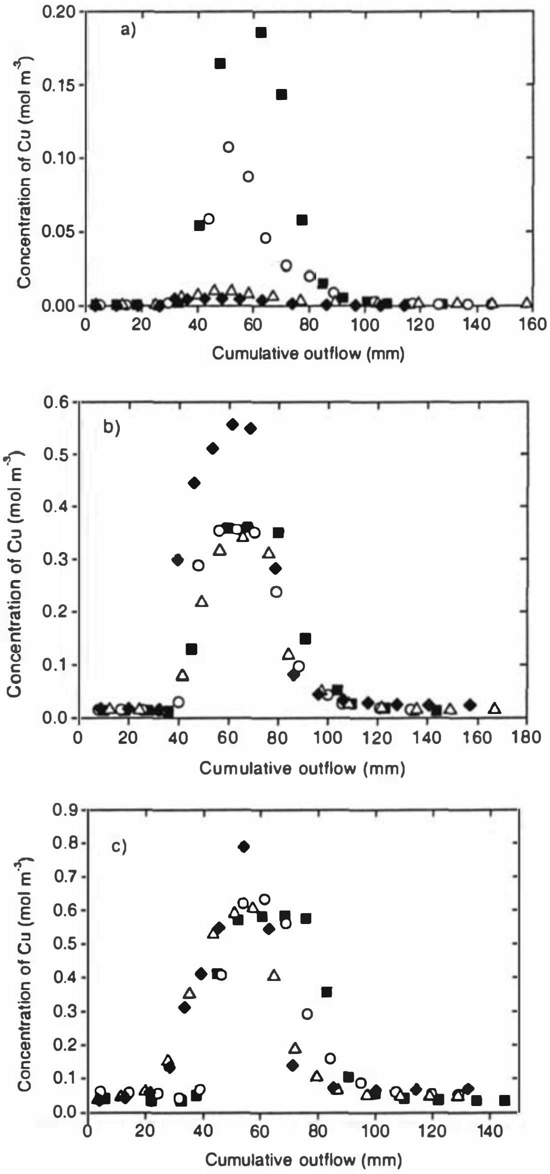

Figure 2-7 Measured effluent concentrations of copper in immediate (■), one day (○), one week (Δ) and one month (◆) delayed experiments. (a) Low-Cu soil (b) medium-Cu soil and (c) high-Cu soil.

Figures 2.7 and 2.8 show the measured effluent concentrations of copper and iron after the 50 ml (31mm) pulse of 0.001 *M* $EDTA_0$ was left in the soil for different time periods before leaching with 0.0025 *M* $CaCl_2$ in the low-, medium- and high-Cu soil column experiments. In the low-Cu soil, the amount of copper leached dropped markedly as the time the EDTA was left in the soil increased (Figure 2.7a; and Table 2.4). With a one-week or longer delay, very little copper was leached. Figure 2.8a also indicates that after a month delay almost 100% of the applied EDTA left the soil complexed with iron. The decreasing amount of copper leached with increasing residence time, coupled with a corresponding increase in the extracted iron, was most likely a result of the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ in the soil. Several other authors have observed similar transformations when they conducted experiments involving flow interruption of metal-EDTA for different periods of time (Mayes *et al.*, 2000), slower flow rates (Brooks *et al.*, 1996), or injected metal-EDTA pulses into aquifers (Davis *et al.*, 2000). Davis *et al.* (2000) reported the transformation of $CuEDTA^{2-}$ together with some other metal-EDTA compounds.

It is likely that for the transformation a chain of reactions occurred, initiated by EDTA complexing with copper, followed by $CuEDTA^{2-}$ reacting with the soil, then the dissociation of $CuEDTA^{2-}$ into Cu^{2+}, and finally the more stable $Fe(III)EDTA^{-}$ coming into solution. The released copper (Cu^{2+}) was re-adsorbed by the soil. This probably caused the increased iron concentrations and decrease in the copper concentrations in the leachate with increased residence time in the soils. However, the $CuEDTA^{2-}$ dissociation was less pronounced in the medium and high-Cu soils as perhaps due to the added copper masking the iron compounds and, so had little effect on the total amount of copper leached (Figures 2.7 b and 2.7c). The leached amount of copper was between 23 and 37 μmol in the medium-Cu soil, and between 40 and 51 μmol in high-Cu soil.

During preleaching, the effluent copper concentration in the last few aliquots of the medium- and high-Cu soils was higher than the effluent copper concentration from the low-Cu soil. This caused the combined molar amounts of copper and iron in the effluent to be greater than the amount of EDTA applied to the medium and high-Cu soil in some cases (Table 2.4). However, they were mostly less than 50 μmol, after doing an approximate correction for the background copper concentration measured during the last stage of preleaching. The values in brackets in Table 2.4 for the amount of copper leached, and the combined amount of copper and iron leached given are after correcting for the background concentrations.

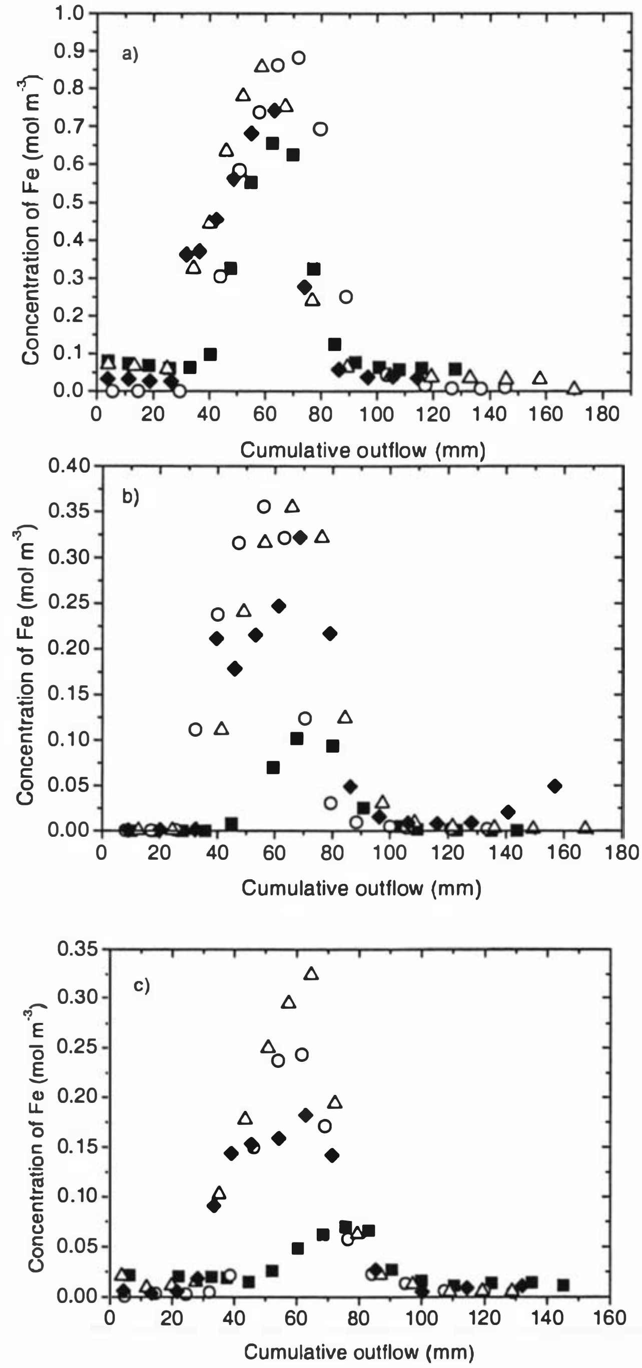

Figure 2-8 Measured effluent concentrations of iron in immediate (■), one day (○), one week (Δ) and one month (◆) delayed experiments. (a) Low-Cu soil (b) medium-Cu soil and (c) high-Cu soil.

Table 2-4 Amount of Fe and Cu leached after leaving a 50 μmol EDTA pulse in the soil for different time periods and then leaching with 0.0025 *M* $CaCl_2$.

	Time EDTA left in soil (d)	Amount of EDTA added (μmol)	Amount of Cu leached (μmol)	Amount of Fe leached (μmol)	Cu + Fe leached (μmol)
Low-Cu soil	0	50	10	43	53
	1	65	4.4	59	63
	7	50	0.8	55	56
	30	50	0.3	43	43
Medium-Cu soil	0	50	27 (24)	5	33 (30)
	1	50	25 (21)	18	43 (39)
	7	50	23 (19)	21	44 (40)
	30	50	37 (33)	20	57 (53)
High-Cu soil	0	50	44 (37)	6	50 (43)
	1	49	40 (34)	12	52 (45)
	7	50	42 (32)	18	60 (50)
	30	50	51 (40)	14	65 (54)

As shown in Figure 2.8 and Table 2.4, in all cases the amount of iron in the effluent increased with EDTA residence time up to a one-week leaching delay. However there was a decrease after a one-month delay. This drop could be due to the reducing conditions prevailing, changed the Fe(III) to Fe(II). The EDTA-Fe(II) formation constant (log K = 14.3) is lower than the EDTA-Fe(III) (log K =25.1).

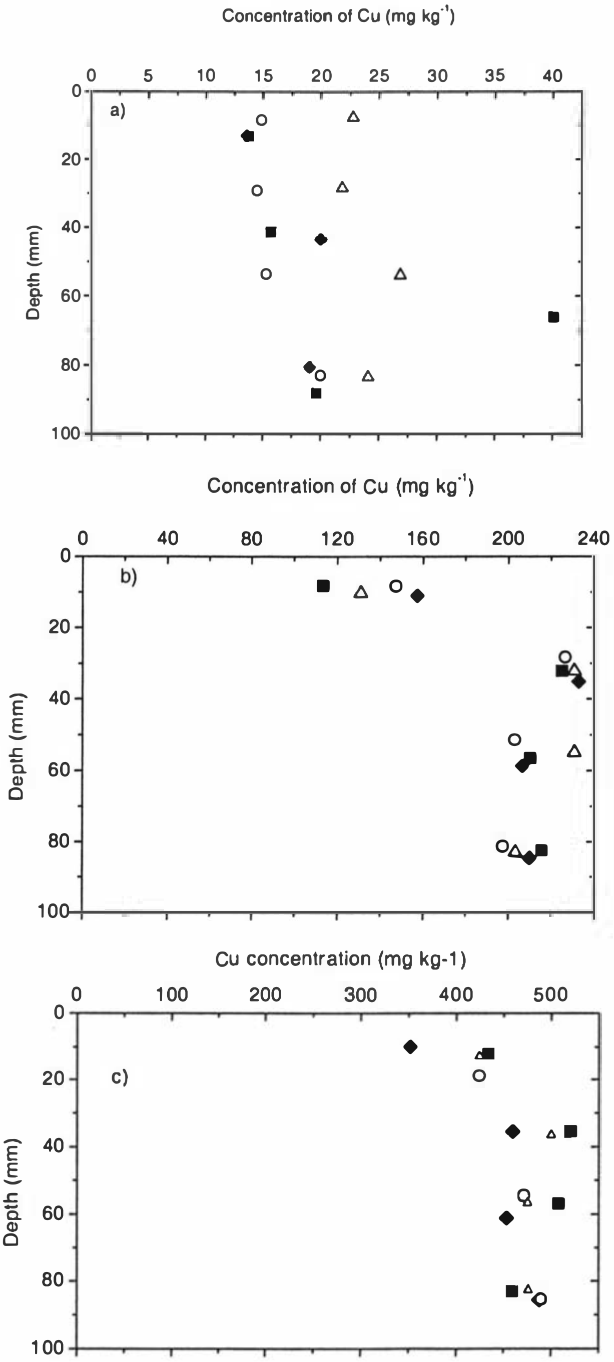

Figure 2-9 Final soil copper concentration as a function of depth in immediate (■), one day (○), one week (Δ) and one month (◆) delayed experiments. (a) Low-Cu soil (b) medium-Cu soil and (c) high-Cu soil.

The copper concentrations in the soil columns at the end of leaching are shown in Figure 2.9. In contrast to the continuous leaching experiments in Section 2.3.2, much of the copper initially present remained in the soil, especially in medium- and high-Cu soil. This was due to the much smaller amount of EDTA added in these experiments compared to the continuous leaching experiments.

2.4 Conclusions

The EDTA that was applied to increase the copper mobility also enhanced the dissolution of iron in the soil. The EDTA moved through the soil without any observable adsorption during the application of 0.001 *M* and 0.01 *M* Na_2H_2EDTA at a flow rate of 28 mm h^{-1}. In the low-Cu soil, more iron than copper complexed with the EDTA. However, in the high-Cu soil, the reverse was found. In both low and high-Cu soils, about 40 mg kg^{-1} of the acid extractable copper was not solubilised by either 0.01 *M* and 0.001 *M* solutions of $EDTA_0$ applied at a flow rate of 28 mm h^{-1} for 5 h at a pH of 6.4.

Leaving the $EDTA_0$ in the low, medium and high-Cu soil for different periods of time before leaching in general showed a time-dependent increase in iron concentration in the leachate. With an increasing time period, the mass of copper leached dropped markedly in the low-Cu soil however, changed little in the medium and high-Cu soils. These results are consistent with $CuEDTA^{2-}$ being gradually adsorbed by the soil, and dissociating to form Cu^{2+} while releasing the more stable $Fe(III)EDTA^{-}$ back into solution. The released Cu^{2+} was apparently re-adsorbed by the soils. In medium and high-Cu soils the added copper masked the iron compounds, so less $CuEDTA^{2-}$ got dissociated. In these soils the time given for ageing of the added copper prior to leaching with EDTA was only 10 days, hence preleaching was insufficient to leach out the less aged copper.

3 EDTA-enhanced copper transport in Opotiki sandy loam: Repacked column experiments

3.1 Introduction

In Chapter 2 EDTA-enhanced transport of copper from repacked columns of Manawatu fine sandy loam soil, and the temporal stability of the $CuEDTA^{2-}$ complex in the soil solution, have been described. The results of the experiments using soil with "native" copper (low-Cu) were different to those for experiments using the same soil that had been artificially contaminated to higher concentrations in the laboratory. In the low-Cu soil the copper released as the EDTA slowly changed from $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ was virtually all re-adsorbed by the soil. In contrast, in the soil that had been artificially contaminated to higher copper concentrations, the $CuEDTA^{2-}$ dissociation process was less pronounced, so had little effect on the total amount of copper leached. It was concluded that these contrasting results could be attributed to the differences in soil copper ageing or its concentration. Hence more understanding is required of the effect of soil copper ageing and the metal concentration on the temporal stability of the copper, as the re-adsorption reaction critically affects the transport of copper following application of EDTA.

Also, in the previous chapter EDTA-enhanced copper mobility was examined in a soil with low organic matter content and crystalline clay mineralogy. As discussed in Chapter1 however, the copper complexation with organic matter and its, sorption on Fe/Al oxides and clay minerals have a direct influence on its mobility. In addition to that, the amorphous clays in volcanic soil exhibit variable charge, which could affect the transport of anionic forms of EDTA. Therefore knowledge of the different desorption kinetics in soils with different binding strengths is necessary for predicting EDTA and copper behaviour in different soils. Further, at contaminated sites the copper is usually concentrated in the topsoil due to its strong binding with organic matter. Hence there is a need to study the transport of copper from contaminated topsoil into essentially copper-free subsoil following EDTA application.

While chelating agents such as EDTA enhance the solubility and transport of metals, it has been well documented that iron/aluminium oxides are effective in de-coupling metal-EDTA complexes with time, as outlined in Chapters 1 and 2. Quantitative prediction of the EDTA-enhanced transport of copper depends on a description of the kinetics of these interactions in soil. Sieved and repacked soil in columns do not have the same spatial relationship between sorption sites and water flow pathways that can be expected under field conditions. In repacked soil, therefore, local physical non-equilibrium is less pronounced, providing a better environment to study the chemical kinetics of the reactions.

This chapter describes the EDTA-enhanced transport of copper in an Opotiki sandy loam soil. This soil is of volcanic origin and has a much higher organic matter than the Manawatu sandy loam soil used for the experiments described in Chapter 2. The chapter investigates the leaching of copper following EDTA application, and its mobility with varying EDTA residence times in soil columns that were uniformly contaminated, and also in soil columns with non-uniform contamination. Additionally a three-month study of the reaction kinetics of $CuEDTA^{2-}$ with soil iron is described.

3.2 Materials and methods

3.2.1 Soil and the site description

The soil used was collected from a site near Opotiki, N.Z. most of which had been used to grow passionfruit for the preceding 10 years. The top 20 mm of the soil had become contaminated with copper due to the heavy use of fungicide sprays. The soil at the site is Opotiki sandy loam, a Typic Udivitrand Ashy Thermic in Soil Taxonomy, and a Vitric Orthic Allophanic soil in the NZ classification system. The top 100 mm had a bulk density of 0.9 Mg m^{-3}, a relatively high cation exchange capacity of 22 cmolc kg^{-1}, and an organic matter content of 12-16%. The pH of the soil in 1:2.5 water was 5.6. The clay mineralogy of A horizon consists of 15% allophane plus imogolite, 25% vermiculite, 18% kandite, and 40% VG Am. SiO_2.

The soil for all the experiments was collected from the top 100 mm of the A horizon and passed through a 2 mm nylon sieve when it was moist. Five leaching experiments were conducted, which I will refer to as A, B, C, D and E. For Experiments A and B described in Section 3.2.2.1 the soil was taken from an area, which had been subject to copper sprays. The acid-extractable copper content was between 265 and 290 mg kg^{-1}. Note that this is at the high end of the range of values reported in Australian orchard soils by Merry *et al.* (1983) and in Australian and New Zealand horticultural regions reported in McLaughlin *et al.* (2000). For Experiment C described in Section 3.2.2.2 the soil was collected from an adjacent area that had not been subject to copper sprays. Its copper content was 13 mg kg^{-1}, similar to reported values for uncontaminated soil (Merry *et al.,* 1983). In the soil columns used for Experiments D and E described in Section 3.2.2.3, the bottom 70 mm of soil was the low-Cu soil used in Experiment C, and the top 30 mm the higher copper soil used in Experiments A and B.

3.2.2 General leaching procedure

A soil depth of 100 mm was packed at a bulk density of 0.65 Mg m^{-3} into acrylic tubes with an internal diameter of 45 mm and with nylon mesh at the base. A peristaltic pump was used to apply the leaching solutions to all the repacked columns at about 44.5 ml h^{-1}, corresponding to a Darcy flux density of about 28 mm h^{-1}. The leachate dripped from the bottom of the columns at atmospheric pressure and aliquots were collected. As the soil columns were only 100 mm high the pressure potential was between –100 mm and 0 both during and in between leaching events.

The influent $EDTA_0$ solutions used in all experiments except C were prepared using Na_2H_2EDTA and either $CaCl_2$ or $CaBr_2$. The solutions were brought to pH 6.2 by the addition of KOH. The $CuEDTA^{2-}$ solution used in Experiment C (described in Section 3.2.2.2) was made by the stoichiometric addition of copper as $CuCl_2$ and EDTA (1:1) as Na_2H_2EDTA, allowing the mixture to equilibrate for 24 hours, then adding $CaBr_2$ to include a non-reactive tracer, and finally adding KOH to raise the pH to 6.2. All these influent solutions contained equal molarities of EDTA and Br^- or Cl^-. Although controls were not included in the experimental design, each of the experiment involved pre-leaching of the soil using $CaCl_2$. Pre-leaching was done in order to wet the soil, to induce steady-state flow conditions, to leach freely available and exchangeable metals including copper and also to leach the DOC present in soil. At the conclusion of all five experiments, the soil was extruded from each column, cut into sections, weighed, and then water content and copper concentration measured as described in the Section 2.2.3.

3.2.2.1 EDTA application to uniformly contaminated soil

Two sets of leaching experiments were conducted, named Experiments A and B. Experiment A involved pre-leaching with about 1 PV of 0.0025 *M* $CaCl_2$ solution, and then continuously leaching a soil column with 616 mm or about 10 PV of 0.01 *M* EDTA$_0$ (Table 3-1). In Experiment B, after an initial application of about 1 PV of 0.0025 *M* CaCl$_2$ solution, 31 mm (0.5 PV) of 0.001 *M* EDTA$_0$ was added to four soil columns. The first of these columns was then leached immediately with about 150 mm (2.5 PV) of 0.0025 *M* CaCl$_2$ solution. The second was leached with same solution after a one-day delay, the third after a one-week delay and the fourth after one-month delay. During the delay periods the columns were wrapped in polythene to minimise evaporation.

3.2.2.2 Copper-EDTA leaching study

The column used in Experiment C was pre-leached with 0.0025 *M* CaCl$_2$. Then a total of 2316 mm (42 PV) of 0.001 *M* CuEDTA^{2-} solution was applied as daily pulses of 28 mm (0.5 PV) over an 83 day period, by which time the effluent copper concentration had reached the influent concentration. The column was then leached with 0.0025 *M* CaCl$_2$.

3.2.2.3 EDTA application to non-uniformly contaminated soil

Two sets of experiments were conducted, namely D and E. Except for using layers of copper contaminated soil and the un-contaminated soil (see Section 3.2.1), they were the same as described in the Section 3.2.1 for Experiments A and B.

A summary of the leaching procedure for Experiments A to E is given in Table 3.1.

Table 3-1 Experiment procedures for Experiments A to E

Experiments A and D (2 columns)	Experiment C (1 column)	Experiments B and E (6 columns)
Pre-leached with 0.0025 *M* CaCl$_2$	Pre-leached with 0.0025 *M* CaCl$_2$	Pre-leached with 0.0025 *M* CaCl$_2$
		↓
		31 mm 0.001 *M* EDTA$_0$ applied
↓	↓	↓
Leached with an excess of 0.01 *M* EDTA$_0$	0.001 *M* CuEDTA^{2-} (as 28 mm pulses for 83 days to give a total of 2316 mm) applied	Wrapped in polythene bags and kept for 0, 1, 7 or 30 days
	↓	↓
	Leached with 0.0025 *M* CaCl$_2$	Leached with 0.0025 *M* CaCl$_2$
↓	↓	↓
Destructively sampled	Destructively sampled	Destructively sampled

3.3 Results and discussion

3.3.1 EDTA and hydraulic conductivity

The air-filled porosity in the columns (calculated from the gravimetric water content and bulk density, assuming a particle density of 2.5 Mg m^{-3}) was between 0.1 and 0.15 m^3 m^{-3}, indicating better aeration in the Opotiki soil compared to the Manawatu fine sandy loam used in Chapter 2. This reflects the better-developed structure, and higher saturated hydraulic conductivity, in the Opotiki soil than the alluvial Manawatu soil.

In contrast to the Manawatu fine sandy loam soil, in Experiments A to E no ponding was observed in any of the Opotiki soil columns, so the saturated hydraulic conductivity remained higher than 28 mm h^{-1}. In fact the measured water content in the columns was between 0.58 and 0.61 m^3 m^{-3}, significantly lower than the porosity of 0.70 m^3 m^{-3}.

3.3.2 EDTA application to uniformly contaminated soil: Experiments A and B

3.3.2.1 *Chloride and EDTA*

The chloride and EDTA results are shown in Figures. 3.1a (Experiment A), 3.3a and 3.3b (Experiment B). Only the immediate leaching and one-month delayed leaching experiment results are shown here for easy comparison although there were four experiments carried out in Experiment B. The dimensionless concentrations shown were found as $(C - C_1)/(C_2 - C_1)$, where C is the measured effluent concentration, C_1 is the concentration of chloride or EDTA in the pre-leaching solution, and C_2 is the concentration of chloride or EDTA applied. There was no evidence of EDTA being adsorbed, as the breakthrough curves for EDTA show no retardation relative to the chloride data. Sometimes chloride adsorption is found in Allophanic soils however, if

$$\int_0^\infty \left(1 - C/C_2\right) d\frac{I}{I_0} = 1 \qquad (3\text{-}1)$$

where I_0 is the cumulative outflow in 1 PV, no adsorption or exclusion has occurred. This is consistent with the chloride BTC in Figure 3-1(a). Moreover, the calculated percentages of the applied chloride recovered in the leachate ranged from 97-99% for the four columns in Experiment B. Non-adsorption behavior of EDTA is in consistent with findings in Chapter 2 for Manawatu soil, but is not always the case, as discussed in Section 3.3.4. EDTA was also resistant to breakdown in the soil, even after a month. In the Experiment B, 54 µmol of EDTA exited with immediately leaching, and 53 µmol when leaching was delayed by 30 d. Both values are close to the 50 µmol of EDTA applied, with the difference attributable to either measurement error, or to not all the DOC being EDTA. As in the Manawatu soil, the EDTA and chloride breakthrough curves showed more dispersed but slightly lower peaks with a one-month delay compared with the immediate leaching, showing the effect of molecular diffusion during no flow periods.

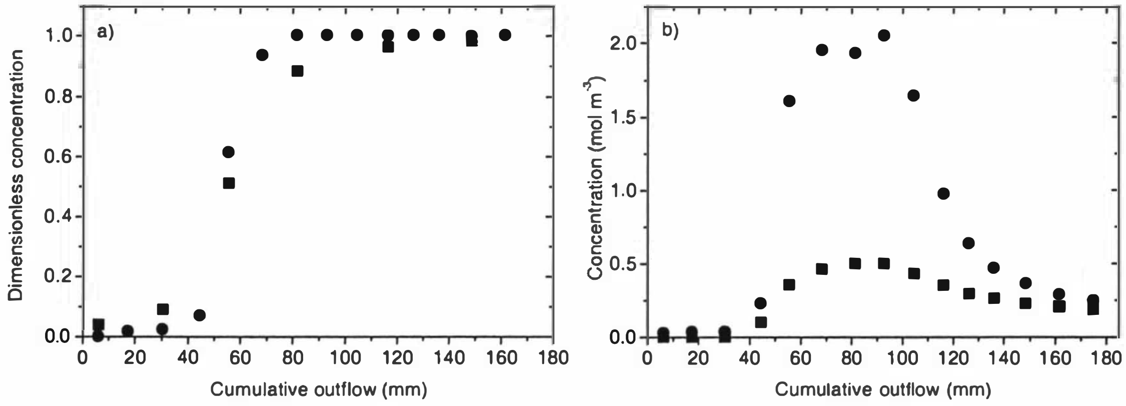

Figure 3-1 Breakthrough data for Experiment A (a) for chloride (●) and EDTA (■) (b) for copper (●) and iron (■).

3.3.2.2 *Copper and Iron*

The effluent concentrations for copper and iron in Experiment A are shown in Figure 3.1b. A small amount of zinc was also measured in the leachate (see below). As insignificant amounts of copper, iron and zinc were found in the leachate during pre-leaching, it is reasonable to assume that the metals present in the leachate following the addition of EDTA were brought into solution by complexation with EDTA. This was confirmed by speciation of the effluent using GEOCHEM-PC (Parker *et al.*, 1995) at various times during the experiment, which indicated that all of the copper, iron and zinc would have been complexed with EDTA at the measured effluent pH of between

5.3 to 5.6. Furthermore copper concentrations in the samples were the same before and after passing through the IC-Chelate cartridges. EDTA that was not complexed with copper, iron or zinc apparently leached with calcium, as insignificant amounts of aluminium and manganese were found in the effluent.

The 9500 μmol $EDTA_0$ applied in the Experiment A extracted 295, 140 and 26 μmol of copper, iron and zinc, respectively. Even though the amount of EDTA was way in excess of the amount needed to complex all the copper present in the soil, only 68% of the soil copper was leached, with about 90 mg kg^{-1} of copper remaining in the soil. This is higher than the 40 mg kg^{-1} remaining after the analogous experiment using Manawatu fine sandy loam in Section 2.3.3. This demonstrates the strong relationship between the organic matter content and the binding strength of copper (McGrath *et al.*, 1988; Barona *et al.*, 2001). The clay mineralogical differences between soils would have also contributed to this. In Manawatu soil the organic matter content was 5-9%, while for the Opotiki soil 12-16%. It is noteworthy that 80% of the copper extracted came out in the first 3 PV of leachate, and only 20% in the remaining 7 PV (for which data are not shown in Figure. 3.1b). So once the weakly adsorbed copper had been removed, the extraction process became much slower and less efficient.

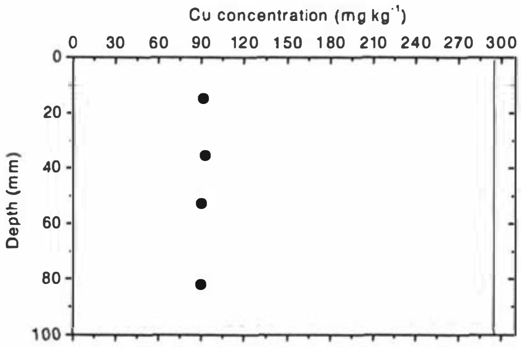

Figure 3-2 The initial (—) and the final measured copper concentrations in the soil (●) in Experiment A.

The final soil copper data are shown in Figure 3.2. EDTA leaching reduced the copper concentration from 290 mg kg^{-1} to about 92 mg kg^{-1}. However all but 28 μg g^{-1} of this remaining copper was extracted by shaking 1g of the soil with 25 ml of 0.01 *M*

$EDTA_0$ solution for 24 h, illustrating the greater efficiency of batch extraction compared to column extraction. This is presumably due to the breakdown in soil structure under batch conditions, allowing the EDTA to get at strongly adsorbed copper which is usually inaccessible (Kookana *et al.*, 1994).

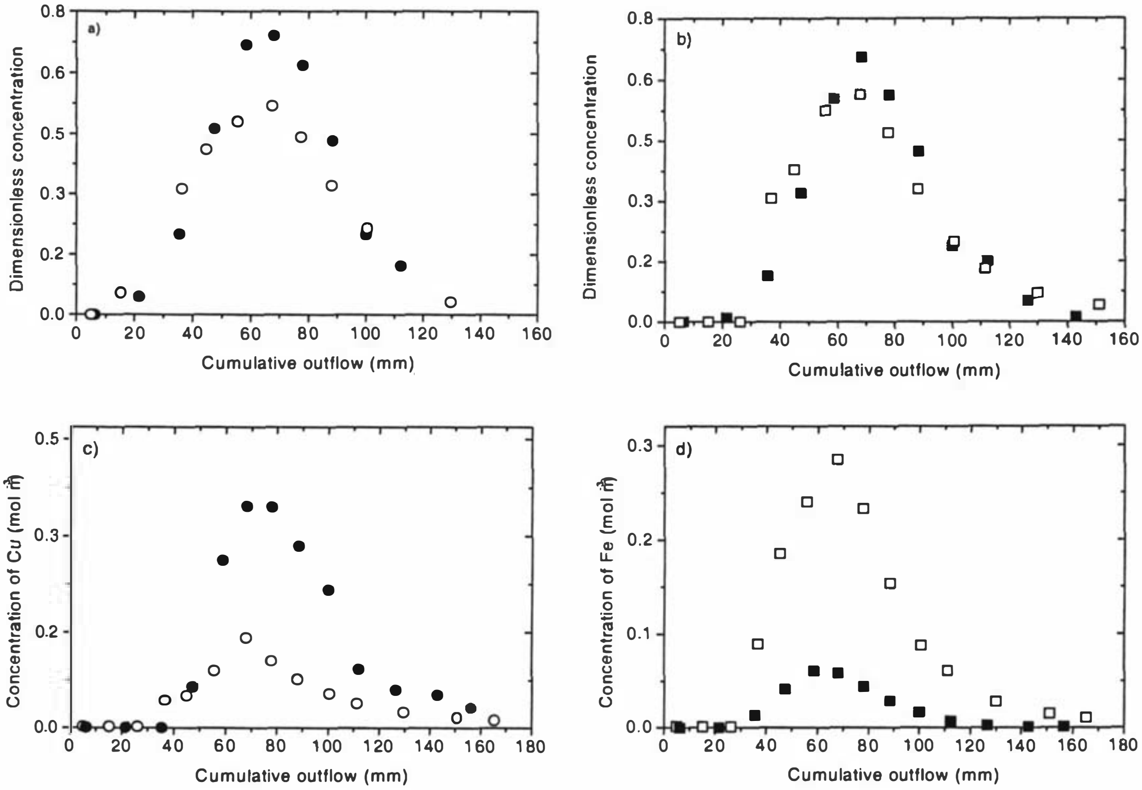

Figure 3-3 Breakthrough data for Experiment B, the closed symbols are for the column leached immediately and the open symbols are for the column left for a month before leaching. (a) Chloride (b) EDTA (c) Copper (d) Iron.

Experiment B was designed to find out how stable $CuEDTA^{2-}$ is in the soil. Four columns were set up to which 50 ml (31mm) pulses of 0.001 M $EDTA_0$ were applied and then left for different time periods (0, 1, 7 and 30 d) before leaching resumed with 0.0025 M $CaCl_2$. Figures 3.3c and 3.3d show the effluent copper and iron concentrations for columns leached immediately and 30 d after the $EDTA_0$ application, and Table 3.2 gives the amounts leached from all four columns. The total amount of copper leached declined markedly as the time the EDTA was left in the soil increased, while the amount of iron leached increased with increasing EDTA residence time. With a one-month delay, only 35% of the copper from the immediately-leached column was leached. Table 3.2 indicates that with a one-month delay only 24% of the EDTA left the soil with copper, compared to 70% in the immediately leached column. This increase in iron and decrease in the copper leaching with increased EDTA residence time is due to the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$. This is similar to the findings in the experiments using low-Cu Manawatu soil described in Section 2.3.3, however the amount of transformed is less. The effluent pH varied in Experiment B. It stayed between 5.5 and 5.6 in the immediately leached column, but increased from 5.6 to 6.1 in the column with the month's delay. This difference can be attributed to the consumption of hydrogen ions during the slow transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ which occurred over the month (Szecsody *et al.*, 1994).

Table 3-2 The iron and copper leached with varying EDTA residence times in Experiment B

Residence time (d)	Cu leached μmol	Fe leached μmol
0	35	5
1	28	10
7	23	18
30	12	24

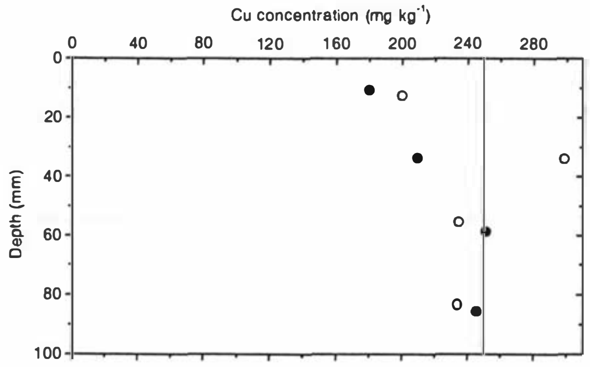

Figure 3-4 The initial copper concentration (—) and the final measured copper concentrations in the soil columns leached immediately (●) and a month (○) after $EDTA_0$ application in Experiment B.

The resident copper concentrations in the soil at the end of leaching for the 0 and 30 d EDTA residence time columns, in Experiment B are shown in Figure 3.4. Note that, in contrast to Experiment A, a large reduction in copper content occurred only in the top 30 mm. This is due to the much smaller amount of EDTA added. In fact, in the column left with EDTA in it for a month, the copper content at 35 mm depth increased, which is attributable to the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ and the associated release and adsorption of copper at that depth.

3.3.3 Leaching non-contaminated soil with CuEDTA: Experiment C

To specifically investigate the time dependent reaction of $CuEDTA^{2-}$ with the iron in soil, $CuEDTA^{2-}$ solution was applied to a column packed with Opotiki sandy loam soil obtained from an area that had not been contaminated with copper sprays. Each day for 83 days, 28 mm of 0.001 *M* $CuEDTA^{2-}$ solution (44.5 μmol) was added. Figure 3.5a shows the average daily bromide, copper and iron concentrations in the leachate. Of the 3685 μmol of the copper applied in total, 2860 μmol exited in the leachate and 720 μmol remained in the soil, which ended up with an average copper concentration of 444 g kg^{-1}. This left just 105 μmol of copper unaccounted for. The 726 μmol of iron in the leachate equaled almost exactly the amount of copper staying in the soil, confirming that the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ was the only significant reaction involving EDTA, and that none of the $Fe(III)EDTA^{-}$ was adsorbed. The iron data showed a fast transformation (peak) followed by a slower transformation (plateau) occurred as seen in Figure 3.5a. This is further discussed in Chapter 6, where the experiment is modeled. As the iron concentration in the leachate during pre-leaching was only 0.0002 mol m^{-3}, it is reasonable to assume that virtually all the iron eluted was complexed with EDTA.

The application of the $CuEDTA^{2-}$ for only about an hour per day, with a 23 h rest period in between applications, and the collection of each day's leachate in three aliquots, allowed the rate dependence of the chemical reactions to be demonstrated. Figure 3.5b shows the bromide, copper and iron leachate concentrations in each aliquot during the first twelve days (300 h) of the experiment. As expected the copper concentration in the three aliquots collected on each day increased with time. However the concentration in the first aliquot on the following day is lower than in the last aliquot on the previous day. After the first 50h the iron concentration shows complementary behaviour, decreasing during each flow event, and then increasing immediately after the non-flow periods. This behaviour is explainable as the gradual replacement of CuEDTA^{2-} in the soil solution with Fe(III)EDTA^{-} during the 23 h non-flow period each day. The behaviour became less pronounced with increasing time, as the system approached equilibrium with the invading CuEDTA^{2-} solution. On the other hand, bromide concentration in the three aliquots collected on each day increased with time, and also increased after the no flow period.

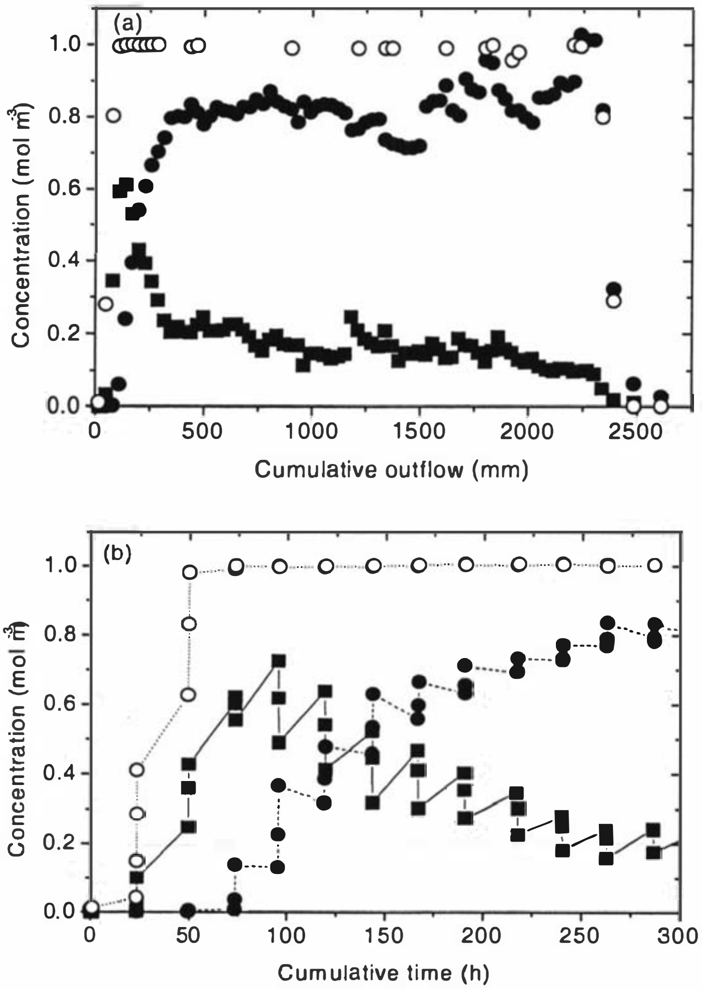

Figure 3-5 Measured effluent concentrations for Experiment C of bromide (○), copper (●), and iron (■) as a function of (a) cumulative outflow (b) cumulative time

Figures 3.5a and 3.5b show that during the first 80 h of the experiment the molar concentration of copper plus iron was less than the concentration of bromide, indicating that some adsorption of $CuEDTA^{2-}$ occurred. But in contrast, during the final step of leaching with 0.0025 M $CaCl_2$, Figure 3.5a shows the decline in copper tracked that of the non-reactive bromide tracer. Also the copper leached during this final phase was 110 µmol, which is only slightly higher than the 99 µmol which would have been in the soil solution prior to the application of the $CaCl_2$. These results indicate that negligible desorption of $CuEDTA^{2-}$ occurred during this final leaching. So either none was adsorbed at this stage of the experiment, or if it was the adsorption was not reversible. I believe that the adsorption was reversible, and that this contrasting behavior at the beginning and end of the experiment was probably due to the gradual increase in pH brought about by the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$. It was noted that the first effluent aliquot had a pH of 4.5 and the last, 83 days later, had a pH of 6.2. This is due to the hydrogen consumption during the $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ transformation. As Brooks *et al.* (1996) showed, the higher the pH, the less likely it is that EDTA is adsorbed, so the $CuEDTA^{2-}$ that was adsorbed had gradually come back into solution as the pH rose. As the total iron plus copper exiting is equal to the mol of EDTA applied, EDTA was not adsorbed at the end.

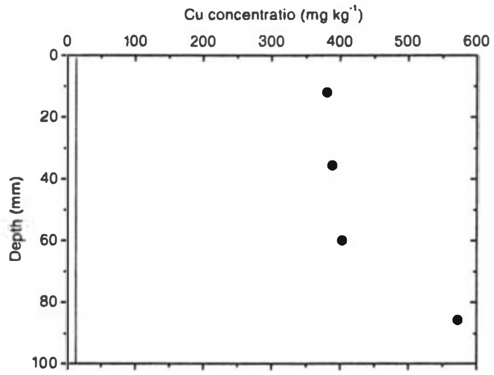

Figure 3-6 Measured initial (—) and final (•) soil copper as a function of depth in Experiment C.

Figure 3.6 shows the final distribution of copper in the soil as a function of depth. Mass balance calculations indicate that 19% of influent $CuEDTA^{2-}$ was dissociated to form Fe(III)EDTA. In other words, only about 397 $\mu g\ g^{-1}$ of iron reacted with $CuEDTA^{2-}$ even though the soil contained a large amount of iron, and iron has a very high formation constant for EDTA. This again clearly indicates that all the iron present in the soil is not readily available for reaction with EDTA under the prevailing experimental conditions.

3.3.4 EDTA application to non-uniformly contaminated soil: Experiments D and E

Experiments D and E involved identical treatments to Experiments A and B, but a different soil. The top 30 mm depth of soil in the columns consisted of the copper contaminated Opotiki soil used in Experiments A and B while the underlying 70 mm of soil was the uncontaminated Opotiki soil used in Experiment C.

3.3.4.1 Bromide and EDTA

The EDTA breakthrough curve for Experiment D in Figure. 3.7a shows obvious retardation compared to the non-reactive halide tracer, indicating some adsorption of EDTA by the soil, as in Experiment C. This is in contrast to findings in Experiment A where, in an analogous experiment, EDTA was not adsorbed. This difference is probably due to the low pH of 4.5 (in water) in the uncontaminated soil relative to that of the contaminated soil, which was 5.6. The pH of the effluent reflected this difference in soil pH. In Experiment D it was between 4.5 and 4.6, while the effluent pH for the comparable Experiment B was between 5.3 and 5.6. Brooks *et al.* (1996) similarly reported greater retardation of $Co(II)EDTA^{2-}$ and $Co(III)EDTA^{-}$ transport through ferrihydrite when they decreased the pH. It is noteworthy the difference in the soil pH is not due to the copper contamination but due to the lime application to the contaminated soil.

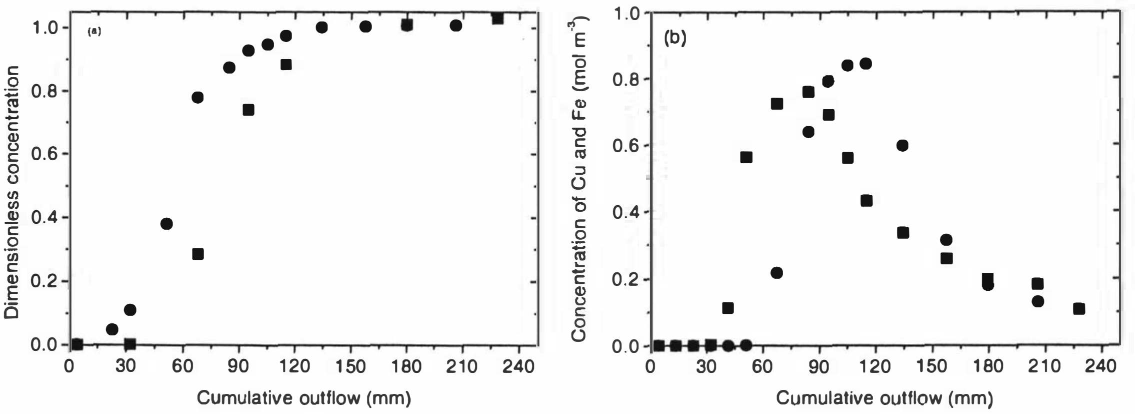

Figure 3-7 Breakthrough data for Experiment D. (a) Measured breakthrough data for bromide (●) and EDTA (■). (b) Measured breakthrough data for copper (●) and iron (■).

Also in Experiment E, Figure 3.9 a and 3.9b show that the observed exiting pulse of EDTA from the column that was leached immediately had a similar retardation to that observed in Experiment D, and its amplitude was lower than that of chloride. However, Figure 3.9b shows the peak EDTA concentration to be greater for the column in which leaching was delayed for a month than the immediately leached one, and also it does not show any retardation. This suggests that the inferred EDTA value is too high due to the presence of organic compounds other than EDTA affecting the DOC analyses in this case, for the reasons discussed in relation to the comparable study reported in Section 2.3.3. This will be discussed more in Chapter 6. The effluent pH was 4.5 in the immediately leached column however it rose to 4.8 in the delayed experiment, probably for the same reason discussed for Experiment B in Section 3.3.2.2.

3.3.4.2 Copper and Iron

Figure 3.7b shows the copper and iron concentrations in the effluent for Experiment D. Due to the smaller amount of copper present in the soil compared to Experiment A, much less copper was leached (110 μmol compared to 295 μmol). Also 118 μmol of iron and 23 μmol of zinc were leached. In contrast to Experiment A, more iron was leached by the same amount of EDTA, due presumably to the lower copper availability and the greater availability of iron at the lower pH in this experiment.

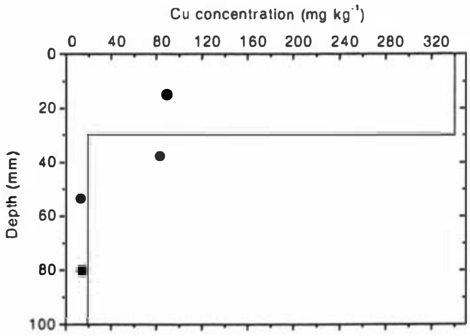

Figure 3-8 The initial copper concentration (—) and the final measured copper concentrations in the soil column (●) in Experiment D.

Leaching with EDTA brought down the copper concentration from 340 to 85 mg kg^{-1} (Figure. 3.8) in the top 30 mm of the copper contaminated soil. The 85 mg kg^{-1} of copper that remained at the surface soil without being leached by the EDTA is a little lower than the non-extractable copper in Experiment A (which was 90 mg kg^{-1}). The copper concentration in the soil at the end of leaching showed little or none of the copper removed from the top 30 mm was re-adsorbed in the almost copper free soil below. This can be attributed to the short residence time of the CuEDTA^{2-} in the soil, and the relative slowness of the transformation reaction involved.

Figure. 3.9 shows the results of Experiment E where 50 ml (31mm) pulses of 0.001 *M* EDTA$_0$ (50 μmol) were left in soil columns for 0 and 30 d before leaching with 0.0025 *M* $CaCl_2$. The amounts of copper leached were 12 μmol with continuous leaching and 0.6 μmol with delayed leaching. The corresponding amounts of iron leached were 10 μmol and 40 μmol. Also 9 μmol of zinc was eluted from the immediately leached column, but virtually none from the column with the month's delay. The amounts of copper leached with both immediate and delayed leaching were much lower than in Experiment B (Section 3.3.2). This was due to the smaller copper content initially present in the column in this study. The appearance of zinc in the leachate in Experiments D and E was probably also be due to the lower levels of copper in these experiments compared to Experiments A and B and to the similar formation constants of ZnEDTA^{2-} to the CuEDTA^{2-} as discussed in Chapter 1.

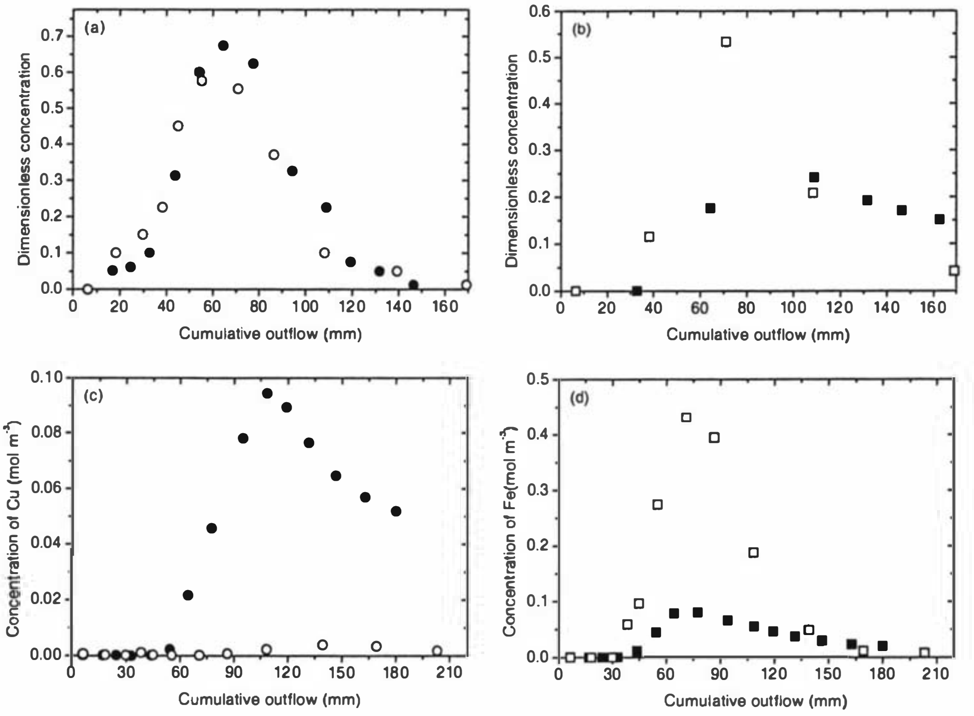

Figure 3-9 Breakthrough data for Experiment E. The filled-in symbols are for the column leached immediately and the open symbols are for the column left for a month before leaching. (a) Chloride (b) EDTA (c) Copper (d) Iron.

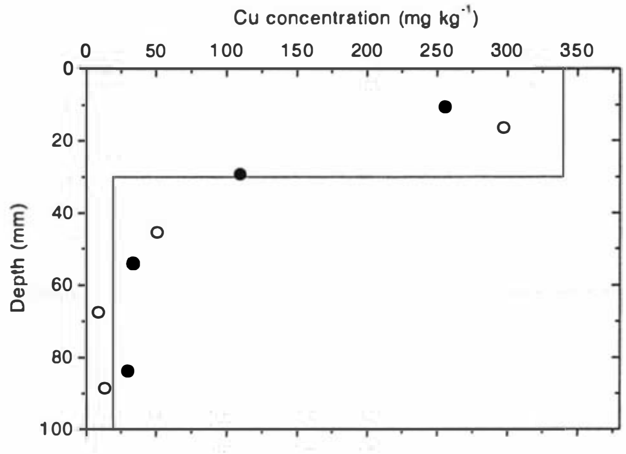

Figure 3-10 The initial copper concentration (—) and the final measured copper concentrations in the soil column leached immediately (●) and a month (○) after $EDTA_0$ application in Experiment E

Figure. 3.10 shows the copper concentration in the two soil columns at the end of Experiment E. Very little copper was leached from the contaminated soil near the surface due to the small amount of EDTA applied. The increased soil copper concentrations at lower depths of the immediate leached column could be due to the incomplete leaching after the EDTA pulse application.

3.4 Conclusions

Leaching with an excess 0.01 *M* EDTA leached more than half of the copper from both uniformly and non-uniformly contaminated soil in repacked columns. Most of this copper was removed in the first 3 PV. About 90 mg kg^{-1} of copper remained in the soil as EDTA-non extractable copper during flow, in contrast to the 40 mg kg^{-1} remaining in Manawatu fine sandy loam. This is attributable to the higher organic matter content in the Opotiki soil compared to the Manawatu soil and to the type of organic matter in the soils. A substantial amount of iron was also leached. The copper contaminated soil with a pH of 5.6 did not adsorb EDTA, but the uncontaminated soil from nearby with a pH of 4.5 did adsorb EDTA to some extent.

In the columns with non-copper contaminated soil, EDTA was adsorbed. The observed adsorption is probably due to the lower pH of the uncontaminated soil, which in contrast to the contaminated orchard soil, had apparently not been limed.

When a small pulse of EDTA was applied to copper contaminated soil and left there for up to a month before leaching, there was a time-dependent drop in the amount of copper leached and a corresponding increase in the amount of iron leached. This trend was observed in both uniformly copper contaminated and non-uniformly contaminated columns. A month's delay reduced the amount of copper leached by at least 65%. Experiment C, in which pulses $CuEDTA^{2-}$ were applied daily to a low copper soil for three months, showed that the time-dependent drop in copper concentration in the leachates, and the corresponding increase in iron concentration, was $CuEDTA^{2-}$ slowly changing to $Fe(III)EDTA^{-}$, and the re-adsorption of the Cu^{2+} released. The results show that the effect of the soil copper ageing and concentration on the stability of $CuEDTA^{2-}$ are inseparable and hence need further investigation.

4 EDTA-enhanced copper transport through undisturbed contaminated soil

4.1 Introduction

The results from the studies described in Chapters 2 and 3 provide a good understanding of EDTA-enhanced copper transport, and of the temporal stability of $CuEDTA^{2-}$ in repacked soil. A question now arises. Is the information obtained from a repacked soil of use in the field? Many investigators of solute transport have concluded that there are fundamental differences between the transport characteristics of repacked soil and the structured soil in the field. For example the dispersivity values measured for field-scale transport is over three times greater than those obtained from packed columns studies (Starrett *et al.*, 1996). This is mainly because sieved and repacked soils do not have the same range of pore sizes, or the same pore connectivity, as found under field conditions. As a result, BTCs for solutes, even non-reactive solutes, from undisturbed cores are often quite different to those of repacked cores, under otherwise similar experimental conditions (Anderson and Bouma, 1977; Perfect and Sukop, 2001). Even greater differences could be expected for reactive solutes for the reasons discussed below.

Further as discussed in Chapter 1, structural voids or other geometric anomalies in intact soil can create preferential flow pathways that channel water and solutes rapidly through a small fraction of the solute transport volume. Consequently, the time scales for mass transfer between regions in which water flows at different rates can become very short in the field. Hence the transformation of information, gathered using repacked soil, to the field scale cannot be achieved without considering the differences in the soil structure.

In the reactions described in the previous chapters, chemical equilibrium was never attained. Therefore, it was concluded that the copper or iron interaction with EDTA, and the $CuEDTA^{2-}$ interaction with soil iron, all involved time-dependent reactions. Solute transport under non-equilibrium conditions is even more complicated by spatial heterogenity in both the physical and chemical properties of porous media. Just as the physical properties vary spatially in field soil, it is also logical to expect the chemical properties to be spatially variable. Copper is usually concentrated in the surface soil at contaminated sites, due to its propensity for adsorption by soil organic matter. Therefore, depending on the spatial distribution of soil organic matter, the proximity of the copper adsorption sites to the major water flow pathways the time-dependent processes occuring in intact soil and repacked soil could be different. Hence the BTC of copper following EDTA application could also be different.

Described here is a study conducted in the laboratory using intact columns of soil brought from the field to the laboratory. The laboratory was used, as better control of the experimental conditions was possible there than can be achieved in the field. This study was aimed at obtaining further understanding of EDTA-enhanced copper transport, and its temporal stability, in undisturbed soil where it is influenced by soil heterogeneity in both transport-related properties and the copper distribution. Leaching was done under unsaturated conditions.

4.2 Materials and methods

Three soil cores were collected, in close proximity to each other, at the Opotiki site where the soil for the experiments described in Chapter 3 was obtained. Some of the chemical characteristics of the soil are given in Section 3.2.1. After the vegetation had been removed, plastic tubes 100 mm in internal diameter and 150 mm long were pressed into the soil, then the cores were retrieved by excavation and transported to the laboratory. These three cores were used for two experiments. Several smaller 35-mm diameter soil cores were taken adjacent to the larger-diameter cores, in order to measure the initial copper distribution in the soil profile.

Apparatus similar to that described by Magesan *et al.* (1995) was used for the application and collection of the influent and effluent solutions under unsaturated conditions. In brief, a disk permeameter sat atop each soil column to allow solution entry at some pre-set pressure potential, which was maintained by a bubbling tower and vacuum system. A similar porous disk and suction apparatus underneath allowed solution removal while it maintained the same pressure potential at the base. The imposed pressure potential at the top and bottom was –100 mm, which resulted in a flow rate of about 24 mm h^{-1} for the core used in the first, and of 14 and 7 mm h^{-1} for the two cores used in the second experiment.

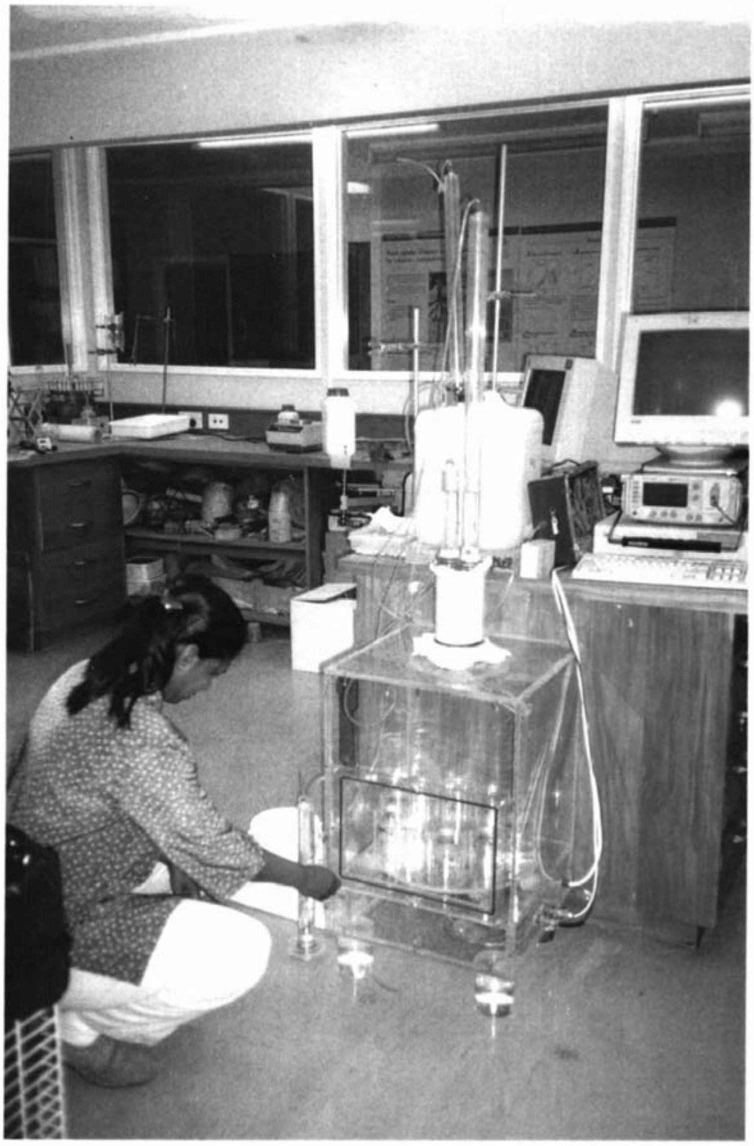

Figure 4-1 Experimental set up on undisturbed core under unsaturated conditions

The influent $EDTA_0$ solutions used in all experiments were prepared using Na_2H_2EDTA and $CaBr_2$ by mixing them at the same molarity level (EDTA:Br). The solutions were then brought to pH 6.2 by the addition of KOH.

Each core was first pre-leached with about 87 mm (1 PV) of 0.0025 *M* $CaSO_4$ solution. In the first experiment the infiltrating solution was then quickly changed to 0.01 *M* $EDTA_0$ solution and this was applied continuously for about 5 PV. In the second experiment, 61 mm (0.7 PV) of 0.001 *M* $EDTA_0$ was applied to the two cores. After the application of $EDTA_0$ solution, the treatment of the cores differed. The first core was immediately leached with about 4 PV of 0.0025 *M* $CaSO_4$ solution and was then allowed to drain. The second core was removed from the leaching apparatus, covered to prevent evaporation, and left for a month. Then 4 PV of 0.0025 *M* $CaSO_4$ solution was applied. Throughout the experiments effluent aliquots were obtained using an automatic leachate collector.

At the conclusion of leaching, each core was extruded from its plastic tube, cut into sections, weighed, and then the water content and copper concentration was measured, as described in Section 2.2.3.

4.3 Results and discussion

4.3.1 Initial soil copper distribution with depth

This paragraph describes how the initial copper concentration with depth was obtained, as there was no way of non-destructively measuring the initial copper distribution in the cores. As mentioned earlier, six smaller cores were taken from adjacent to each large core and the copper distribution in them measured. But due to soil variability, this need not necessarily give an accurate indication of the copper concentration in the large cores. However, by adding the amount of copper leached and left in the soil after leaching, the total amount of copper initially present in each of the three large soil cores was calculated. To ensure the correct mass balance for each core those total values were used, in conjunction with the shape of the distribution measured in the smaller soil cores taken adjacent to the large cores, to infer the initial copper distribution in each of the large core.

4.3.2 EDTA and hydraulic conductivity

During the intact core experiments using the Opotiki soil, the gravity induced flow at −100 mm pressure head varied by less than 15%, except for the core in which leaching was delayed for a month after EDTA application. In that core the flow rate during the final leaching dropped to 3 mm h^{-1} from the 7 mm h^{-1} found during pre-leaching and EDTA application a month earlier. As just the removal and replacement of the disk permeameter can cause such changes, it was concluded that the effect of the EDTA on unsaturated hydraulic conductivity was negligible or slight.

Significant preferential flow was not observed in any of the experiments, probably due to the unsaturated flow conditions.

4.3.3 Continuous application of EDTA to the contaminated soil

4.3.3.1 EDTA and bromide

The two experiments involved the same treatments as the two experiments A and B described in Section 3.2.2.1, and D and E described in Section 3.2.2.3, but used intact soil cores of Opotiki sandy loam rather than repacked soil columns. In the first experiment 0.01*M* $EDTA_0$ was applied continuously and for the second experiment a pulse of 0.001 *M* $EDTA_0$ was applied to two columns, then one was leached immediately and the other after a month.

Figure 4-2 shows the BTC of non-reactive solute obtained from the repacked and intact cores of the Opotiki soil. Bromide BTC from the intact core is more dispersed compared to the repacked column, which shows the well-developed structure of the Opotiki soil.

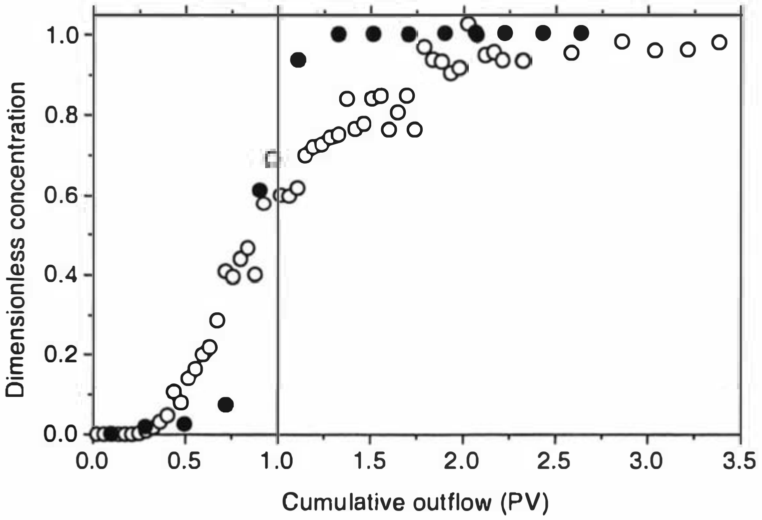

Figure 4-2 Breakthrough curves for the non-reactive solute obtained from repacked and intact columns. Open symbols are for the intact column and closed symbols for the repacked column.

Figure 4-3a shows the dimensionless effluent concentrations of bromide and EDTA as a function of cumulative outflow when 0.01 *M* $EDTA_0$ was applied. In contrast to Figure 3-7a shown in Section 3.3.4.1, the EDTA data is only slightly retarded relative to the bromide, indicating little EDTA adsorption. This is probably due to the soil pH in the lower part of the intact soil core being higher than in the soil used in the Experiment D described in Section 3.3.4.1. The pH there was 4.5 compared to 5.0 in this experiment. However, the EDTA retardation in this experiment is more than for the EDTA data shown in Figure 3-1a for the Experiment A (Section 3.3.2.1), performed on uniformly copper contaminated soil where the pH was 5.6.

4.3.3.2 Copper and Iron

The 40 000 μmol of EDTA applied to the soil only extracted 641, 75 and 1076 μmol of copper, zinc and iron respectively in a cumulative volume of about 7 PV of leachate (Figure 4-3b). The 641 μmols of copper were 54% of that present in the soil. The GEOCHEM speciation program showed that the Cu, Fe and Zn in the leachate were entirely complexed with EDTA. The finding that less copper than iron was leached in this experiment contrasted with the similar experiment described in Section 3.3.2.2. However, these results are similar to the findings from the Experiment D (Section 3.3.4.2) where about same amount of copper and iron was leached. This difference is probably due to the smaller amount of copper present in the intact-core and the non-uniformly copper contaminated repacked column relative to the uniformly contaminated repacked column.

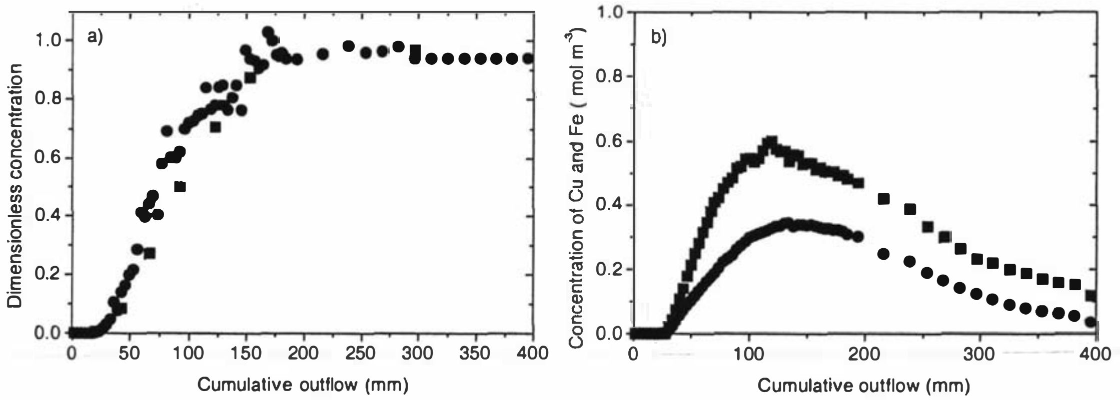

Figure 4-3 Breakthrough data for the intact core in the first experiment. (a) Normalised breakthrough data for bromide (●) and EDTA (■). (b) Measured breakthrough data for copper (●) and iron (■).

Figure 4-4 shows the distribution of copper in the soil at the end of the leaching experiment, and also the inferred initial copper distribution in the soil core. EDTA application brought the copper concentration down from 240 mg kg^{-1} to 80 mg kg^{-1} in the top 30 mm of soil. In contrast, in the corresponding experiment described in Section

3.3.2.2 using repacked Opotiki soil, the same treatment could only reduce the copper concentration to 90 mg kg^{-1}. It could be that sieving and homogenizing the soil, and then leaving it for some days in the laboratory, changed the organic matter - copper relationship in a way that reduced the amount of non EDTA-extractable copper, perhaps partly due to the increased pH compared to the intact soil. It was surprising to see how effective the EDTA was in removing copper from the intact soil, given the non-uniform flow pathways usual in intact soil with well-developed structure. This was probably due to the highly permeable nature of the soil and the flow being under non-ponding flow conditions (as occur in the field in this soil). If the leaching had been under saturated conditions and the soil had been less permeable and ponding had occurred, then the flow probably would have been highly preferential, and much less effective in removing the copper.

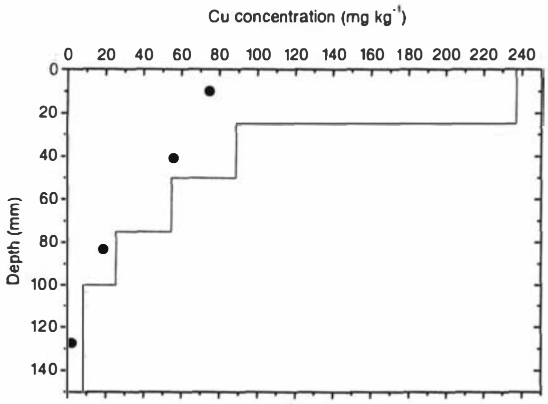

Figure 4-4 The initial copper concentration (—) and the final measured copper concentrations in the soil core (●) in the first experiment.

A further 56 mg kg^{-1} of the remaining 80 mg kg^{-1} of copper at the surface soil was extracted by the batch method. This is in consistent with the results of the experiment described in Section 3.3.2.2 for repacked soil, and again illustrates the higher efficiency of the batch extraction method.

4.3.4 $CuEDTA^{2-}$ stability with varying residence time

4.3.4.1 EDTA and bromide

Figures. 4-5a shows bromide and EDTA effluent concentrations as a function of cumulative outflow for the column leached immediately after the $EDTA_0$ application. The dimensionless concentrations shown were found as $(C - C_1)/(C_2 - C_1)$, where C is the measured effluent concentration, C_1 is the concentration of bromide or EDTA in the pre-leaching solution (i.e. zero), and C_2 is the concentration of bromide or EDTA in the $EDTA_0$ solution. Figure 4-5b shows the comparable data for the column with a month's delay before leaching. The calculated percentages of the applied bromide recovered in the leachate were 115% with immediate leaching and 94% with delayed leaching. These are reasonable recoveries, considering that some interference from nitrate occurred in the HPLC-AS5 column used to measure bromide concentration. With immediate leaching, the EDTA breakthrough data show significant retardation and tailing relative to bromide (Figure 4-5a). This indicates some adsorption of EDTA by the soil. This behavior is less evident for the column in which leaching was delayed for a month (Figure 4-5b). Likely reasons for this are given when the simulations are discussed in Chapter 6. Adsorption of $0.001M$ $EDTA_0$ in the immediately leached column is more pronounced than the adsorption shown in the first experiment where $0.01M$ $EDTA_0$ was used (Figure 4-2).

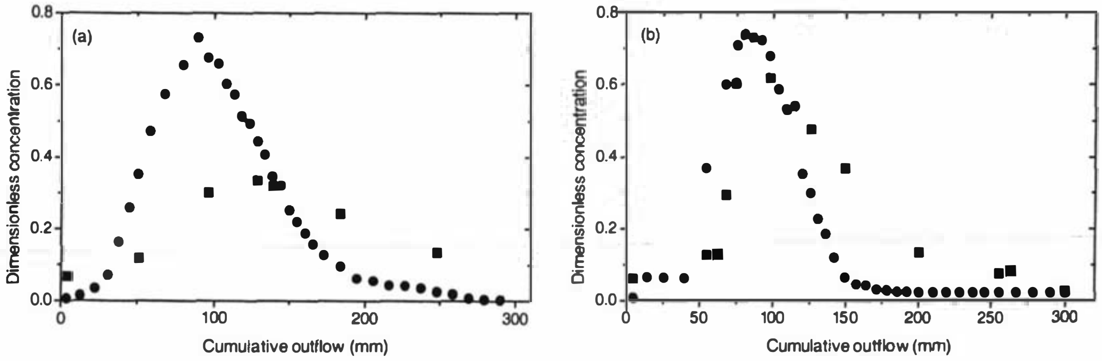

Figure 4-5 Normalised breakthrough data for bromide (●) and EDTA (■) for the second experiment. (a) Immediately leached column (b) one month delayed leached column.

4.3.4.2 Copper and Iron

While the one-month pause in leaching when the cumulative outflow was 61 mm did not cause any noticeable discontinuity in the bromide concentration (Figure 4-5b), the pause induced a pronounced drop in the copper concentration when leaching resumed, and a large increase in the iron concentration (Figure 4-6b). These changes reflect the time-dependent chemical reaction of CuEDTA^{2-} in the soil. As discussed in Chapter 1, flow interruption has frequently been used to study the effects of physical and chemical non-equilibrium in soil (Murali and Aylmore, 1980; Brusseau *et al.*, 1989). The absence of a concentration drop in the non-reactive bromide tracer concentration shows that physical non-equilibrium was not a major factor in this experiment, verifying that the discontinuities in the copper and iron concentrations were due to the slow chemical transformation of CuEDTA^{2-} to Fe(III)EDTA^{-}.

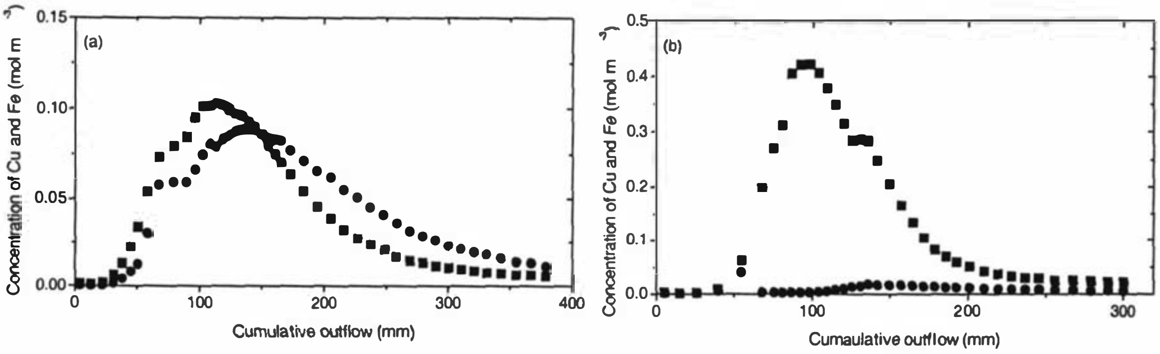

Figure 4-6 Measured breakthrough data for copper (●) and iron (■) for the second experiment. (a) Immediately leached column (b) One month delayed leached column.

Leaving the 480 μmol of EDTA$_0$ pulse in the soil for a month caused a decrease from 126 μmol to 23 μmol in the amount of copper leached. The increase in iron leached was from 116 μmol to 286 μmol. This decrease in copper and increase in iron is roughly similar to the data for the corresponding experiment described in Sections 3.3.2 and 3.3.4. The variation in the amount of CuEDTA^{2-} changing to Fe(III)EDTA^{-} in these experiments was probably due to the different pH, copper distribution and flow pathway heterogeneity.

Figures 4-7a and 4-7b show the distributions of copper in the soil after immediate and delayed leaching. Figure 4-7a shows that the addition of just 61 mm of 0.001 *M*

EDTA, followed within a few days by rain or irrigation, could reduce the copper concentration in the top 20 mm of the soil from 300 mg kg^{-1} to 180 mg kg^{-1}. In the delayed leaching experiment (Figure 4-7b), except in the top 20 mm, the final copper concentration was generally greater than that initially present. Following the application of the 61 mm $EDTA_0$ pulse, some copper, after complexing with the EDTA, would have traveled all through the column due to the relatively high dispersivity. The presence of some EDTA and copper in the first 61 mm of leachate confirms this. Hence, in contrast to the Experiment B described in Section 3.3.2 using repacked soil, where most of the copper was re-adsorbed in a narrow band at a depth of 35 mm, Figure 4-7b shows that in the intact soil the copper was re-adsorbed over most of the 150 mm column depth.

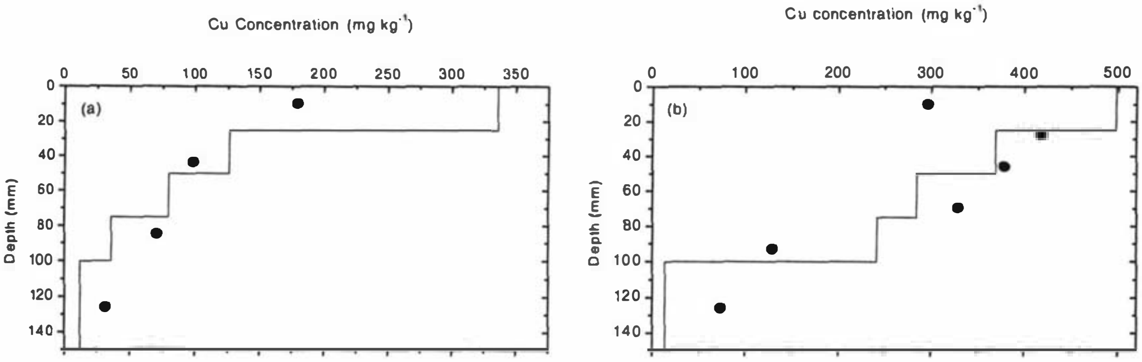

Figure 4-7 The initial copper concentration (—) and the final measured copper concentrations in the soil core (●) in the second experiment. (a) Immediately leached column (b) One month delayed leached column.

4.4 Conclusions

In the undisturbed columns, no obvious preferential flow occurred during the experiments and hence, the EDTA was as effective in leaching the copper as it was in the repacked soil. But the BTC was more dispersed in the intact cores than the repacked columns.

Leaching with excess of 0.01 *M* EDTA reduced the copper concentration in the top 25 mm of the intact core from 240 to 80 mg kg^{-1}, despite the less uniform flow pathways. EDTA was only slightly retarded relative to the bromide, indicating little EDTA adsorption. The adsorption was less in intact cores compared to the repacked column with non-uniformly contaminated soil, but greater than in the column with uniformly contaminated soil.

A month's delay in leaching the pulse of EDTA reduced the amount of copper leached to a negligible amount and increased the amount of iron leached. This was due to the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$, as explained for the repacked soil in Section 3.3.2. The absence of a drop in the bromide concentration following the resumption of the leaching suggests that physical (transport controlled) non-equilibrium was not a factor, and that the sharp concentration changes observed in the copper and iron concentrations were primarily due to time-dependent chemical reactions. The copper released following the transformation reaction of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ was re-adsorbed by the soil over the whole 150-mm column depth. This can be attributable to the more dispersed flow.

5 Plant uptake and leaching of copper during EDTA-enhanced phytoremediation of repacked and intact contaminated soil

5.1 Introduction

Phytoremediation has been suggested as an economic and environmentally sound method for heavy metal remediation of moderately polluted soils since plant cultivation and harvesting are relatively inexpensive processes compared to conventional engineering-based solutions (Cunningham *et al.,* 1996; Brooks, 1998). Although several conditions must be met in order for phytoremediation to be effective, the availability of the target metal in the soil is the first critical factor for the plant uptake to occur.

More recently, many glass house studies and a few field studies (Kayser *et al.*, 2000) have demonstrated the potential for chelates to enhance the plant uptake of metals that exist in soil predominantly in a sorbed state. A range of metals have been targeted, either individually, or collectively in a multi-metal contaminated environment. The metals that have been targeted individually are Pb (Blaylock *et al.*, 1997; Epstein *et al.*, 1999; Cooper *et al.*, 1999), Zn (Ebbs and Kochian, 1998), Cs (Lasat *et al.,* 1998), U (Huang *et al.,* 1998) and Au (Anderson *et al.,* 1998). Whereas Lombi *et al.* (2001); Grčman *et al.* (2001) and Kayser *et al.* (2000) have evaluated chelate-assisted phytoremediation in a multi-metal contaminated environment.

This chelate-enhanced phytoremediation approach makes use of high-biomass crops that are induced to take up large amounts of a metal when its mobility in soil is enhanced by the chelates. One crop plant that produces high rates of biomass under field condition, and also has the capacity to accumulate substantial metal concentration in its shoots, is *Brassica juncea* (Kumar *et al.,* 1995; Blaylock *et al.,* 1997). Of the chelates tested for this technology, ethylene diamine tetra-acetic acid (EDTA) has been found to be the most effective (Brooks, 1998; Blaylock *et al.,* 1997; Huang *et al.*, 1997; Ebbs and Kochian, 1998; Epstein *et al.,* 1999; Deram *et al.,* 2000; Grčman *et al.*, 2001; Lombi *et al.,* 2001).

As an initial step towards EDTA-enhanced copper phytoremediation, the mobility of copper in contaminated soils following EDTA application was studied in repacked soil columns and discussed in Chapters 2 and 3. Then, in Chapter 4, EDTA-enhanced copper transport, and its temporal stability, in undisturbed contaminated soil has been described. These studies clearly showed the ability of EDTA to enhance the copper concentration in the soil solution of contaminated soils, and so indicate that copper is potentially available for uptake by plants used for phytoremediation.

It was also clear from these studies that if the copper so mobilised is not all taken up by plants, there is a risk of contamination of groundwater. However, the EDTA-enhanced phytoremediation studies published to date, and discussed above, have focussed on plant uptake. Little attention has been given to the risk of target metals solubilised by the chelate being leached below the root zone to the ground water. The exception is the study of Grčman *et al.* (2001). While they found that EDTA did enhance heavy metal uptake by *Brassica rapa*, it also resulted in 38% of the Pb, 10% of the Zn and 56% of the Cd present being leached out of the soil. Clearly the potential mobility of chelated metals during phytoremediation needs to be evaluated before commercialisation of this technology is attempted.

The key to chelate-induced phytoremediation is to maintain an increased concentration of the target metal concentration in the root zone soil solution long enough for a significant amount of plant uptake to occur. Hence, the soluble target metal-EDTA complex needs to be relatively stable. Although EDTA itself is quite stable in soil, many metal-EDTA complexes are not. In particular, as discussed already, $CuEDTA^{2-}$ has been found to react with soil iron over time, leaving the more stable $Fe(III)EDTA^{-}$ in solution, with the copper released being re-adsorbed by the soil. Therefore it seemed worthwhile to study the effect on plant uptake of numerous small EDTA applications over time compared to just one or two widely spaced applications.

The chelate-induced phytoremediation studies described above used repacked soil. Water movement and root growth in repacked soil may not be the same as in soil with its structure intact and thus quite different pore geometry.

In this chapter an investigation of the possibility of EDTA-enhanced phytoremediation of copper contaminated soil using a copper tolerant grass, *Agrostis tenuis,* is described. The main objective of our study was to investigate the relative importance of plant uptake and leaching of copper following the addition of EDTA. Another objective was to compare EDTA-induced copper uptake by grass grown in repacked soil columns, with that of grass in intact soil cores. The third objective was to compare the effect on the plant copper uptake of numerous small EDTA applications over time, as compared to just two widely-spaced applications. The experiments described in this chapter were carried out both on repacked copper contaminated soil, and on intact cores of the same soil.

5.2 Materials and methods

A copper-tolerant grass from Parys Mountain, Amlwch, Anglesey, UK, *Agrostis tenuis* was used in this study. A copper tolerant grass was used rather than a hyperaccumulator, as the copper hyperaccumulators discovered to date have a small biomass, and are not tolerant of temperate climatic conditions, as they are native to the Democratic Republic of Congo (Deram *et al.*, 2000).

Opotiki soil was collected from the same orchard site where the soil for the experiments described in Chapter 3 and 4 was collected.

Two experiments were conducted, which will be referred to as I and II. Experiment I used repacked soil columns while Experiment II used intact soil cores. The soil for Experiment I was collected from the top 100 mm of the A horizon in the copper contaminated orchard and passed through a 2 mm nylon sieve while still moist. A soil depth of 150 mm was packed at a bulk density of 0.75 Mg m^{-3} into plastic tubes with an internal diameter of 100 mm and a nylon mesh base. The average acid-extractable copper content in the sieved soil was 276 mg kg^{-1}. Experiment II used intact cores collected from the same orchard site. Plastic cylinders 150 mm long and 100 mm in diameter were pressed into the soil with minimal disturbance to the soil, and the cores retrieved by excavation. The bulk density ranged from 0.91 to 0.96 Mg m^{-3}. Six smaller 35 mm diameter soil cores were taken adjacent to the larger cores to measure the copper distribution in the soil profile. The cores and repacked columns were placed in a glasshouse and grass seed (*Agrostis tenuis)* was sown in each.

In all cases EDTA application commenced five weeks after seedling emergence. The EDTA solution applied was 0.01 *M* Na_2H_2EDTA raised to a of pH 6.0 with KOH. The columns/cores received various applications of EDTA solution (Table 5-1). Where there were 9 or 18 applications, the EDTA solution was mixed with the required amount of irrigation water and applied to the columns or core. However, when there were only one or two EDTA applications, the EDTA solution was applied without mixing with water. No nutrients were applied to the soil.

In Experiment I three repacked columns were used. The first column was kept as a control with no EDTA addition. The second column had a total of 1800 μmol of EDTA sprinkled on to it in two applications of 900 μmol, the second 18 d after the first. The third column also received a total of 1800 μmol, but in 18 applications, each of 100 μmol, applied on alternate days. As the columns contained soil with a dry mass of 880 g and the gram molecular weight of EDTA is 372, the 1800 μmol of EDTA added corresponded to 0.74 mg of EDTA per g of dry soil.

Experiment II involved five intact soil cores. The same three treatments used in Experiment I were imposed on three of the cores. The other two cores both had 900 μmol of EDTA added to them. This was added as single application to one core, and as nine 100 μmol applications applied at 4-day intervals to the other core.

Every day the water loss due to plant uptake from each of the columns and cores was measured gravimetrically, and water sprinkled on to correct for the weight loss. No leachate emerged from the base of the columns, as the soil water content was just brought back to ‘pot capacity’ each day. Forty four days after EDTA was first applied, the grass was harvested from all columns and cores and placed in a drying oven at 80° C until a constant weight was achieved. The herbage samples were analysed for copper as described below.

After harvesting, the columns and cores were leached with about 7 liquid-filled pore volumes of water under unsaturated conditions. The apparatus used to do this is described in Section 4.2 of Chapter 4. The leachate was collected and analysed for copper and iron as described previously. Then the soil in each column or core was cut into six segments. The soil in each segment was homogenised, sub sampled, and analysed as described earlier.

The plant material analysed for copper was prepared in the following manner. Sub-samples (about 1g) of grass were weighed into 10-ml borosilicate test tubes. The tubes were heated in a muffle furnace overnight at 500° C. The next day 5 ml of warm 2 *M* HCl was added to each tube, mixed in with a vortex mixer and then the solution analysed for copper using flame atomic absorption spectroscopy.

The acid-extractable copper concentrations in the soil were determined by digesting the soil as described in Section 2.2.3.

5.3 Results and discussion

As only one set of the complex apparatus (Figure 4-1) was available for leaching the columns and cores under unsaturated conditions, it was not possible to replicate the treatments and to apply statistical analysis to the results in the usual way. However some of the differences found were large enough, and consistent enough across treatments, for some inferences to be made.

The dry matter yields at harvest are shown in Table 5.1, and ranged from an equivalent of 336 g m^{-2} to 433 g m^{-2}. There was no observable decrease in yield attributable to EDTA application, probably because the grass had been allowed to grow and establish for about 45 days before the EDTA was applied. During the 44 day period between the first application of EDTA and harvest, the evapotranspiration from the columns and cores ranged from 10 to 13 mm/day.

In the repacked soil columns, pre-mixing of the soil meant that the initial soil copper concentration was reasonably uniform with depth, although some variation was observed in the total amount of total extractable copper in the columns (Table 5.1). In contrast, in the intact cores the copper was concentrated near the surface. This would be due to the surface-applied copper binding strongly to organic matter and so having limited mobility. As there was no way of non-destructively measuring the initial copper distribution in the cores, the copper data from the smaller cores taken close to each large core were used to infer the copper distribution in the larger cores. The total amount of copper in each large core and the copper distribution with depth were calculated as described in Section 4.3.1. The results are shown in Figure 5.3. Again some variation was observed in the total amount of copper in the cores, as is expected in the field (Table 5.1). The repacked columns contained about 50% more copper than the intact cores.

The 1800 μmol of EDTA applied to the contaminated soil corresponded to 0.74 mg g^{-1} in the repacked columns and 0.67 mg g^{-1} in the intact cores. This EDTA was sufficient to complex about half of the acid-extractable copper present, assuming a 1:1 molar reaction between copper and EDTA. However as shown in Chapters 2, 3 and 4 EDTA not only complexes and brings copper into solution, but also complexes with most heavy metals and has a strong affinity for iron when applied to soil. Therefore less than half of the total amount copper was expected to be brought into solution by the EDTA.

Figure 5-1 *A. tenuis* on copper contaminated soil in (a) repacked columns and (b) intact cores

5.3.1 Copper uptake by *A.tenuis*

Figure 5.2 shows that the addition of EDTA to the copper-contaminated soil resulted in a substantial increase in the copper concentration in the leaves of *A. tenuis*. This was observed in both the repacked columns and intact cores. In the absence of EDTA, copper uptake was minimal. The highest herbage copper concentration measured, 300 μg g^{-1}, is comparable to the 472 μg g^{-1} measured by Aseni *et al.* (1999) in *Erica andevalensis* (a metal-tolerator) grown in crushed copper ore containing 1926 mg kg^{-1} of copper with 2 mg g^{-1} of EDTA added. But it was well below the 2500 μg g^{-1} found in *Arrhenatherum elatius* (also a metal-tolerator) by Deram *et al.* (2000) after the addition of EDTA at a rate of 0.5 mg g^{-1} to a copper ore with a total concentration of just 187 mg kg^{-1}. These variations in the copper concentration in the leaves could be due to differences in the form of copper present in the substrate, and/or to differences between plant species. Copper ores mostly contain copper in inorganic form, whereas the copper in the orchard topsoil would have been mostly associated with organic matter.

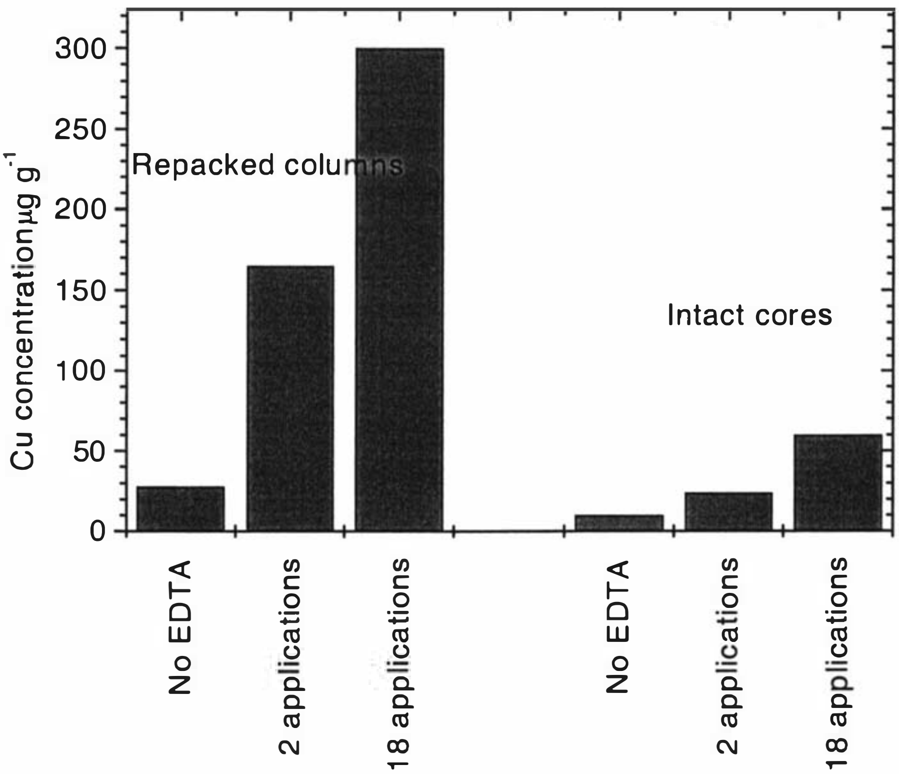

Figure 5-2 Copper accumulation in shoots of *A.tenuis* grown on copper contaminated (a) repacked soil columns and (b) intact soil cores in response to the addition of EDTA (1800 μmols/column or core).

The herbage copper concentration was much higher for the repacked columns than for the intact cores (Figure 5.2). In part this can be attributed to more copper being present in the repacked soil than the intact cores (Table 5.1). It is likely that the higher shoot copper concentration found in the repacked columns was mainly due to a greater spatial separation between the copper adsorption sites and the roots in the intact cores than the repacked soil columns. In intact cores the humus responsible for the copper adsorption sites tends to be more associated with clay inside the aggregates, while roots tend to grow in larger cracks and bio-pores. In contrast, in the repacked soil columns, the roots and the copper would both have a more uniform distribution, while the physical disturbance caused by sieving would increase the exposed surface area, making some of the copper adsorption sites more accessible to the roots. The copper concentration in the roots ranged from 26-34 μg g^{-1}. Lower copper concentration in the roots measured in this study could be due to the continuous leaching of the soil with water for 7 PV after the harvest of the above ground material.

Table 5-1 Summary of Experiment I and II results

	Number of EDTA applications	Initial copper in soil (μmol)	EDTA applied (μmol)	Copper leached (μmol)	Iron leached (μmol)	Dry matter produced (g)	Copper in shoot (μmol)
Experiment I (Repacked)	0	3831	0	5	2	3.3	1.54
	2	3075	1800	480	788	3.0	7.8
	18	3522	1800	363	686	3.1	14.9
Experiment II (Intact)	0	3453	0	1	1	3.0	0.4
	1	2484	900	109	467	2.6	0.9
	9	2597	900	169	407	2.7	1.0
	2	2120	1800	115	1045	3.2	1.2
	18	1720	1800	340	816	3.4	3.2

The amount of copper uptake by the plants also varied with the amount and frequency of EDTA application (Table 5.1). As might be expected, the addition of 1800 μmol of EDTA induced more uptake from repacked soil columns than did the addition of 900 μmol. But also when 1800 μmol of EDTA was applied in 18 small aliquots rather than two large dollops, the copper concentration in the herbage (Figure 5.2), and amount of copper uptake (Table 5.1), doubled in both the repacked columns and intact cores. The reasons for this are not clear. But it could be that the application of 900 μmol of EDTA on one day produced such high local concentrations of copper in the soil solution near the surface that the roots became less active there. Thus they may have taken up more of their water from lower down, where there was little EDTA, and so copper, in the soil solution. This explanation is consistent with the finding that the uptake difference due to this treatment was less pronounced when only 900 μmol of EDTA was applied either as one dollop or in nine aliquots (Table 5.1).

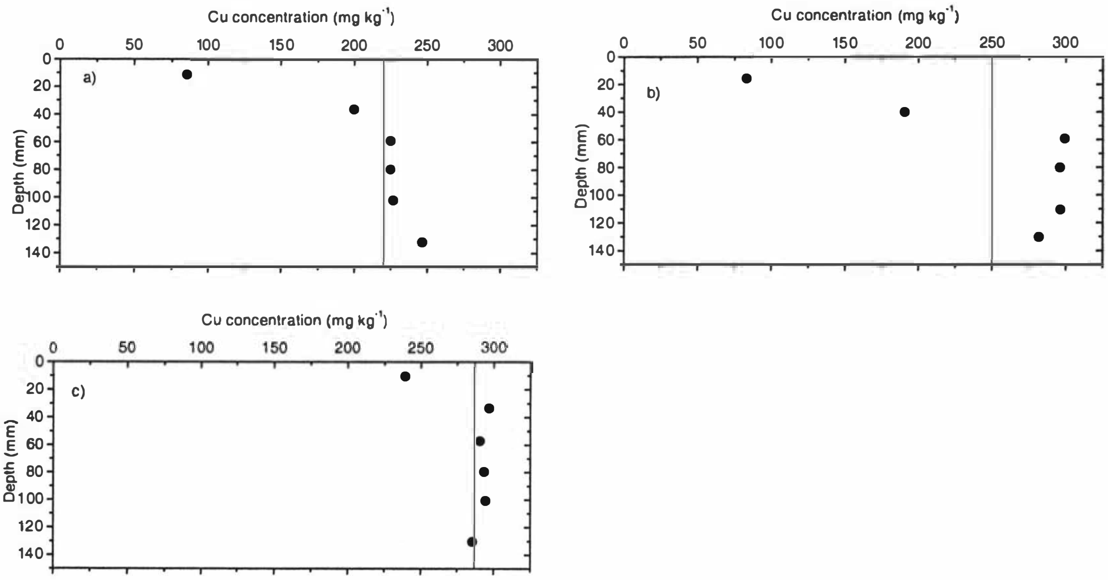

Figure 5-3 The initial copper concentration (—) and the final measured copper concentrations in the repacked soil columns (●) in Experiment 1. (a) Two EDTA applications (b) Eighteen EDTA applications and (c) control column.

5.3.2 Plant uptake and leaching of copper

Thus far the discussion has mainly been about plant uptake. Uptake occurred because EDTA brought copper into the soil solution. But if this copper is not all taken up by the plants, there is the risk that it can be leached and end up in the groundwater. To assess this risk, I measured the amount of copper leached from each of the columns and cores when 7 PV (about 500 mm) of water was applied. Table 5.1 shows that between 10% and 20% of the copper in the soil was leached from it when EDTA had been applied. A lot of iron was also leached. About 23-58% of the EDTA applied apparently was complexed with iron when it was leached from the soil.

Figures 5.3 and 5.4 show the copper distributions in the columns and cores after leaching. In the repacked columns, most of the copper from the top 30 mm was brought into solution by the EDTA and then leached downward. The final copper concentration was about 84 μg g^{-1} on the surface soil in the two repacked columns to which EDTA had been applied. This concentration is similar to the 92 μg g^{-1} of copper that remained in contaminated Opotiki sandy loam after leaching with excess EDTA solution (Section 3.3.2.2). The higher copper concentration measured in the top 30 mm of the intact cores could be due to the amount of EDTA applied not being enough to solubilize the higher initial copper concentration at the surface soil.

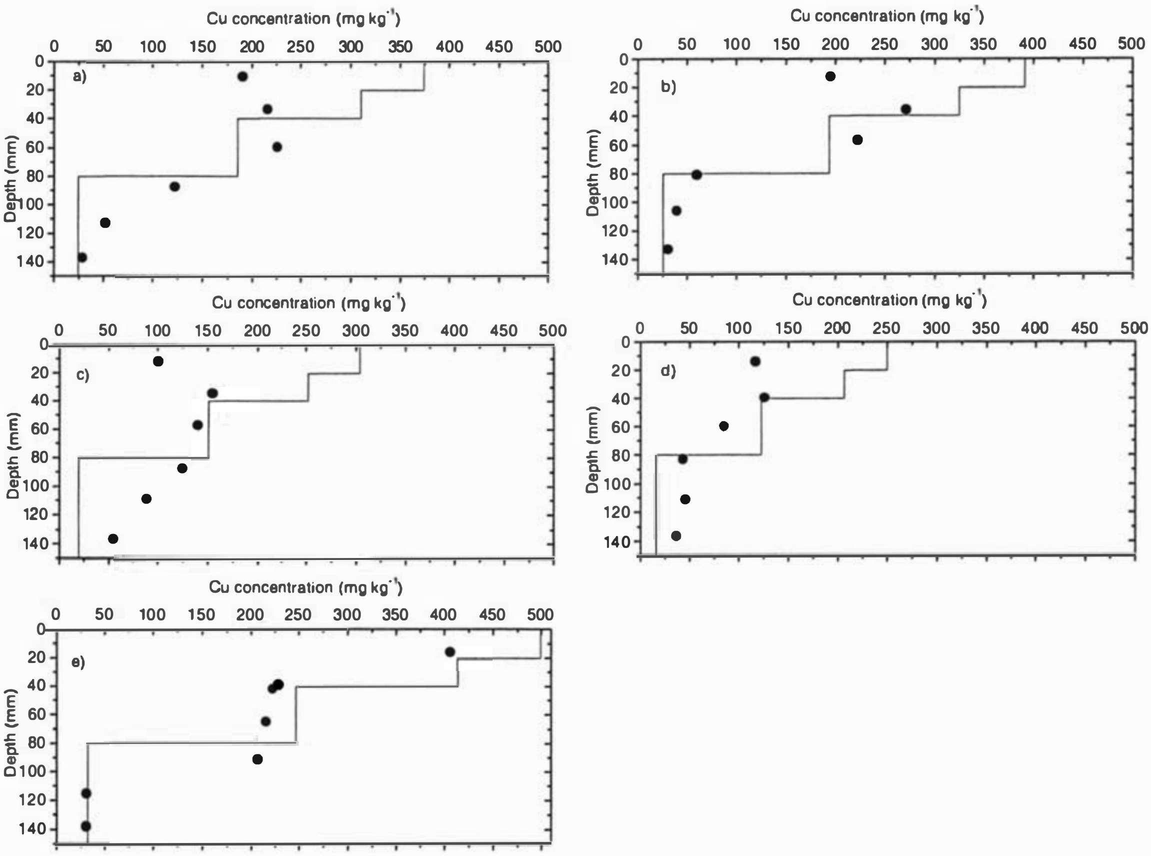

Figure 5-4 The initial copper concentration (—) and the final measured copper concentrations in the soil cores (●) in Experiment II. (a) One EDTA application (b) nine EDTA applications (c) Two applications (d) Eighteen EDTA applications and (e) control core.

Below 80 mm depth the final copper concentration in the soil was greater than the initial concentration in all columns and cores apart from the controls (Figures. 5.3 and

5.4). This increase can be attributed to the re-sorption of EDTA-solubilised copper. As shown in Section 3.3.2.2 with EDTA residence times of a week or more, $CuEDTA^{2-}$ slowly reacts with iron in the soil to form $Fe(III)EDTA^{-}$ and copper ions, which are then adsorbed by the soil. The negligible amount of copper measured in the leachate at the end of the 7 PV of leaching confirmed that it was not due to incomplete leaching of the copper present in the soil solution.

Assuming that all the copper and iron in the leachate was complexed with EDTA, between 58% and 70% of the applied EDTA was leached in association with copper and iron. The rest of the EDTA probably was complexed with calcium or the small amount of zinc in the soil, or alternatively was either adsorbed or broken down by the soil.

It is interesting to compare the amount of copper uptake by the grass with the amount leached. This gives an indication of how effective the EDTA-enhanced phytoremediation would be in terms of the beneficial removal of copper by plant uptake, relative to the detrimental increase in risk of polluting the groundwater. For the two repacked columns with EDTA added, 25 and 62 times more copper was leached than was taken up by plants. This uptake-leaching ratio was even higher for the intact cores, ranging from 99 to 169. This suggests that EDTA-enhanced phytoremediation is unlikely to be successful and safe unless a drainage system can be installed and the leachate collected or recycled. If the leachate is collected, it rather than plant uptake will provide the major copper removal pathway.

An interesting question is, to what extent did the grass roots exclude copper? An approximate calculation provides an answer. Consider the repacked soil column with the highest copper concentration in the leaves. Over the forty-four days between the first EDTA application and harvest, 450 mm or 3.5 kg of water was evaporated, which can be reasonably assumed to have all been lost as transpiration. During that period the *A. tenuis* leaves took up 14.8 μmol or 941 μg of copper. So the average copper concentration in the water entering the roots was 0.27 $\mu g\ g^{-1}$. A total of 363 μmol or 23 mg of copper was leached from that column after harvest. This provides a way of regularly estimating the copper concentration in the soil solution over the forty-four days. The volume of soil in the column was 1.2 litres and the water content at 'pot capacity' was 0.5 $m^3\ m^{-3}$, so the column would have typically contained 600 g of water. Thus the average copper concentration in the soil solution was about 23 mg / 600 g or 38 $\mu g\ g^{-1}$. Looked at this way, the soil solution copper concentration was two orders of magnitude greater than the concentration entering the roots, so the grass was quite effective at screening out the copper in the soil solution.

5.4 Conclusions

EDTA application of 1800 μmol to 0.9 kg of contaminated soil in the repacked column increased the shoot copper concentration of *A.tenuis* from about 30 μg g^{-1} to 300 μg g^{-1}. However the EDTA-enhanced phytoremediation was less effective in the intact cores, where the same EDTA application to 1.0 kg of soil only increased the herbage copper concentration from about 10 μg g^{-1} to 60 μg g^{-1}. More copper accumulated in the herbage when the EDTA was applied in numerous small doses than in just one or two larger amounts. The concentration of copper in the water taken up by the grass was two orders of magnitude lower than that in the soil solution.

Leaching about a month after the EDTA application removed 25 to 169 times more copper than was taken up by the herbage. This means that a strategy for managing leaching losses needs to be a major part of any plan for EDTA-enhanced phytoremediation.

6 Modelling EDTA-enhanced transport of copper and copper uptake by plants

6.1 Modelling EDTA-enhanced transport of copper

6.1.1 Introduction

The use of mechanistic models for simulating the fate and transport of copper and CuEDTA complex is a key tool for environmental impact assessment, and for planning the rates and timing of EDTA applications for remediation purposes. The aim in developing a model in this study was to be able to describe quantitatively the main physical and chemical processes involved in the EDTA-enhanced transport of copper from copper contaminated soils. These processes were outlined in Chapters 1, 2, 3, and 4 and occur in a soil when copper and EDTA are present, both during and in between leaching events.

A number of models in the literature have the potential to describe the interaction and transport of metals and EDTA in soil. Some models, such as PHREEQC (Parkhurst and Appelo, 1995) and HYDROGEOCHEM (Yeh and Salvage, 1995), are comprehensive and complex. They involve multiple metal species, and their associated geochemistry. Such models were not considered, as the detailed chemical information required was neither available nor readily obtainable. In terms of practical application, it was believed that their adoption by most other potential users would be precluded by similar limitations. Other simpler models considered were those of Jardine *et al.* (1993), and Kedziorek *et al.* (1998). However neither of these take into account the competition between the contaminant metal and the soil iron for EDTA. In a number of the experiments described in Chapters 2, 3 and 4, a relatively small amount of EDTA had been added which had then complexed with both copper and iron from the soil. Once complexed with the more stable Fe(III), negligible interaction between EDTA with copper would be expected at the range of pH used in this study. Hence competition between the copper and iron for the added EDTA was a major determinant of how much copper came into solution, and a description of it was needed in the model. So it was concluded that, while some of the elements in the earlier models could be used, in particular the model of Kedziorek *et al.* (1998), it was necessary to develop a model to describe the processes observed in the experiments described in the previous chapters.

In this chapter, the development of the model to describe EDTA-enhanced copper transport through contaminated soil is first explained. Next the evaluation of the parameters required in the model is described. Data from the Experiments A and B in Section 3.3.2 were used to evaluate the parameters. However, the usefulness of the model parameterised using these experimental data depends on whether it can be extrapolated to other conditions. So described and tested in this chapter are simulations of how a different soil under similar experimental condition behaves, of what happens if copper is leached from a contaminated topsoil into an essentially copper-free subsoil, and finally of how EDTA applied to unsaturated intact soil columns behaves. Lastly, the model was used to simulate the copper leaching at different flow rates.

The EDTA-enhanced transport of copper from contaminated soils described in this chapter was modelled using the convection-dispersion equation, coupled with descriptions of the key chemical reactions.

6.1.2 Model development

Although the imposed flow was sometimes intermittent in all experiments described in Chapters 2, 3 and 4 the soil water content changed little with time. Thus the water content was assumed to be constant with time, but not necessarily with depth. Apart from a small concentration of zinc, copper was the only heavy metal present in the soil in significant quantities. So copper was the only one considered. All experiments showed that virtually all the copper and iron present in the soil solution was complexed with EDTA, therefore this was assumed in the model. Thus solute transport for the three forms of EDTA of interest (free, Cu- or Fe(III)-EDTA), as well as that of the halide tracers, was described by the CDE given earlier as equation (1-22), but with a source/sink term included in it. The equation is

$$R\frac{\partial C}{\partial t} = D_h\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} + S \qquad (6\text{-}1)$$

where R is a dimensionless retardation constant accounting for any reversible instantaneous adsorption as described by a linear adsorption isotherm, C is the concentration of the halide, or of the free-, Cu- or Fe-EDTA in the soil solution (mol m^{-3} of solution), and S is a term accounting for any chemical reactions bringing that chemical species into or out of solution (mol m^{-3} of soil s^{-1}). Other variables are defined in Chapter 1. When R is defined this way, it is the total amount of the halide or EDTA form present in unit soil volume divided by the amount dissolved in the water in unit soil volume. R equals one if there is no adsorption to the matrix, and is greater than one if there is adsorption.

As in some experiments flow was stopped for up to a month, while molecular diffusion continued, both hydrodynamic dispersion and longitudinal molecular diffusion needed to be considered. So, D_h was defined as (Wagenet, 1983)

$$D_h = cD_o + \lambda q_w/\theta \qquad (6\text{-}2)$$

where c is a dimensionless tortuosity factor, and D_o is the molecular diffusion coefficient in solution ($m^2 s^{-1}$).

For the inert halide tracers $S = 0$. For EDTA, three source/sink reactions were considered. The first two involve the added EDTA, which denoted as $EDTA_0$, reacting with copper and iron in the soil to form complexes as $CuEDTA^{2-}$ and $Fe(III)EDTA^{-}$. The third reaction was $CuEDTA^{2-}$ reacting with iron in the soil to form $Fe(III)EDTA^{-}$ and copper ions. These copper ions would then be adsorbed by the soil. In all reactions it was assumed that one mole of metal ion (Cu^{2+} or Fe^{3+}) reacts with one mole of EDTA (Kedziorek *et al.* 1998; Sparks 1995). Therefore,

$$S_{Cu} = k_1(C_o \rho_b M_{Cu})^n - k_3(C_{Cu} \rho_b M_{Fe})^n \qquad (6\text{-}3)$$

$$S_{Fe} = k_2(C_o \rho_b M_{Fe})^n + k_3(C_{Cu} \rho_b M_{Fe})^n \qquad (6\text{-}4)$$

and

$$S_o = - S_{Cu} - S_{Fe} \qquad (6\text{-}5)$$

In the above equations S_o, S_{Cu} and S_{Fe} are the source/sink terms for $EDTA_0$, $CuEDTA^{2-}$ and $Fe(III)EDTA^{-}$ respectively, and n is a dimensionless constant indicating the order of the reaction. In equations (6-3) and (6-4), k_1 is the rate constant for the reaction between $EDTA_0$ and the extractable copper, k_2 is the rate constant for the reaction between $EDTA_0$ and the extractable iron, and k_3 is the rate constant for the reaction between $CuEDTA^{2-}$ and the extractable iron. All rate constants have units of s^{-1}. The soil solution concentrations of C_o, C_{Cu} and C_{Fe} are for $EDTA_0$, $CuEDTA^{2-}$ and $Fe(III)EDTA^{-}$

respectively. M_{Cu} is the EDTA-extractable copper concentration in the soil (mol kg^{-1}), and M_{Fe} is the EDTA-extractable iron concentration (mol kg^{-1}).

During the dynamic experiments described in Chapters 2, 3 and 4 chemical equilibrium was not obtained. So stability equilibrium constants, that are commonly used in other models, are not used here. However equations (6-2), (6-3) and (6-4) imply that at equilibrium all the EDTA in the soil would be complexed with iron, provided enough iron is available. This is consistent with the fact that the stability constant for the Fe^{3+} complex with EDTA is much greater than that for Cu^{2+}. The log $K_{M\text{-}Y}$ values given in GEOCHEM PC version 2.0 (Parker *et al.*, 1995) are 20.5 for CuEDTA^{2-} and 27.7 for Fe(III)EDTA^{-}.

Equations (6-1) to (6-5) were solved numerically, using the appropriate boundary and initial conditions (Section 1.2.2.3). This involved simultaneous solution for the halide tracer, for free EDTA and for EDTA complexed with both copper and iron. An explicit finite-difference scheme, written in Visual Basic™ within Excel™ was used to do this, and employed a forward-difference approach, with numerical dispersion taken into account. Examples of the various computer programs used are given in Appendix A, Programs 1-5.

6.1.3 Results and discussion

6.1.3.1 Evaluation of model parameters for repacked Opotiki soil

Solution of equations (6-1) to (6-5) requires that parameter values be found. Some of these values were directly measured, or obtained from the literature. The remainder were determined indirectly using the results of the experiments. Mostly the results from Experiments A and B described in Chapter 3 were initially used for this purpose. In the case of the Darcy flux density (q_w), the measured values were used. The gravimetric water content measured at the time of final destructive sampling of the columns, and the measured bulk density, allowed the θ in each column at the conclusion of the experiment to be found. As already mentioned, these values were assumed constant with time. The volumetric moisture content ranged from 0.57 to 0.62 m^3 m^{-3} for the repacked Opotiki soil. The traditional value of 0.66 was assumed for the tortuosity factor c (Penman, 1940), as all the soil columns were near saturation. A molecular diffusion coefficient (D_o) value of 1 x 10^{-9} m^2 s^{-1} was used for chloride and bromide

(Robinson and Stokes, 1959). A molecular diffusion coefficient value for EDTA was not found in the literature, so this value was also used for EDTA (Jardine *et al.*, 2002). It will be shown later in this chapter that the model is fairly insensitive to any error in this assumption.

The λ for the repacked soil was determined by optimising the appropriate analytical solutions of the convection-dispersion equation (equation 1-35), for the imposed boundary and initial conditions (equations 1-31 to1-33), to the effluent chloride data. Data from Experiment A, and the immediately leached column in the Experiment B in Chapter 3, were used and λ found using the least squares method. Longitudinal molecular diffusion was negligible during flow, so could be ignored in this case. Dispersivity values of 1 and 5 mm were found for these two experiments, and these are close to the typical value of 4 mm given for repacked soil by Wagenet (1983). The average of the two values, 3 mm, was used for all solutes in all simulations of experiments conducted on repacked Opotiki soil.

The optimised values of R were close to unity for chloride in Experiment A, and in the immediately leached column in the Experiment B. This indicated that neither adsorption nor exclusion had occurred. Therefore a value of 1 was used for R.

In Experiment A, excess of $EDTA_0$ was added. Therefore, it was assumed that the applied $EDTA_0$ removed all the iron that was EDTA-extractable at the prevailing pH. Thus an initial value of 1.25 mmol kg^{-1} was found for M_{Fe} from the area under the iron breakthrough curve. The first part of this curve is shown in Figure 6-1b. This value for M_{Fe} was used in all the simulations of Opotiki contaminated soils. It was also assumed that, in the Experiment A, all the copper, which could be removed by leaching with $EDTA_0$, had been removed. So the 90 mg kg^{-1} (1.4 mmol kg^{-1}) of copper remaining was effectively inert as far as EDTA extraction was concerned. Thus the initial value of M_{Cu} for the simulations was the acid-extractable value, less 1.4 mmol kg^{-1}.

Kedziorek *et al.* (1998) found that metal-EDTA reactions, over a wide range of EDTA concentrations, could be described using an equation similar to the equation (6-3) with n =1. This implies a first order reaction with respect to both the EDTA and the extractable metal concentrations. However I found that n = 0.5 better described the way the EDTA concentration, over a 10-fold difference in concentrations, affected extraction. So this value for n was used in the model. Values for the rate-coefficients k_1

and k_2 were obtained by visually fitting the model predictions to the data in Figure 6-1b. During this optimisation process k_3 was assumed to be zero, as little transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ was expected during the relatively short resident times of the Experiment A. Subsequent checks showed that this assumption was reasonable. The values obtained were 4×10^{-5} s^{-1} for k_1, and 9×10^{-6} s^{-1} for k_2.

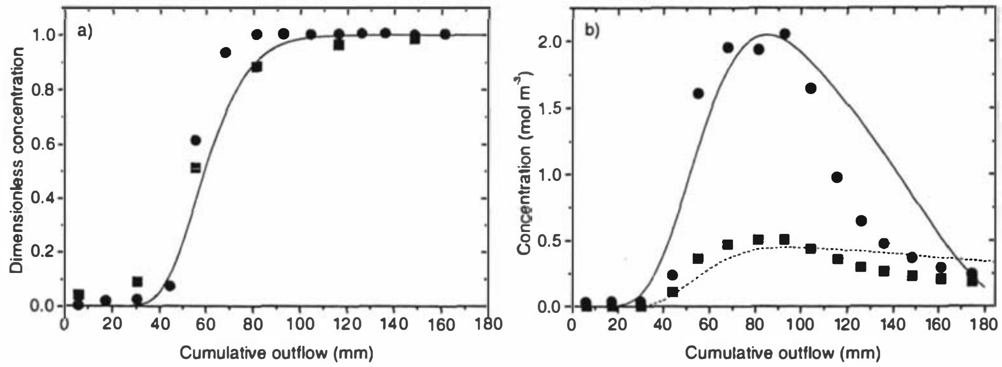

Figure 6-1 Breakthrough data for Experiment A of Chapter 3. (a) Measured and simulated values for chloride (● and —) and EDTA (from DOC) (■ and ----). (b) Measured and simulated values for copper (● and —) and iron (■ and ----).

It remained then to find a value for k_3, which controlled the rate of $CuEDTA^{2-}$ transformation to $Fe(III)EDTA^{-}$. The data from Experiment B were used for this purpose. Here EDTA was left in the soil for varying periods of up to a month. Optimisation gave a k_3 value of 2.2×10^{-7} s^{-1}. Note that k_3 is two orders of magnitude lower than k_1, justifying the assumption in the previous paragraph that relatively little of this transformation reaction is likely to occur within any one day.

6.1.3.2 Experiments on uniformly contaminated repacked Opotiki soil

This section outlines the simulation of Experiments A and B described in Section 3.3.2, with uniformly contaminated repacked Opotiki soil.

The simulated breakthrough curves for chloride are shown in Figures 6-1a and 6-2a. The simulations of EDTA behaviour in the same experiments are shown in Figures 6-1a and 6-2b, assuming $R = 1$. EDTA transport was modelled successfully, implying little or no adsorption occurred. Note that in Figure 6-1a the simulated curves for chloride and EDTA coincide, so a single curve is shown.

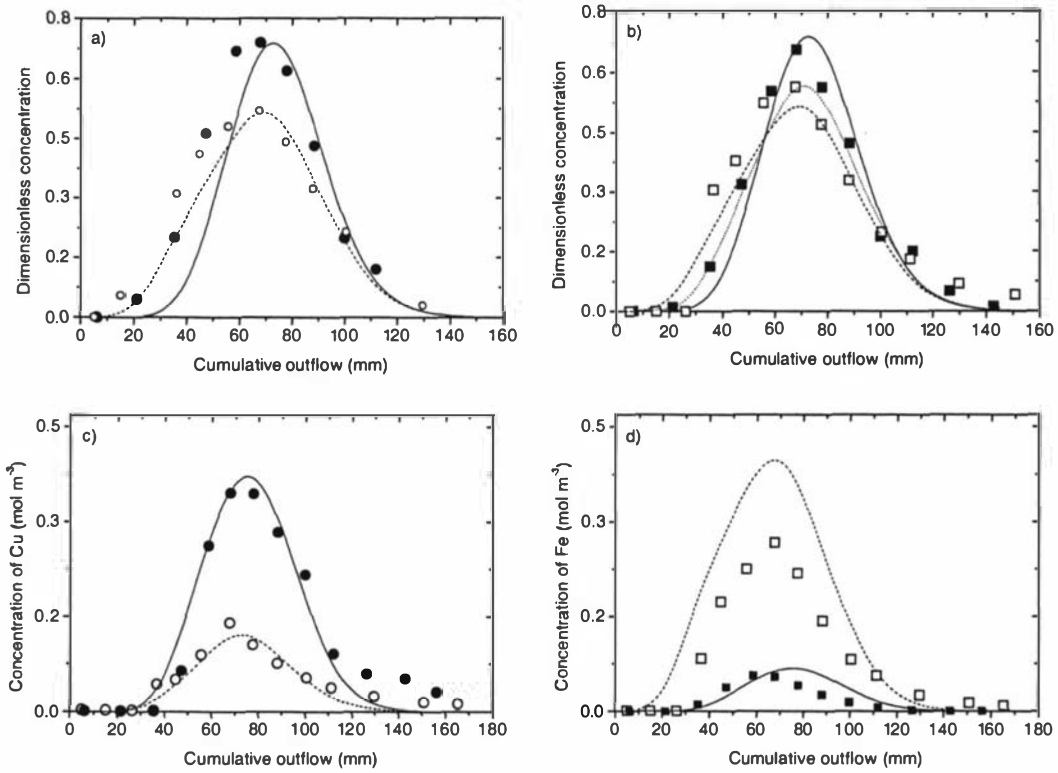

Figure 6-2 Breakthrough data for Experiment B of Chapter 3, the filled-in symbols and full lines are for the column leached immediately; the open symbols and broken lines are for the column left for a month before leaching. (a) Chloride (b) EDTA (c) Copper. (d) Iron.

Comparison of the chloride breakthrough with immediate leaching, and after one month's delay (Figure 6-2a), shows the effect of molecular diffusion over the month. The amplitude of the pulse was reduced and the spreading increased. Both the measured and simulated values show this behaviour. The EDTA-breakthrough curves show the same behavior, but it is less pronounced. Two simulated curves are shown for EDTA with one month's delay in leaching in Figure 6-2b. The curve with the higher peak uses the molecular diffusion coefficient for chloride, 1 x 10^{-9} m^2 s^{-1}, and the other uses a lower value of 2.5 x 10^{-10} m^2 s^{-1}. This lower value is half the value given for atrazine, a similar large organic molecule, by Hu and Brusseau (1996). Note that the two simulations are not very different, and indeed it is hard to say which fits the data better, especially given some uncertainty as to whether, after one month, all the DOC in the leachate was in fact EDTA. Therefore, same values were used for both chloride and EDTA.

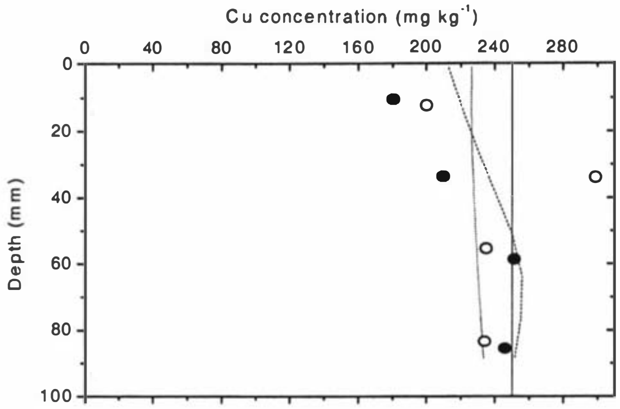

Figure 6-3 The initial copper concentration (—) and the final measured and simulated copper concentrations in the soil column leached immediately (● and ......) and a month (○ and ------) after EDTA$_0$ application in Experiment B of Chapter 3.

With the parameter set defined in Section 6.1.3.1, the model described quite successfully the copper concentration in the leachate in Figures 6-1b and 6-2c, despite the different amounts and concentrations of EDTA applied, and the varying lengths of time it was left in the soil. The model also reasonably described the decreasing amounts of CuEDTA^{2-} in the leachate with increasing EDTA residence time in the soil (Table 6-1, Figure 6-2c). However there were some aspects of Experiment B that the model did not describe well. While the model correctly estimated the amount of copper leached, both immediately and with a one-month delay, it overestimated the amounts leached after one day and one week (Table 6-1). This simple model can only describe approximately the range of reaction rates, and the availability.of the soil copper, which is bound to the solid phase to varying degrees. This is also probably the reason for the discrepancies between the measured, and simulated, final copper distributions in the soil after leaching (Figure 6-3).

The iron concentration in the leachate of both Experiments A and B was also quite closely simulated, except for the column with the one-month delay before leaching (Figures 6-1b and 6-2d and Table 6-1). The overestimation in this case was possibly due to some degradation, or slow irreversible adsorption, of EDTA over the month.

Table 6-1 The iron and copper leached with varying EDTA residence times in Experiment B

Residence time	Cu leached	(μmol)	Fe leached	(μmol)
(d)	Experiment	Model	Experiment	Model
0	35	34	5	6
1	28	40	10	10
7	23	31	18	19
30	12	12	24	38

6.1.3.3 Experiments using repacked Manawatu soil

6.1.3.3.1 Parameterising the model

In order to use the model developed to simulate the experimental results described in Chapter 2, new values for some parameters had to be found, as a different soil was used. For the q_w and θ, the measured values were used. The water content in the Manawatu soil ranged from 0.49 to 0.58 m^3 m^{-3}. Values for D_o, c and n were the same as those used in Section 6.1.3.1 for the Opotiki soil.

An average dispersivity of 3 mm was found by fitting the bromide data in Figure 6-4a and chloride data in Figure 6-11a to the appropriate analytical solutions of the convection-dispersion equation. This value is similar to that found for the repacked Opotiki soil. Optimization for R in the Manawatu soil experiments also gave a value close to unity, indicating that neither adsorption nor exclusion of chloride or bromide occurred.

As for the Opotiki soil in Section 6.1.3.1, it was assumed for the continuous leaching with excess 0.01 M $EDTA_0$ experiment (Section 2.3.2) that all the copper that could be removed by leaching with $EDTA_0$ had been removed. So the 40 mg kg^{-1} (0.63 mmol kg^{-1}) that remained in the Manawatu soil was effectively too strongly bound to be extracted. Thus the initial value of M_{Cu} for the simulations was taken as the acid-extractable value, less 0.63 mmol kg^{-1}. A value for the EDTA-leachable iron of 4.2 mmol kg^{-1} was obtained from another experiment where the soil was continuously leached with $EDTA_0$. Here enough of $EDTA_0$ was added to leach all iron that was EDTA extractable under the prevailing conditions. Note that this value is 3.3 times greater than the value found for the Opotiki soil. Values for k_1, k_2 *and* k_3 were obtained by fitting to the data of experiment conducted on Manawatu soil as discussed below.

6.1.3.3.2 Continuous leaching with EDTA of different concentrations

This section describes the simulation of leaching experiments using 0.001*M* and 0.01*M* EDTA$_0$ on low and high-Cu soil. The experimental results are described in Section 2.3.2.

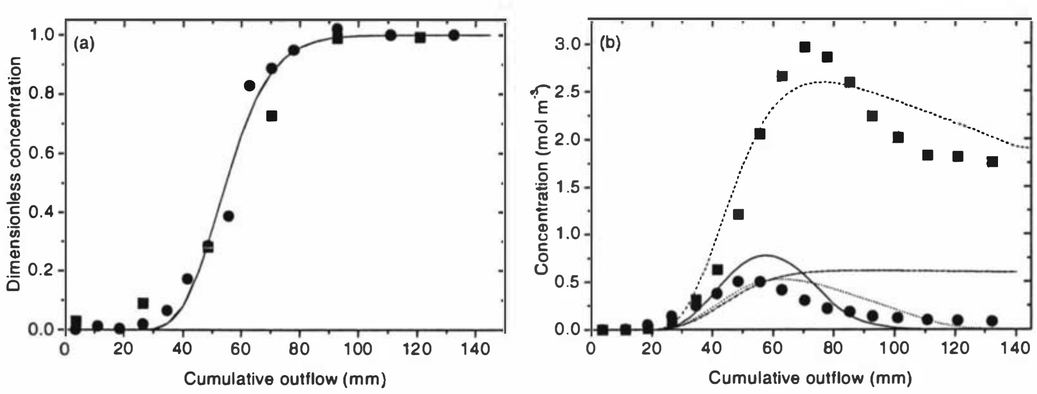

Figure 6-4 Breakthrough data for leaching the low-Cu soil with 0.01*M* EDTA$_0$ described in Chapter 2. (a) Measured and simulated breakthrough data for bromide (● and —) and EDTA (■ and ----). (b) Measured and simulated breakthrough for copper (● and — or ....) and iron (■ and ---- or–·–·–). Details of the alternative simulations are given in the text.

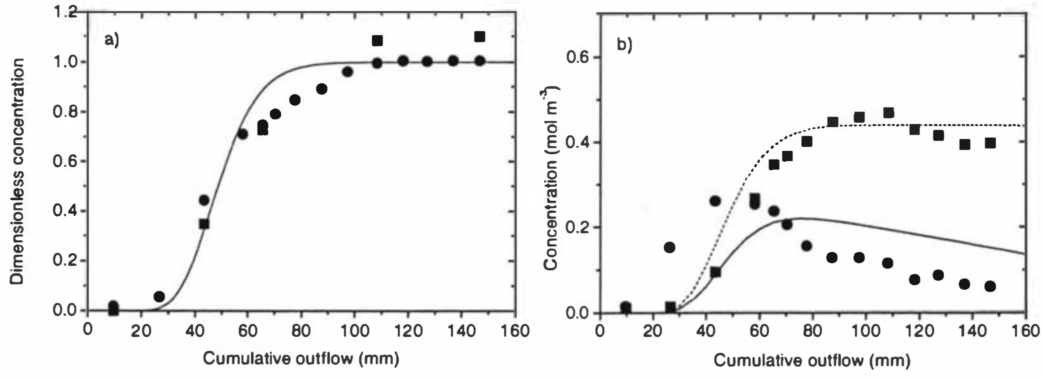

Figure 6-5 Breakthrough data for leaching the low-Cu soil with 0.001*M* EDTA$_0$ described in Chapter 2. (a) Measured and simulated breakthrough data for bromide (● and —) and EDTA (■ and ----). (b) Measured and simulated breakthrough for copper (● and —) and iron (■ and ----).

Figures 6-4 and 6-5 show the measured and simulated data for the leaching experiments using 0.01and 0.001*M* EDTA$_0$ on low-Cu soil. Figures 6-6 and 6-7 shows the measured and predicted results for similar leaching experiments on high-Cu soil.

Using the dispersivity obtained for chloride, the simulations for EDTA transport was successful on both low and high-Cu soils (Figures 6-4a, 6-5a, and 6-6a) except in Figure 6-7a. Again, the curves for bromide and EDTA fall on top of each other and as the model with $R = 1$ describes the EDTA measured data, little or no adsorption of EDTA occurred.

Simulation of the copper and iron leachate results for the 0.01 *M* EDTA$_0$ leaching experiment (Section 2.3.2), using the values for the rate-constants k_1, k_2 and k_3 used for the Opotiki soil (… and-.-.. respectively), grossly underestimated the iron concentration in the leachate, and also predicted slower leaching of copper than was observed (Figure 6-4b). This was attributed to the copper and iron being adsorbed with different strengths in the Opotiki and Manawatu soils. Hence, there was a need for new values for the rate-constants, which would better describe the data for experiments conducted using Manawatu soil. It was found that assuming all three rate constants were 2.5 times greater in the Manawatu soil than in the Opotiki soil greatly improved the simulations. Thus the values used for k_1, k_2 and k_3 were 1×10^{-4} s^{-1}, 2.3×10^{-5} s^{-1} and 5.5×10^{-7} s^{-1} respectively. The simulated breakthrough curves for copper and iron using these modified k values are shown as — and ---- respectively. The faster rate constants in the Manawatu soil are probably due to its lower organic matter content.

Using the adjusted k values above, the model also simulated the copper and iron concentrations in the leachate reasonably well for the continuous leaching experiments using 0.001*M* EDTA$_0$ on a low-Cu soil (Figure 6-5b).

There is generally close agreement between the simulated and measured copper and iron data for the other two experiments where 0.001*M* (Figure 6-6b) and 0.01*M* EDTA$_0$ (Figure 6-7b) were used to leach the high-Cu soil. However, the effluent iron in the high-Cu soil was over- estimated in both the leaching experiments. This over prediction of iron could be attributed to much of the copper being easily available in high-Cu soil for complexation with EDTA$_0$. This reduces the chance for iron to complex with the added EDTA$_0$ even though it has a higher affinity for EDTA. However, the value for M_{Fe} used for simulation was obtained from the experiment on low-Cu soil. In low-Cu soil, more iron leached out with the EDTA, probably because there was less copper available for masking the iron from the EDTA$_0$.

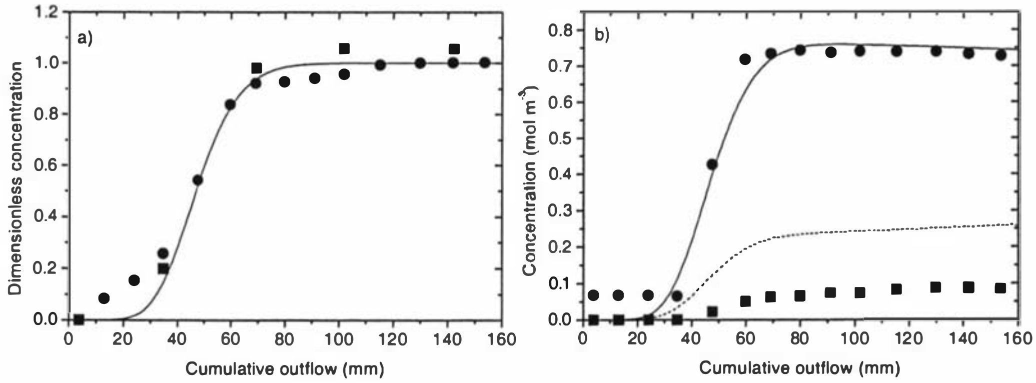

Figure 6-6 Breakthrough data for leaching the high-Cu soil with 0.001*M* EDTA$_0$ described in Chapter 2. (a) Measured and simulated breakthrough data for bromide (● and —) and EDTA (■ and ----). (b) Measured and simulated breakthrough for copper (● and —) and iron (■ and ----).

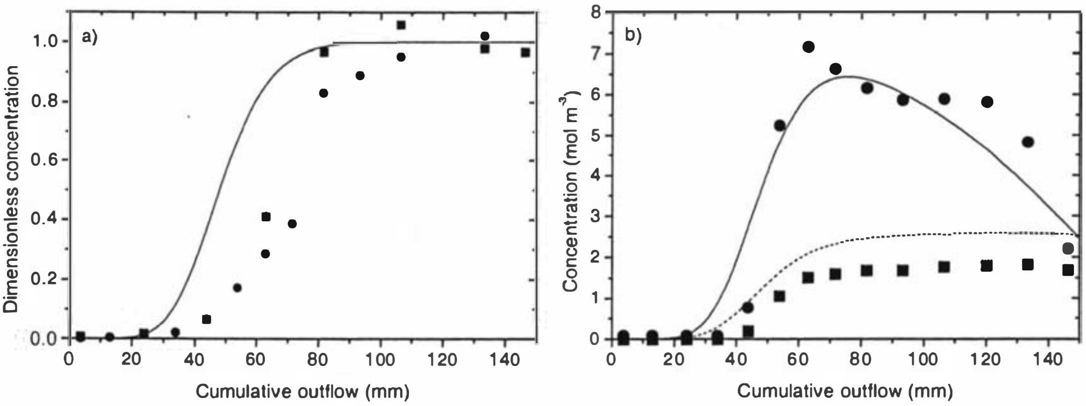

Figure 6-7 Breakthrough data for leaching the high-Cu soil with 0.01*M* EDTA$_0$ described in Chapter 2. (a) Measured and simulated breakthrough data for bromide (● and —) and EDTA (■ and ----). (b) Measured and simulated breakthrough for copper (● and —) and iron (■ and ----).

In general, the model was capable of simulating the results of EDTA-enhanced copper transport in a soil with a wide range of copper contamination, and also when different EDTA concentrations were used for leaching.

Figure 6-8 shows the measured and predicted final soil copper concentration in the low and high-Cu soils. It can be observed that for all the experiments the soil copper concentrations after leaching were predicted reasonably well by the model.

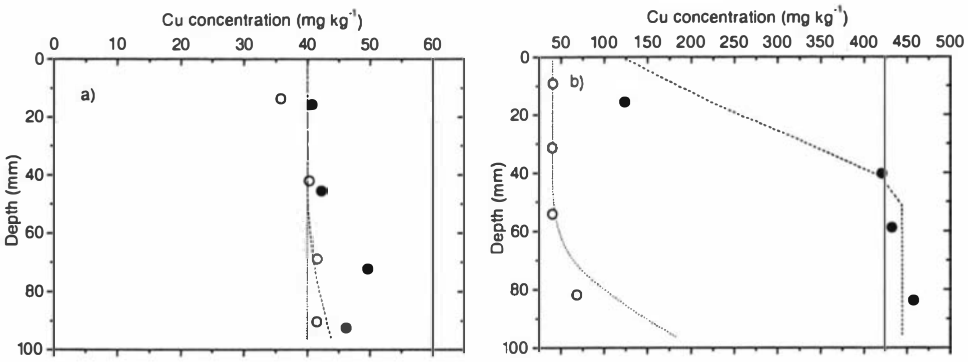

Figure 6-8 Final resident concentration of copper in the soil as a function of depth for a) Low-Cu soil and b) high-Cu soil. Closed symbols indicate leaching with 0.001 *M* EDTA$_0$ and open symbols indicate 0.01 *M* EDTA$_0$. Also shown are the simulations for the 0.001*M* (-----) and 0.01 *M* (...) EDTA$_0$ leached columns. Solid lines indicate the initial copper concentration in soil.

6.1.3.3.3 Three step applications of EDTA to high-Cu soil

Figures 6.9 and 6.10 show the measured and simulated data for the three-step EDTA$_0$ application on high-Cu soil (Section 2.3.1). For the first two steps there was a close agreement between the measured and simulated data of bromide, and EDTA in Figure 6.9. The model with an *R* of 1 well simulated the EDTA$_0$ at both concentrations (0.001 *M* and 0.01 *M*) confirming there was no retardation due to adsorption.

The amount of copper leached was well simulated by the model for all three EDTA$_0$ pulses. The model overestimated the amount of iron leached after the first two pulses of EDTA$_0$ for the reason discussed above in relation to the assumption of M_{Fe} in the model. The model also overestimated the peak concentrations of both metals for the second and third pulses of EDTA$_0$ and did not simulate the shape of the BTC correctly (Figure 6.10). This could be due to the value used for n = 0.5 in the model predicting that the reactions happened faster than they actually did.

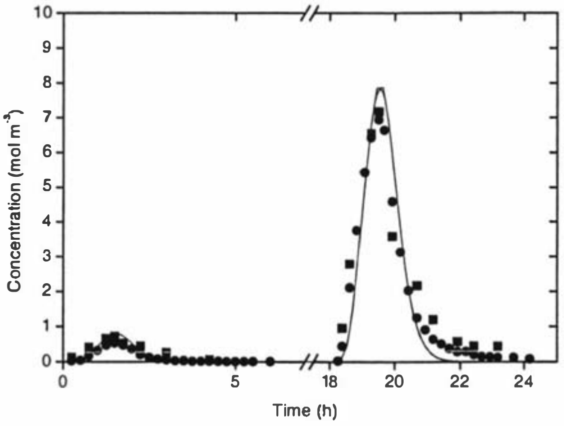

Figure 6-9 Breakthrough data of bromide (●) and EDTA (■)for the three-step pulse application of EDTA$_0$ on high-Cu soil described in Chapter 2. Also shown are the simulated breakthrough data for bromide (—) and EDTA (----).

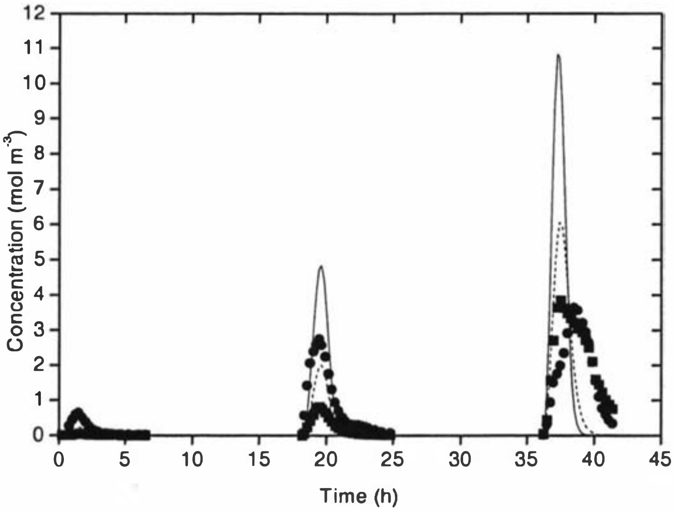

Figure 6-10 Breakthrough data of copper (●) and iron (■) for the three-step pulse application of EDTA$_0$ on high-Cu soil described in Chapter 2. Also shown are the simulated breakthrough data for copper (—) and iron (----).

6.1.3.3.4 CuEDTA stability with varying residence time in soil

Figure 6-11 shows the measured and simulated results for the 0.001 *M* EDTA$_0$ leaching experiments conducted with varying residence time (Section 2.3.3). The measured and modeled chloride data in Figures 6-11a are in close agreement. Both the data and the model demonstrate how molecular diffusion during the one-month pause in leaching reduced the amplitude of the pulse, and spread it out.

The simulations for EDTA transport were also successful (Figures 6-11b), except for the column with a one-month delay. The probable reason for this exception is the uncertainty, in this case, of using the DOC data to infer EDTA concentration, as discussed in Section 2.3.3. However, the assumption of $R = 1$ gives the modelled peak in the same place as the experimental data, showing no or little adsorption of EDTA occurred.

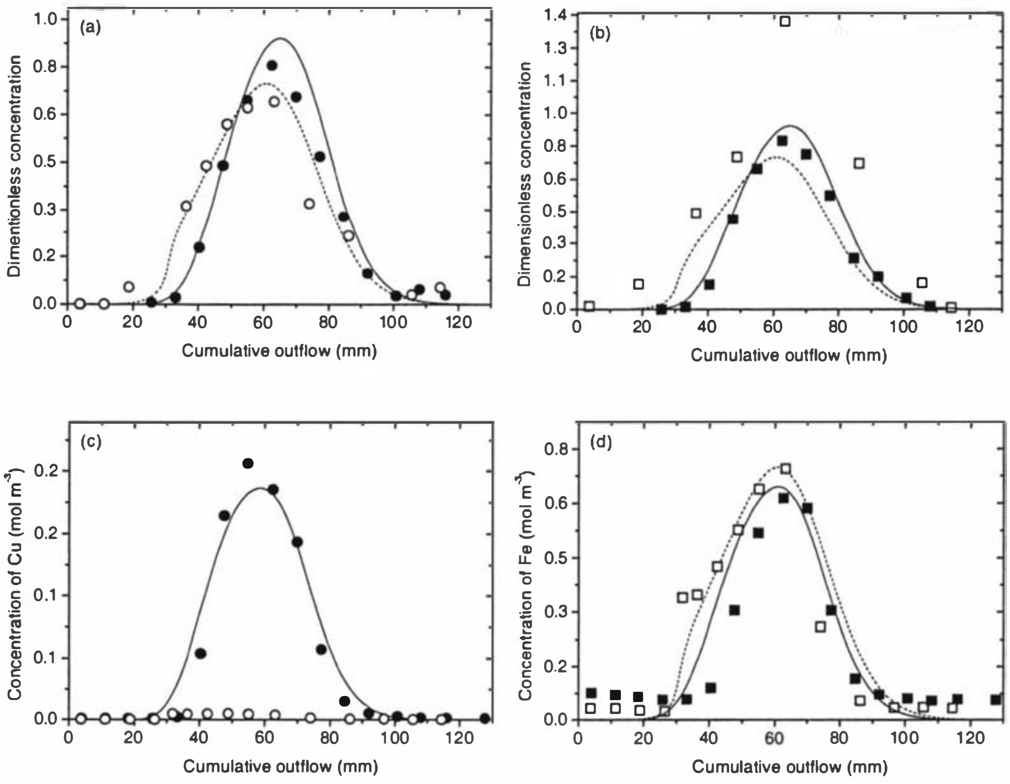

Figure 6-11 Breakthrough data for the low-Cu soil delayed EDTA$_0$ leaching experiment described in Chapter 2. The filled-in symbols and full lines are for the column leached immediately; the empty symbols and broken lines are for the column left for a month before leaching. (a) Chloride (b) EDTA (c) Copper. (d) Iron.

To simulate the copper and iron results, the parameter set described above for Manawatu soil in Section 6.1.3.3.1 was used except for M_{Cu}. The soil used for this experiment (described in Section 2.3.3) was collected from a different spot, or slightly different depth, so apparently contained less organic matter. Therefore the copper concentration measured in the top layer of the column leached immediately after the $EDTA_0$ application, was taken as the non- EDTA extractable copper. This was found to be 0.20 mmol kg^{-1}. With this adjustment, the model simulated the results for leachate copper and iron (Figure 6-11c, 6-11d and Table 6-2) well. This is despite the much lower copper concentration, the smaller amount of EDTA applied in this experiment compared to experiments described in Section 6.1.3.3.2, and the varying periods it was left in the soil. Thus the simple model developed appears quite robust, and is capable of predicting the results of experiments done in a quite different soil, given that the values for a few key parameters are adjusted appropriately.

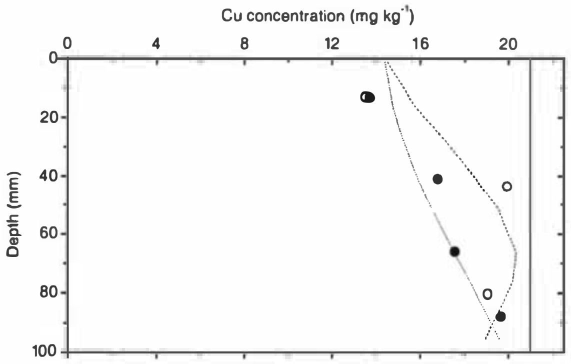

Figure 6-12 The initial copper concentration (—) and the final measured and simulated copper concentrations in the soil column leached immediately (● and ......) and a month (○ and ------) after $EDTA_0$ application.

Figure 6-12 shows that the final copper concentrations in the soil were well simulated by the model using the parameters derived for Manawatu soil. The model data successfully described the re-adsorption of the gradually-released Cu^{2+}, as shown by the increased copper concentration below the 40 mm depth of the soil in the delayed leaching experiment.

The experiments described in Section 2.3.2 and 2.3.3, that involved delayed leaching on medium and high-Cu soils, could not be successfully simulated by the model. In the low-Cu soil the transformation processes of $CuEDTA^{2-}$ involved release of $Fe(III)EDTA^{-}$ and Cu^{2+} into the soil solution, and the subsequent re-adsorption of released Cu^{2+} by the soil. However, these processes were less pronounced in the medium and high-Cu soils and more of the copper stayed in the soil solution. This may be due to the fact that the soil was only left for 10 d to "age" in the laboratory after the extra copper was added to increase the copper levels in the soil. Also the preleaching of the medium- and high-Cu soil columns was insufficient to leach out the water-soluble copper completely.

Table 6-2 The iron and copper leached with varying EDTA residence times

Residence time	Cu leached	(μmol)	Fe leached	(μmol)
(d)	Experiment	Model	Experiment	Model
0	10	10	40	40
1*	5	7	59	57
7	0.8	0.2	50	49
30	0	0	50	50

*The amount of EDTA applied in this particular experiment was 65 μmol and in the others 50 μmol.

6.1.3.4 *$CuEDTA^{2-}$ leaching experiment on Opotiki soil*

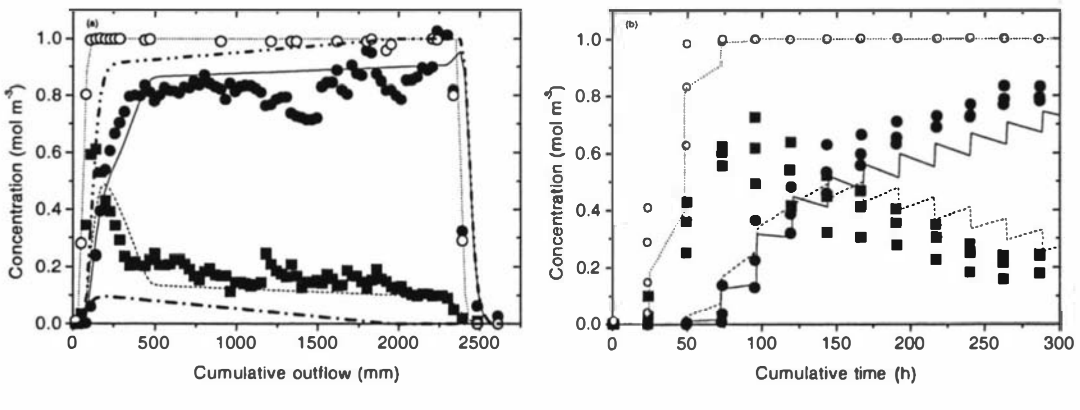

Figure 6-13 Observed and simulated effluent concentrations for Experiment C of bromide (○ and ....) copper (● and — or—··—··-), iron (■ and ------- or -·-·-) as a function of (a) cumulative outflow and (b) the first 300 h of cumulative time. Details of the two simulations for iron are given in the text.

In this section simulation of Experiment C, described in Section 3.2.2.2, is outlined. Figure 6-13 shows the measured and predicted results of Experiment C. During the leaching with $CuEDTA^{2-}$, the only significant reaction taking place was the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$. This allows the study of this transformation in some detail. The model, with the values for M_{Fe}, and k_3 used for Experiments A and B for the same Opotiki sandy loam, but from a contaminated area, grossly underestimated the amount of iron leached (–·–·– in Figure 6-13a), and so the reaction rate of the $CuEDTA^{2-}$. This also resulted in an overestimation in the amount of copper leached (–··–··–). This is believed due to the soil's pH, which was 4.5, and significantly lower than the 5.6 of the contaminated soil. The lower pH would have made iron in the soil more easily extractable by EDTA (Brooks *et al.* 1996). This suggests the use of a higher value for k_3. It also seems likely that more iron would have been extractable by EDTA, implying a higher value for M_{Fe}. However the shape of the iron breakthrough curve with an initial sharp peak of 0.6 mol m^{-3}, followed by a long plateau of around 0.2 mol m^{-3}, suggests another approach. It is consistent with two EDTA-extractable iron fractions being present in the soil; a smaller and rapidly reacting fraction (M_{Fe}), and a larger more-slowly reacting one (M_{Fe}^{*}). The introduction of this second iron fraction implies that two additional terms are required in the model. One describes the reaction between $EDTA_0$ and M_{Fe}^{*}, and the other describes the reaction between $CuEDTA^{2-}$ and M_{Fe}^{*}. Thus equations (6-3) and (6-4) given in Section 6.1.2 now become

$$S_{Cu} = k_1(C_o\,\rho_b\,M_{Cu})^n - k_3(C_{Cu}\,\rho_b\,M_{Fe})^n - k_5(C_{Cu}\,\rho_b\,M_{Fe}^{*})^n \tag{6-6}$$

$$S_{Fe} = k_2(C_o\,\rho_b\,M_{Fe})^n + k_4(C_o\,\rho_b\,M_{Fe}^{*})^n + k_3(C_{Cu}\,\rho_b\,M_{Fe})^n + k_5(C_{Cu}\,\rho_b\,M_{Fe}^{*})^n \tag{6-7}$$

Here k_4 is the rate constant for the reaction between $EDTA_0$ and the slowly extractable soil iron, and k_5 is the rate constant for the reaction between $CuEDTA^{2-}$ and the slowly extractable soil iron. Both have units of s^{-1}. The other symbols have already been defined in Section 6.1.2.

To use this modified model to simulate the data in Figure 6-13, values for M_{Fe}^{*} and k_5 have to be found. Also a new value is needed for k_3, as it is expected to have a higher value in the more acid soil. The protracted, slow decline in the iron concentration in the leachate suggests a relatively high value for M_{Fe}^{*}, and a relatively low value for k_5. Fitting-by-eye provided values of 6.3 mmol kg^{-1} for M_{Fe}^{*}, 1.3 x 10^{-6} s^{-1} for k_3 and 1.3 x

10^{-7} s^{-1} for k_5. Some adsorption of EDTA by the soil was also expected at pH 4.5 soil, and an R value of 2 was assumed, for reasons discussed below in Section 6.1.3.5 in relation to Experiment D.

The saw-tooth shape of the simulated curves in Figure 6-13b mirrors the observed behavior (described in Section 3.3.3) nicely. However, during the first 100 h, the iron concentrations were much higher than simulated. This suggests that there was some iron in the soil that was more readily available, and/or reacted more quickly, than assumed in the simple model which divided the soil iron into just two fractions.

Figure 6-14 shows the measured and simulated copper concentration at the end of the experiment as a function of depth. The model was able to simulate the Cu^{2+} adsorption to the soil reasonably well at least for the soil depth of 60 mm.

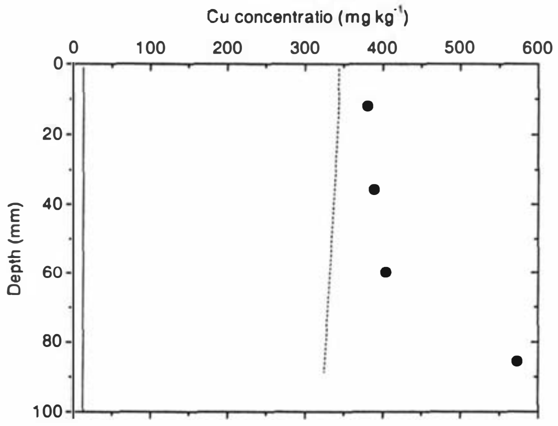

Figure 6-14 The initial copper concentration (—) and the final measured (●) and simulated (......) copper concentrations in the soil column in Experiment C.

6.1.3.5 Repacked experiments using non-uniform copper Opotiki soil

In this section, simulation of Experiments D and E (Section 3.3.4) which used layers of copper contaminated and non-contaminated soil is described. To apply the model to Experiments D and E, the greater availability of the iron at the lower pH in the soil used in the bottom 70 mm of the columns has to be taken into account. As discussed above in relation to Experiment C in Section 6.1.3.4, soil iron becomes more reactive as the pH decreases. So it was assumed that the values for k_2 and k_4 changed with pH in the same way as the k_3 and k_5 were assumed earlier. Thus for both Experiments D and E, k_2 was assumed as 6×10^{-5} s^{-1} and k_4 as 6×10^{-6} s^{-1} in the bottom 70 mm of soil. For the copper contaminated soil in the top 30 mm of the columns, the k values used were those found in Section 6.1.3.1 and used for Experiments A and B.

As shown in Figure 6-15a in Experiment D, the breakthrough of EDTA was retarded relative to bromide, as a result of the lower pH in the bottom 70 mm of soil. Fitting by eye showed that an R value of 2 described this retardation for EDTA movement through the lower 70 mm of the columns reasonably well (Figure 6-15a). This value was also assumed in the lower pH soil used in Experiments C and E.

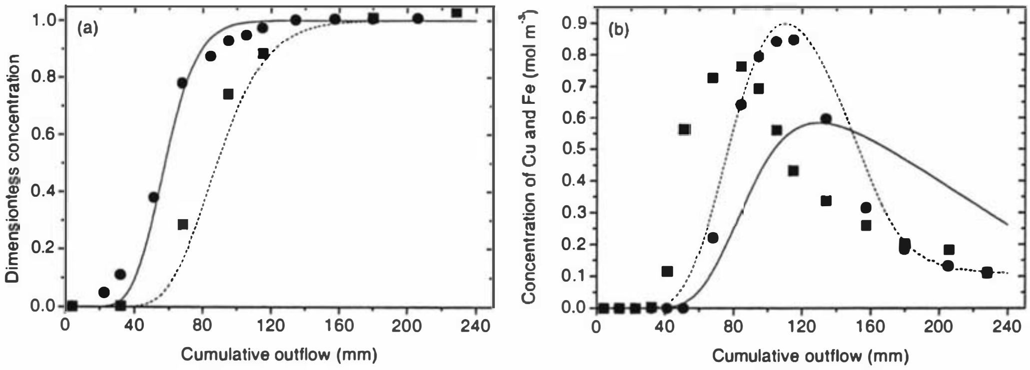

Figure 6-15 Breakthrough data for Experiment D. (a) Measured and simulated breakthrough data for bromide (● and —) and EDTA (■ and ----). (b) Measured and simulated breakthrough for copper (● and —) and iron (■ and ----).

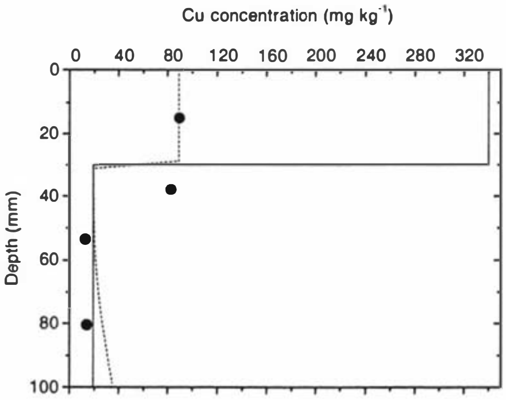

Figure 6-16 The initial copper concentration (—) and the final measured (●) and simulated (......) copper concentrations in the soil column in Experiment D.

In Experiment D, the observed copper breakthrough was more peaked than the simulated curve, and further the iron came out somewhat earlier (Figure 6-15b). This could perhaps be due to $CuEDTA^{2-}$ and Fe(III)$EDTA^{-}$ being less subject to adsorption than the Na_2H_2EDTA and calcium-EDTA as they moved through the lower 70 mm of the columns. The model, as shown in Figure 6-16, closely simulated the final copper concentration in the soil at the end of the Experiment D.

In the immediately-leached column of Experiment E, while the observed exiting pulse of EDTA from the column had roughly the expected retardation, its amplitude was about half that of the simulation (Figure 6-17b). This suggests more adsorption of EDTA than implied by the assumed *R* value of 2. This simple model implies a linear adsorption isotherm, whereas isotherms are usually non-linear. Such non-linearity is the probable reason for the *R* value derived for 0.01 *M* EDTA (in Experiment D) underestimating the adsorption of 0.001 *M* EDTA.

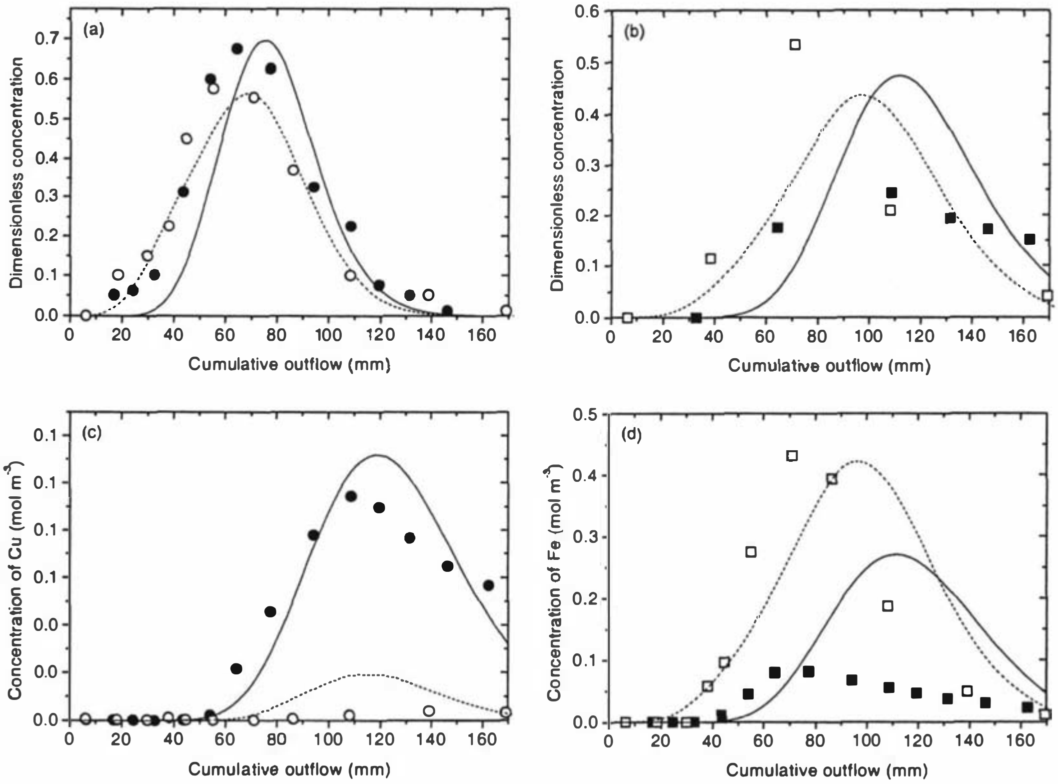

Figure 6-17 Breakthrough data for Experiment E. The filled-in symbols and full lines are for the column leached immediately; the open symbols and broken lines are for the column left for a month before leaching. (a) Chloride (b) EDTA (c) Copper (d) Iron.

In contrast to the immediately leached column, Figure 6-17b shows the peak EDTA concentration to be greater than the simulated value for the column in which leaching was delayed for a month. The inferred EDTA peak from the DOC analysis is too high here, due to the presence of organic compounds other than EDTA affecting the DOC analyses. This is discussed in Section 6.1.3.3.4 in relation to similar experiments conducted on Manawatu soil.

Figure 6-17c shows that the concentrations of copper in the leachate from the immediately leached column in Experiment E were closely simulated by the model. However for the column with delayed leaching the copper concentration in the leachate was overestimated. At these lower concentrations it seems the model underestimated the rate of conversion of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$. In contrast Figure 6-17d shows the model grossly overestimating the iron in the leachate from the immediately-leached column, but quite accurately simulating it for the column with delayed leaching. This may be due to the procedure used for selecting a value for k_2 in the lower pH soil. The simulated iron concentration in the immediately leached column was found to be very sensitive to this rate constant. The measured and simulated final copper distributions in the two soil columns in Experiment E are shown in Figure 6-18, and they are in approximate agreement.

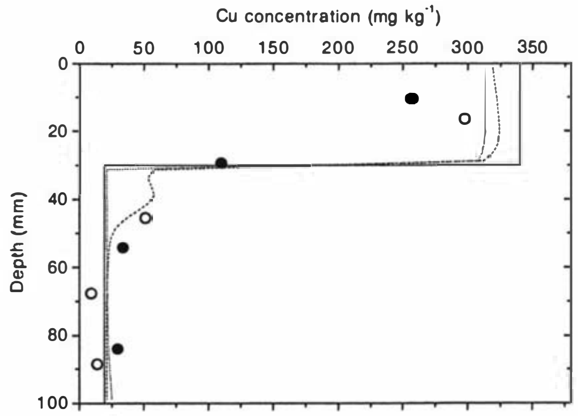

Figure 6-18 The initial copper concentration (—) and the final measured and simulated copper concentrations in the soil column leached immediately (● and ......) and a month (○ and ------) after $EDTA_0$ application in Experiment E.

6.1.3.6 Experiments on intact cores

One of the main aims of this study was to see if the model that was developed for repacked soil could be applied to intact soil. To simulate the intact-soil core data from first and second experiments described in Sections 4.3.3 and 4.3.4, the parameters derived in Section 6.1.3.1, from experiments conducted on repacked Opotiki soil, were used, as the soil used was the same. The main exception was the quite different soil structure, and so flow pathways. Hence a very different dispersivity was expected. The bromide breakthrough data in Figure 6-19a yielded a fitted value of 23 mm for λ, an order of magnitude greater than the value for the repacked soil. The simulated curve obtained using this value is shown in Figure 6-19a. The same curve, which assumes negligible adsorption (R = 1), simulated the EDTA breakthrough. The observed EDTA data for the first experiment show only a slight retardation relative to the bromide data, much less than in Figure 6-15a, indicating little adsorption. This was expected, as the intact soil pH was much closer to that of the repacked soil used in Experiment A than that used in Experiment E.

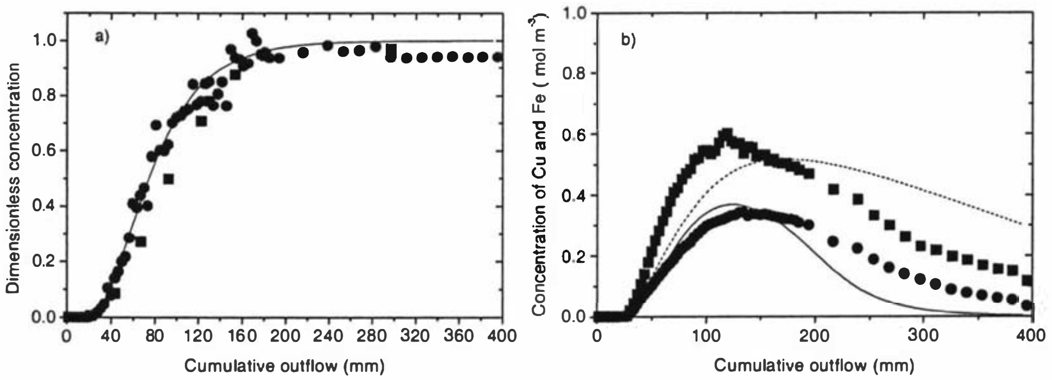

Figure 6-19 Breakthrough data for the intact core in the first experiment of Chapter 4. (a) Measured and simulated breakthrough data for bromide (● and —) and EDTA (■ and ----). (b) Measured and simulated breakthrough for copper (● and —) and iron (■ and ----).

The simulated copper and iron breakthrough curves for the first experiment in Figure 6-19b approximate the observed curves, as does the final copper distribution in the soil (Figure 6-20), despite the radically different soil structure. This is encouraging, although the amount of copper leached was 640 μmol, while the model predicted 480 μmol. This discrepancy can be partly attributed to an overestimation of the amount of non-EDTA extractable copper in the soil, as discussed above.

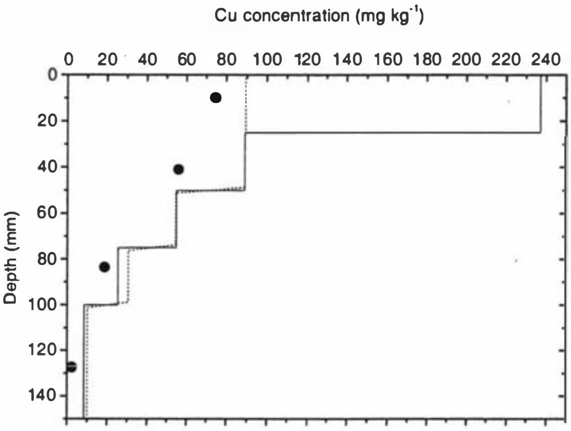

Figure 6-20 The initial copper concentration (—) and the final measured and simulated copper concentrations in the soil core (● and ----) in the first experiment of Chapter 4.

For the immediately-leached column in the second experiment of Chapter 4, Figure 6-21a shows that while the breakthrough of bromide is well described, the measured values for EDTA have a much lower maximum, and the breakthrough is retarded. This suggests that some of the relatively small pulse of EDTA applied was adsorbed. Similar behaviour was observed in Experiment D (Figure 6-15a). It is interesting, however, that Experiment B showed no EDTA adsorption. This is probably due to the higher soil pH in Experiment B compared to the soil pH in Experiment A and in this experiment.

Again, for the immediately leached column, there was approximate agreement between the measured and simulated values for the copper and iron concentration in the leachate, and for the final copper concentrations in the soil (Figures 6-21c and 6-21e). As might be expected, close agreement was not found between the observed and simulated concentrations of copper and iron in the leachate, due to the discrepancy between the observed and simulated EDTA behaviour evident in Figure 6-21a. Also, in the early leachate, the iron concentration was higher than the copper concentration, while the simulation predicted the opposite. This could be due to the leading edge of the EDTA pulse encountering some very reactive iron as it moves through the soil.

For the reasons given in the discussion of the Experiment E in Section 6.1.3.5, the month's delay in leaching in this experiment, coupled with the low soil-solution copper concentration, means that the inferred EDTA values are suspect due to the likelihood of additional organic carbon contributing to the measured DOC. So the peak EDTA concentration in Figure 6-21b is probably erroneous. The actual peak EDTA concentration in the leachate was probably somewhat lower than the simulated value, due to adsorption. If so, that would explain the peak iron and copper concentrations found in the leachate being lower than the simulated values (Figure 6-21d). The drop in the leachate copper concentration, and the sudden increase in iron concentration, following the month-long pause were simulated reasonably well.

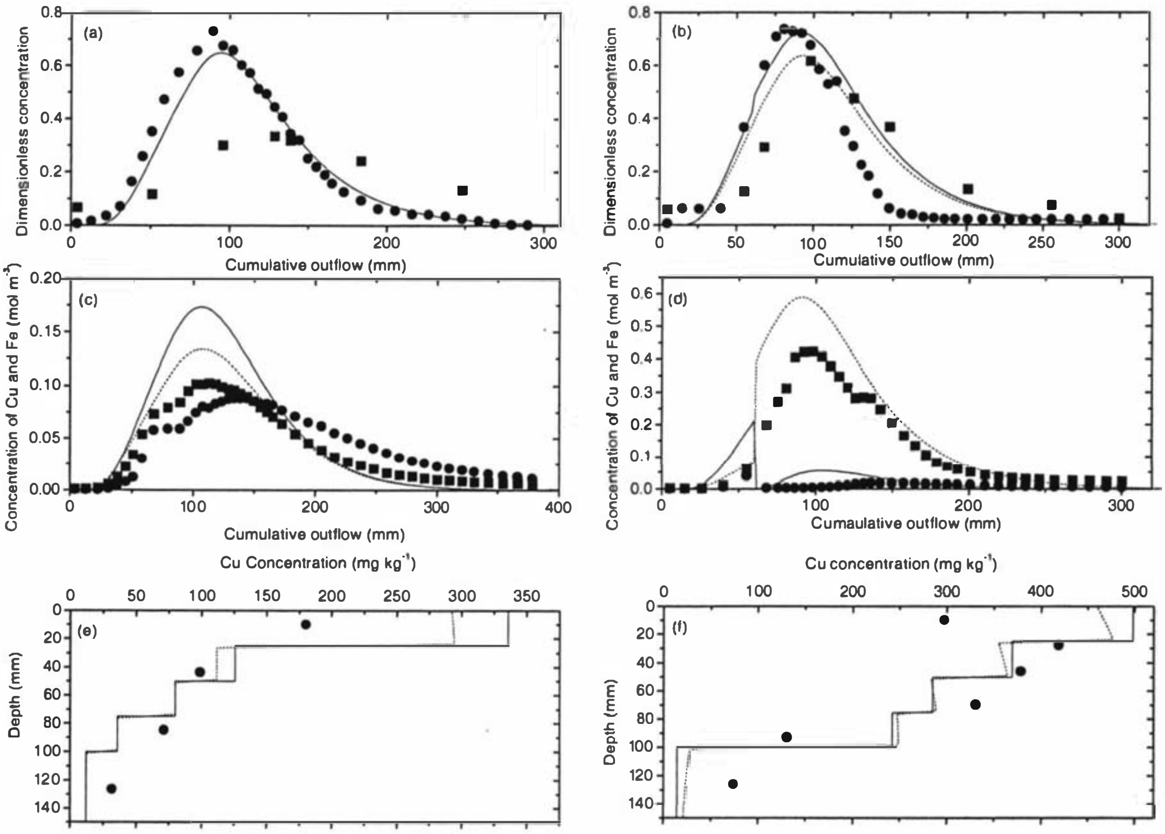

Figure 6-21 Results of the second experiment of Chapter 4. Figures (a), (c) and (e) show results for immediate leaching. Figures (b), (d) and (f) show results with a month's delay before leaching. Figures (a) and (b) show measured and simulated breakthrough data for bromide (● and —) and EDTA (■ and ----). (c) and (d) show measured and simulated breakthrough data for copper (● and —) and iron (■ and ----). (e) and (f) show the initial copper distribution (—) and the final measured (●) and simulated (----) copper concentrations in the soil cores.

The simulated final copper-concentrations shown in Figure 6-21e and 6-21f underestimate the amount of copper removed from the top 20 mm of soil. This could be due to the copper being less strongly bound to the intact soil than the repacked soil, and so the assumed values for k_1 and /or M_{Cu} being too low or the copper in the intact soil being in places less accessible to the EDTA compared to the repacked soil.

6.2 Modelling copper uptake by plants following the application of EDTA

6.2.1 Introduction

An understanding of the influence of plants on water and chemical movement in soil aids in developing phytoremediation strategies. Such an understanding can be obtained by descriptions of the physical and chemical processes that control the water flow and chemical transport through the root zone, as well as the uptake strategies by the plant (Vogeler *et al.*, 2001). Many studies have investigated and modelled these processes, either separately or in combination, mostly using one-dimensional approach.

In Section 6.1 the modelling of EDTA-enhanced transport of copper through contaminated soil under various initial and boundary conditions has been described in detail. Here the model is extended to incorporate processes such as transient water movement in soil, and water uptake by plant roots, to simulate the copper uptake by grass, following EDTA application.

6.2.2 Model development

6.2.2.1 Water movement in soil

As discussed in Chapter 1, water movement through unsaturated soil is described by the Richards' equation (equation 1-7), upon which most simulation models are based. To solve Richards' equation, information about the soil's hydraulic conductivity $K(\theta)$ and its water retention properties is required. Partly because detailed data on the hydraulic properties of the soil were not available, a simpler cascade approach was used here to describe transient water movement, similar to that described by Diekkrüger *et al.*, (1995). As before, an explicit finite-difference approach is used. As before, the soil columns are treated as a number of layers each Δz thick. Time is divided into segments each Δt long.

The cascade approach takes the soil water conservation or continuity equation into consideration and so obeys equation (1-5). The change in the water content of a layer of soil over a time interval is equal to the input from the layer above, minus the loss to the layer below less any plant uptake. Any water in excess of field capacity (θ_{FC}) present in a layer at the start of a time interval is assumed to drain into the layer below during the time interval. This implies that gravity driven-percolation only occurs once the local water content exceeds θ_{FC}, and occurs at the rate needed to bring the water content back to θ_{FC} over the time interval. Thus during any time step the flux out of each layer (q_w) is computed as

$$q_w = (\theta_i - \theta_{FC})\frac{\Delta z}{\Delta t} \qquad \text{if } \theta_i > \theta_{FC}\text{, else } q_w = 0 \tag{6-8}$$

where, θ_i is the water content in the layer at the start of the time step. The new θ_i ($\theta_{i,\ new}$) value for use in the next time step is then found by writing equation (6-8) in finite difference form, and rearranging it to get

$$\theta_{i,new} = \theta_{i,old} + (q_{w,in} - q_{w,out})\Delta t/\Delta z - U_w \Delta t \tag{6-9}$$

where $q_{w,\ in}$ is the flux into the top of the layer and $q_{w,\ out}$ is the flux out of the bottom of the layer during the time interval.

6.2.2.2 *Water uptake by roots*

Water uptake by plant roots varies in space and time and depends mainly on,

- the spatial distribution of active roots
- availability of soil water (as controlled by the matric potential and hydraulic conductivity)
- atmospheric demand

For most field crops, the spatial distribution of roots is observed to decline exponentially with depth, and the root uptake activity can be considered proportional to root density (Gardner, 1983). Instead of an exponential decline, a linear decline was assumed in this study for the water uptake, which was maximum at the surface and zero at the base of the column (Prasad, 1988). Actual root water uptake not only depends on the root distribution and its functioning, but also on soil water availability. However, irrigating the columns/cores every day to the field capacity maintained the soil water content at near optimal values for water uptake, so this effect could be ignored. Further, the EDTA addition and the final leaching were performed after the grass was well established. Thus it could be assumed that the roots had grown to the maximum rooting depth (the length of the column) and that the root density did not change during that phase of the experiment. It was also assumed there was no evaporation from the soil surface, as there was full grass coverage. Thus the integral of U_w with depth, from the surface to the maximum depth of the root system (the length of column), equalled the total transpiration flux T_{tot} (m s^{-1}). The water uptake as a function of depth can thus be derived as below.

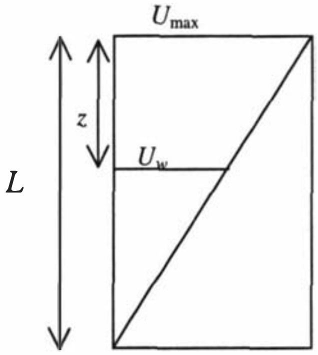

Figure 6-22 Column or core showing the root water uptake pattern as a function of depth

In Figure 6.22, the total uptake rate [m s^{-1}] is

$$T_{tot} = \frac{1}{2} U_{max} L \tag{6-10}$$

where U_{max} is the water uptake from the surface and L is the maximum rooting depth (length of the column). Then, using the similar triangle rule, the water uptake as a function of depth could thus be described by,

$$\frac{L}{L-z} = \frac{U_{max}}{U_w}.$$

Substituting for U_{max} from equation (6-10) and rearraging gives the following equation

$$U_w = \frac{2T_{tot}}{L}\left(1 - \frac{z}{L}\right). \tag{6-11}$$

6.2.2.3 *Solute transport in soil*

To describe solute movement, the model described in Section 6.1 was used. It is a simple model using the convection-dispersion equation, incorporating a source/sink term describing the competing time-dependent reactions of copper and iron with EDTA, and the reversion of $CuEDTA^{2-}$ to adsorbed Cu^{2+} and $Fe(III)EDTA^{-}$ in solution. Rate constants for the sink/source reactions were the same as used in Section 6.1. With a solute uptake term in it, the basic transport equation [1-22] can be written as

$$\frac{R\partial(\theta C)}{\partial t} = \theta D\frac{\partial^2 C}{\partial z^2} - q\frac{\partial C}{\partial z} + S + U_s \tag{6-12}$$

where U_s is a term accounting for copper uptake by the roots (mol m^{-3} of soil s^{-1}).

6.2.2.4 *Copper uptake by plants*

The simplest assumption one can make is that the uptake of a solute by plants is just passive convection with the water. Then the local solute uptake is just the product of the local water uptake (U_w) and the local solute concentration (C). However, experimental evidence shows that roots usually control the solute uptake by either excluding, or actively taking up each solute to some extent at least. Although there are different theories for describing the way plant roots control uptake, an exclusion mechanism is introduced here in two contrasting ways.

Case I. The product of the local water uptake and the local solute concentration was multiplied by a reduction factor (f). This implies the uptake was always proportional to the local concentration.

Case II. Roots throttled the uptake whenever the local concentration exceeded a certain threshold concentration, C_{crit} (Vogeler *et al.*, 2001). In the model solute uptake is thus described by either,

Case I. $U_s = f\, U_w C$

or

Case II. $U_s = U_w C$ if $C < C_{crit}$

Else $U_s = U_w\ C_{crit}$ (6-13)

where C is the local concentration of CuEDTA$^-$ in mol m^{-3} and C_{crit} is the critical concentration triggering exclusion by the roots. It means that at concentrations lower than C_{crit} solute moves passively into the plant, along with the transpiration flow. But all concentrations higher than C_{crit}, the solute concentration entering the roots is limited to C_{crit}.

As before, the above equations were solved numerically using the appropriate boundary and initial conditions. An explicit finite-difference scheme, written in Visual Basic within Excel™ was used to do this. A forward-difference approach was used.

6.2.3 The parameters in the model

Solution of equations (1-7) and equations from (6-8) to (6-13) requires that values be found for the parameters in them. These parameters were either directly measured, determined indirectly using the results of the experiments, or used the parameters found earlier for repacked soil. Flux density in these experiments was variable with time and depth. The upper boundary for q_w was taken as 6 mm h^{-1} during water or EDTA addition, calculated from the time taken to apply the 90 ml of EDTA or water. This value remained constant for all days and for all experiments, except for the time when water was applied using the disc permeameter at a pressure head of –100 mm to wash out the EDTA. During that final leaching it increased to 12 mm h^{-1}.

For θ_{FC}, the measured volumetric water contents at the end of leaching experiments conducted under steady state conditions using repacked soil and cores of the same Opotiki sandy loam was used. The procedure for measuring this is described in Chapter 2. The value for θ_{FC} thus found was 0.59 for both the repacked and intact cores.

The measured transpiration water loss from the columns/cores ranged from 10-12.7 mm d^{-1}. This was assumed to be equal to the transpiration loss, as dense vegetative cover meant that evaporation from the soil surface was minimal. In the model a constant value of 11.4 mm d^{-1} was used for the transpiration flux.

The parameter values needed to describe the solute transport such as dispersivity, diffusion coefficient, reaction rate co-efficients and iron concentrations were the same as those used in Section 6.1.3, as the same soil was used. M_{Cu} was estimated as the initial acid-extractable copper minus the EDTA non-extricable copper (90 mg kg^{-1}). In the intact cores, the depth wise initial acid-extractable copper distribution was obtained as described in Section 4.3.1. For the dispersivity, the average values found for the repacked and intact Opotiki fine sandy loam soil without grass were used. These were 3 mm for the repacked columns and 23 mm for the intact cores (Chapters 3 and 4). However, the dispersivity of the soil with and without roots could be different (Vogeler *et al.,* 1997). Also for undisturbed soil considerable spatial variability is expected.

The concentration of $EDTA_0$ applied was $0.01M$ for the treatments with one and two applications. However, for the treatments with 9 and 18 times applications the $EDTA_0$ was diluted with the water that was added to compensate for transpiration loss. Although the amount of water mixed with 10 ml of $0.01M$ EDTA varied from 68 ml to 89 ml, an average 80 ml was used in the model, giving an EDTA concentration of $0.0011\ M$.

Given there is enough iron and copper in the soil, the model assumes that at equilibrium all the EDTA is complexed with iron and copper. However, most of earlier experiments using the same soil showed that only about 70% of the applied EDTA complexed with copper and iron. The remaining 30% of the EDTA had apparently either complexed with calcium and/or zinc, or broken down in the soil. Therefore, an EDTA input of 70% of the EDTA applied was assumed in the simulation.

As already mentioned, solute uptake was modelled in two ways, for Case I, a value of 0.0006 was obtained using trial and error for the dimensionless factor (f), using the data from the 2-times-EDTA applied repacked column. For Case II, the critical concentration C_{crit} was estimated as 0.004 mol m^{-3}. This is the product of the maximum copper concentration found in leaves (mol g^{-1}) and the dry matter produced per unit amount of water during EDTA application (g m^{-3}).

6.2.4 Results and discussion

The above value for f and C_{crit} show that the grass roots did exclude copper. For Case I type of copper uptake, an exclusion factor of 0.0006 was used to model all experiments, regardless of the soil concentration. The model predicted an uptake of 9.0 μmol of copper for all experiments. It failed to show the differences in uptake in repacked and intact cores (Table 6-3).

The Case II type of uptake, C_{crit} was introduced to limit the passive uptake at higher concentrations. Although the grass roots were found to be dense at the surface in both repacked and intact cores, structural differences in the soil, and the greater non-uniformity in copper distribution in the intact cores could have caused differences in the uptake with depth. In the cores, the high dispersivity means that the highly concentrated copper band in the topsoil becomes dispersed, and thereby increases the depth over which the soil solution copper concentration becomes greater than the maximum uptake concentration. However, in the repacked soil, due to the much smaller dispersivity, and initially uniform copper distribution, this spreading of copper over the depth is less. Hence, it was hoped that fixing the C_{crit} in the model would show the difference in copper uptake between the repacked and intact cores.

Although the model uptake expressed by Case II type did show a difference in uptake between the intact and repacked columns, it over-predicted the copper accumulation in the intact cores (Table 6-3). In fact the model predicted more uptake in the intact cores than in repacked columns. This was the reverse of what was actually found.

Table 6-3 Measured and modelled amounts of copper leached and uptake in the repacked columns and intact cores.

		Experiment I (Repacked)			**Experiment II (Intact)**		
		EDTA applications			EDTA applications		
		None	Two	Eighteen	None	Two	Eighteen
EDTA applied (µmol)		0	1800	1800	0	1800	1800
Cu leached (µmol)	Measured	5	480	363	1	115	340
	Model	-	488	590	-	444	478
Fe leached (µmol)	Measured	2	788	686	1	1045	816
	Model	-	757	658	-	796	770
Copper taken by the grass (µmol)	Measured	1.54	7.78	14.8	0.42	1.2	3.2
	Model I	-	9	9	-	9	9
	Model II	-	9	9	-	13	10

It is not worth trying to get an optimum value for C_{crit} to predict the correct plant uptake in the absence of an independent measurement of the dispersivity, particularly in this study. The results from the sensitivity analysis of a similar solute uptake model showed that various combinations of C_{crit} and dispersivity could give similar results for the plant uptake (Vogeler *et al.*, 2001).

The failure of the model to explain the difference in copper uptake by grass grown in repacked columns and intact cores in this study implies that the lower copper accumulation measured in the intact cores was not entirely due to the copper distribution or to exclusion, but was controlled by some other factor. It could be the heterogenity in the location of copper adsorption sites or in local root distribution limiting the accessibility of the copper.

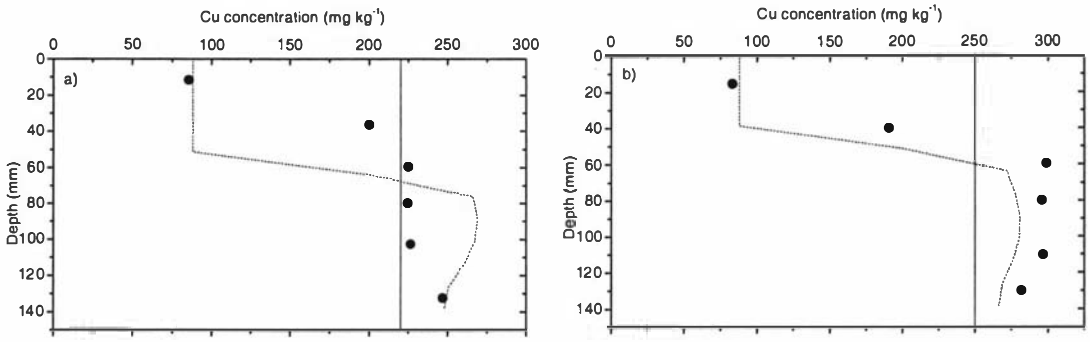

Figure 6-23 The initial copper concentration (—), and the final measured and simulated copper concentrations in the soil after leaching (● and ......) in the repacked columns. a) two EDTA applications b) 18 EDTA applications.

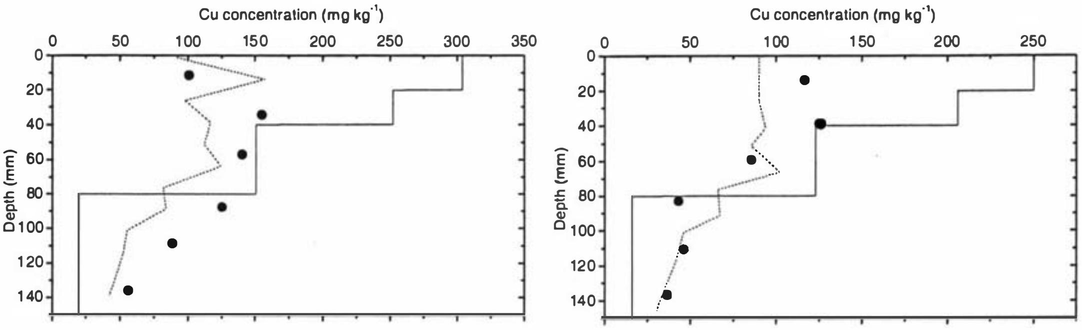

Figure 6-24 The initial copper concentration (—), and the final measured and simulated copper concentrations in the soil after leaching (● and ......) in the intact cores. a) two times applications b) 18 times applications.

The depth-wise final copper concentration measured in the columns and cores after the final leaching is shown in Figures 6-23 and 6-24. Also shown are the model outputs assuming the Case II type for plant uptake. The overall shape of the copper profile in the soil is quite well reproduced by the model both in the repacked columns and the intact cores. In the repacked columns, both measured and the model predictions on the copper concentration at the surface soil are in agreement, showing the EDTA-non extractable copper (90 mg kg^{-1}). However, in the intact cores, the copper concentration measured at the surface soil was a little higher than the model predictions. The model also has leached more copper from the 25 - 70 mm depth compared to the measured amount in the 2 times-EDTA applied column and core. These discrepancies could be due to the assumptions made about the dispersivity, root water extraction rates, and also uncertainty in the determination of initial soil copper distribution in the cores.

For most of the experiments, a reasonable agreement was found between the amount of leached copper and iron, and the model predictions (Table 6-3).

6.3 Extrapolating the model to other conditions

Models can be used to predict what would happen under a much wider range of experimental conditions than it is practicable to study experimentally. To illustrate the power of modelling in this regard, the model was used to predict the copper and iron leaching at different flow rates. The model was used to predict copper and iron leaching after a 50 µmol pulse application of EDTA and the leaching it out at different flow rates. A repacked column of Opotiki soil 100 mm long, and a core of 150 mm were considered. Figure 6-25 shows the simulated amounts of copper and iron leached as a function of flow rate.

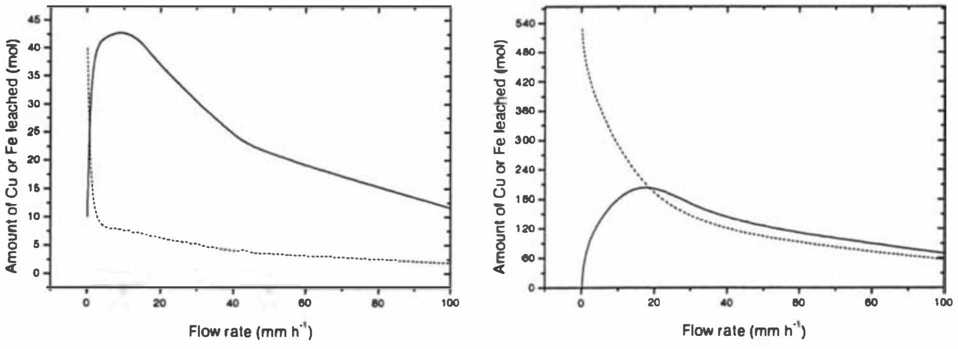

Figure 6-25 Simulated amounts of Cu (—) and Fe (-----) leached as a function of flow rate in (a) repacked (b) and intact Opotiki soils after a pulse application of 50 µmol of EDTA in the repacked column and 540 µmol of EDTA in intact cores and leaching with 3 PV of water.

In both the repacked and intact Opotiki soils, copper and iron leaching show similar trends. Copper shows an increase to reach a peak followed by a decline, and the iron shows a decline with the greater flow rates. However, in the intact core, with a flow rate greater than 18 mm h^{-1}, the amount of copper and iron leached is about the same. This is attributable to the lower amount of available copper in the intact cores compared to the repacked soil. At low flow rates, both in the repacked and intact soils the amount of copper leached was less than the amount of iron. This is due to the longer time available for the transformation reaction of $CuEDTA^{2-}$ to Cu^{2+} and $Fe(III)EDTA^{-}$ followed by the re-adsorption of the Cu^{2+}. It is interesting to note that the pulse application of EDTA at a flow rate of 28 mm h^{-1} followed by leaching a month later (Experiment B in Section 3.2.2.1), and the same size EDTA pulse applied at a rate of 0.1 mm h^{-1} and leaching it immediately, leach out about the same amount of copper and iron. When high flow rates were used in the model, smaller amounts of copper and iron were leached. The relative ineffectiveness of extraction of copper and iron at greater flow rates is attributable to the short contact time. The model suggests a steady flow rate of between 3 and 14 mm h^{-1} optimises the extraction of copper from the repacked soil, and of between 5 and 25 mm h^{-1} optimises it for the intact soil.

6.4 Conclusions

In the studies described above, EDTA-enhanced transport of copper and iron species through contaminated soils was modelled using the CDE coupled with a source/sink term accounting for the chemical reactions bringing that chemical species into or out of solution. In general, the model described reasonably well the copper concentration in the leachate and soil, despite the different amounts and concentrations of EDTA applied, and the varying lengths of time it was left in the soil. However there were some aspects of the experiments that the model did not describe well. The discrepancies are probably due to the fact that this simple model can only describe approximately the range of reaction rates, and the range in availability of the soil copper. Copper is bound to the soil matrix components to varying degrees, depending in part on how long it has been in contact with the soil.

The model was quite robust, as it was capable of predicting the copper and iron leaching successfully in both the Opotiki and the Manawatu soil, given that the values for the key parameters such as rate constants were adjusted appropriately. In the

Manawatu soil, the rate constants for the reactions between the copper, iron and EDTA were found to be 2.5 times higher than for the Opotiki soil. This can be perhaps attributed to the different forms and lower amount of organic matter in the Manawatu soil compared to the Opotiki soil.

Opotiki soil with a low pH required a different parameter set to simulate the EDTA-enhanced transport of copper and iron. An *R* of 2 was obtained by optimisation to describe the retardation measured for the EDTA adsorption. However, for the experiment where the soil was leached using 0.001*M* EDTA, the model only approximately simulated the EDTA adsorption. This could be due the linear adsorption isotherm implicit in a constant value for *R,* whereas isotherms are usually non-linear.

Further, the iron becomes more available and active as the pH decreases. Therefore, the rate constants used were higher than the ones used for the same Opotiki soil at a higher pH (5.6). With an introduction of two iron fractions in the soil: a smaller rapidly reacting fraction, and a larger more-slowly reacting fraction, the model was able to describe the $CuEDTA^{2-}$ transformation reaction to $Fe(III)EDTA^{-}$ as shown by the saw-tooth shaped simulated curves in Figure 6-11. The disagreement between measured and modelled amounts of iron during the first 100 h suggests the presence of a more reactive iron fraction than assumed in the model.

By changing just the dispersivity from 3 mm to 23 mm, the model with the same chemical parameters used to describe the repacked Opotiki soil experiments, was able to simulate the intact soil experiments. Also the drop in the leachate copper concentration, and the sudden increase in iron concentration following the month-long pause, were simulated reasonably well. This implies that the chemistry was adequately described with model, and that the changes to the dispersivity, a physical property, described the effects of different flow patterns in repacked and intact soil. It is important that the initial copper distribution with depth is accurately known in order to predict the EDTA-facilitated copper leaching in the field.

Using the model to extrapolate to conditions other than those used in the experiments allowed study of the interaction between the chemical kinetics and the transport properties of the soil. It suggests what flow rates to use for maximum copper extraction using a pulse of EDTA and steady leaching.

The same model proposed for describing the EDTA-enhanced transport of copper was expanded to simulate the plant uptake of copper, by including transient water movement, water uptake and solute uptake processes. Although this simple one-dimensional model simulated the copper concentration profile in the soil after the final leaching, it could not predict the plant copper uptake correctly. The model with the simplified assumption, that the roots of *A.tenuis* excluded copper with an optimised exclusion factor (f) of 0.0006 could not simulate the differences in uptake between treatments. The alternative exclusion mechanism described by defining a C_{crit} critical concentration to trigger the mechanism did simulate some differences in uptake between the grass grown in repacked and intact soils. But, it predicted more copper uptake by the grass grown in the intact soil than in repacked soil. While in the experiment the plant uptake was more from the repacked soil than the intact core. The failure of the model in predicting this difference could be due to heterogenity in the copper distribution, in the location of copper adsorption sites, and in the local root distribution in the intact soil limiting the accessibility of the copper to the roots.

7 General conclusions

7.1 Introduction

As stated in Chapter 1, the primary objectives of this study were:

- to better understand the physical and chemical processes that influence the EDTA-enhanced transport of copper in contaminated soils,
- to model EDTA-enhanced transport of copper through the root zone based on the understanding obtained, and
- to investigate the relative importance of plant uptake and leaching of copper following the addition of EDTA to a copper-contaminated soil.

To achieve these objectives, various column leaching experiments were performed under various initial and boundary conditions using two contrasting soils, an alluvial Manawatu fine sandy loam with a low organic matter content, and a volcanic Opotiki sandy loam with a higher organic matter content. The uptake and leaching of copper was studied following the addition of EDTA to repacked and intact Opotiki soil growing *A. tenuis*. Lastly, an attempt was made to model the observed behaviour. This chapter summarises the findings, and the conclusions that can be drawn from them.

7.2 Experimental techniques

Column leaching experiments rather than batch extractions were the basis of this study, in order to more closely simulate what would happen in the field. Batch studies are easier, faster and easier to replicate than column experiments. However, as discussed in Chapter 1, batch experiments often do not accurately represent the field situation, and so the results obtained from them have only limited ability to predict the fate of reactive solutes. Differences between these two approaches in the solid to solution ratio, in the agitation used, in the removal of the de-sorbed ions from the system, and in the contact time for the solutes to react with the sorbent, result in quite different reaction kinetics.

In this study, leaching experiments were first performed on sieved, homogenous soil to get an indication of the nature and kinetics of the interactions between the EDTA and copper in the soil. Sieved and repacked soil does not have the same spatial relationships between sorption sites and water flow paths as field soil with its structure intact. In repacked soil columns local physical non-equilibrium was greatly reduced, allowing the study of the chemical kinetics of the reactions by minimising the almost insolvable problem of deconvoluting the interactions between the physical and chemical non-equilibrium.

Later in the study, leaching experiments were conducted using intact soil cores in order to gain some understanding of the interactions between the rate-limited chemical reactions and the physical non-homogenous flow paths induced by the complex pore geometry that results from the soil structure. At the price of ignoring the pedon-scale spatial heterogeneity in both the physical and chemical properties of soil in the field, laboratory studies using undisturbed cores allow much better control of the experimental conditions than can be achieved in the field. For example in the repacked columns experiments, a steady flow rate could be applied using a peristaltic pump. Also a special apparatus with disc permeameters and bubbling towers could be used to create unsaturated flow conditions at a set pressure potential in the undisturbed cores.

The glasshouse experiments, studying the relative importance of plant uptake and leaching of copper following the EDTA application, also provided better control of the experimental conditions than is possible in the field. For example, the mass balance of the copper could be tracked, and the irrigation could be controlled so that no drainage occurred. Rain was excluded. These experiments could also carried out both in repacked and intact soil, to investigate the effects of the different pore geometry on water movement, root growth and copper uptake by the grass.

Given the aims of the study, the experimental techniques adopted proved to be appropriate and robust. In hindsight, I believe the decision to concentrate on column leaching experiments, rather than either laboratory batch studies, or field studies, was the correct one.

7.3 Experimental results

In both the Manawatu and Opotiki soil, all forms of EDTA moved without any observable adsorption at a pH (in water) of between 5.6 and 6.0. However, the uncontaminated Opotiki soil, with a pH of 4.5, did adsorb EDTA to some extent. In the intact Opotiki soil cores there was little adsorption, as the pH was in between that of the contaminated and non-contaminated soils.

Leaching with an excess of 0.01 *M* $EDTA_0$, extracted all but 40 mg kg^{-1} of the copper that was initially present in the repacked Manawatu soil. All but 90 mg kg^{-1} of the copper was extracted from the repacked Opotiki soil. This difference demonstrates the strong relationship between the organic matter content and the binding strength of copper. However all but 28 mg kg^{-1} of this remaining 90 mg kg^{-1} copper was extracted by shaking 1g of the Opotiki soil with 25 ml of 0.01 *M* $EDTA_0$ solution for 24 h. This illustrates the greater efficiency of batch extraction compared to column extraction. This was presumably due to the breakdown in soil structure caused by agitation under batch conditions, allowing the $EDTA_0$ to get at strongly adsorbed copper which would otherwise be inaccessible. The $EDTA_0$ was as effective in leaching the copper from the intact Opotiki soil cores, as it was from the repacked soil. Leaching with excess of 0.01 *M* $EDTA_0$ reduced the copper concentration in the top 25 mm of an intact core from 240 to 80 mg kg^{-1}.

$EDTA_0$ induced not only the leaching of copper, but also a substantial amount of iron from the soil. When the contaminated soil contained a large amount of copper, the amount of iron leached by excess $EDTA_0$ was less than the amount of copper leached. However when the copper content of the soil was lower, the converse was true. This difference could have been due in part to the adsorbed copper masking the potential iron desorption sites from the percolating $EDTA_0$. Also copper, being a relatively recently added soil contaminant, was apparently adsorbed in such a way that was more readily available for complexation with $EDTA_0$ than the iron, which is a constituent of soil mainly present as oxides with varying degrees of crystallisation.

EDTA extraction of copper during leaching, and the transformation of the $CuEDTA^{2-}$ complex to $Fe(III)EDTA^{-}$ in the soil solution, were both found to be a time-dependent processes. Columns of Opotiki soils with pulses of $EDTA_0$ left in them 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 low, medium and high-Cu Manawatu soil prior to leaching in general also showed a time-dependent increase in iron leached. However the amount of copper leached showed a different trend. With increasing EDTA residence time in the soil, the mass of copper leached dropped markedly in the low-Cu 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 soils. These results are consistent with $CuEDTA^{2-}$ being gradually transformed to the more stable $Fe(III)EDTA^-$ and Cu^{2+} in all cases. In these soils, the time given for ageing of the added copper prior to leaching with EDTA was only 10 days. Therefore the difference could be due to the lack of ageing of the copper in the soil. Further work would be needed to confirm this.

As in the repacked Opotiki soil, in the undisturbed Opotiki soil cores, a month's delay before leaching a pulse of EDTA also reduced the amount of copper leached to a negligible amount, and increased the amount of iron leached. The absence of a sudden drop in the effluent bromide concentration following the resumption of the leaching suggests that physical (transport controlled) non-equilibrium was not a factor, and that the sharp concentration changes observed in the copper and iron concentrations were primarily due to time-dependent chemical reactions.

Daily application of $CuEDTA^{2-}$ pulses to repacked low-copper Opotiki soil for three months confirmed that the time-dependent drop in copper concentration in the leachate, and the corresponding increase in iron concentration, were due to $CuEDTA^{2-}$ slowly changing to $Fe(III)EDTA^-$. Furthermore, the amount of copper that remained in the soil after the final leaching with $CaCl_2$ was equal to the iron leached. This confirmed that the Cu^{2+} dissociated from the $CuEDTA^{2-}$ was re-adsorbed by the soil.

In all the experiments in which it was assessed, the effluent EDTA concentration was inferred from DOC measurements. In some experiments where the EDTA residence time was a month, the inferred EDTA values are suspect, due to the likelihood of additional soluble organic carbon contributing to the measured DOC values. In these cases the assumption of a 1:1 correspondence between DOC and EDTA is not reasonable. Ideally, studies of EDTA-enhanced transport of metals should use ion chromatography to measure the various EDTA species independently, but the equipment need to do this was not available for this study.

In general, the addition of $EDTA_0$ to copper-contaminated soil resulted in a substantial increase in the copper concentration in the leaves of *A. tenuis*. For example, application of 1800 µmol of $EDTA_0$ to 0.9 kg of contaminated repacked Opotiki soil increased the shoot copper concentration of *A. tenuis* leaves grown in the soil from 30

μg g^{-1} to 300 μg g^{-1}. However, EDTA-enhanced phytoremediation was less effective in the intact cores, where the same EDTA$_0$ application to 1 kg of soil only increased the herbage copper concentration from 10 μg g^{-1} to 60 μg g^{-1}. More copper accumulated in the herbage when the EDTA$_0$ was applied in numerous small doses rather than in just one or two larger amounts.

In the above experiments, the estimated average soil solution copper concentration was two orders of magnitude greater than the concentration entering the roots, so the grass was quite effective at screening out the copper in the soil solution. This is probably the reason why leaching the soil about a month after the EDTA application removed 25 to 169 times more copper from the soil than was taken up by the herbage.

7.4 Modeling techniques

A relatively simple model, considering only the dominant processes, was considered more useful for predicting the EDTA-enhanced transport of copper and its consequences than more complex models, which require detailed chemical information that is not readily available. Thus in this study the convection dispersion equation (CDE), coupled with a source or sink term accounting for reactions bringing the chemical species of interest into or out of the solution, was used to describe the EDTA-enhanced transport of copper in contaminated soils. This model is less complex than public-domain models such as PHREEQC and HYDROGEOCHEM. But it does take into account the competition between the copper and iron for EDTA, and the rate-dependent reaction of CuEDTA^{2-} changing to Fe(III)EDTA^{-}. The equations describing the source/ sink terms with the CDE were solved numerically, as they could not be solved analytically. The model allowed the study of the interactions between the chemical and physical processes involved in the dissolution and transport of copper.

Some of the parameters in the model were directly measured (q_w, and θ). The remainder were determined from the experiments, either directly (λ, M_{Cu} and M_{Fe}), or by optimisation (k_1, k_2, k_3, k_4, and k_5). Using batch results to obtain rate constants or M_{Cu} or M_{Fe} was found to be inappropriate, as they gave a higher value for the EDTA extractable copper (M_{Cu}) compared to the column leaching experiments. Therefore, parameters like M_{Cu} and M_{Fe} were obtained in one experiment, and then used to predict the results of all other experiments with that soil. The optimisation approach used to quantify the rate constants for the reactions between the EDTA and copper or iron in the soil was not ideal.

To infer the initial copper distribution in each of the large intact cores, the total copper values were used in conjunction with the shape of the distribution measured in the smaller soil cores taken adjacent to the large cores. Although it was found that the shape of the copper distribution was quite similar in all the small cores taken, the total mass of copper was variable. Better prediction of the EDTA-facilitated copper leaching in the field could be achieved if the initial copper distribution with depth had been known exactly. However a non-invasive measurement technique would be needed to obtain such data.

7.5 Modelling results

In general, the model described reasonably well the copper concentration in the leachate and the soil, despite the differing amounts and concentrations of EDTA applied, and the varying lengths of time it was left in the two soils. However the values for some key parameters had to be adjusted for the two soils. Faster rate constants were needed for the Manawatu soil than the Opotiki soil. This could be due to the Manawatu soil having a lower organic matter content. For the Opotiki soil, the lower the pH, the more reactive was the iron in it. Also the dispersivity of the Opotiki intact soil was much higher than the repacked soil.

There were some aspects of the experiments that the model did not describe well, even with adjusted parameters. It seems that these discrepancies were due to the fact that this simple model can only describe approximately the wide range of reaction rates and the availability of the soil copper. Copper is bound to the soil matrix to varying degrees, and the binding strengths to some extent depend on how long the copper has been in contact with the soil. Also in the model the soil iron was divided into just two fractions. However the experimental results suggest that there was some iron more readily available, and/or reacted more quickly, than was assumed in the simple model. Another simplification was that, an optimised R value of 2 was used in the model to describe the EDTA adsorption in the Opotiki soil at a low pH, which implied linear reversible adsorption isotherm for EDTA. But isotherms are usually non-linear, and non-linearity probably accounted for the model's underestimation of the adsorption of 0.001 M $EDTA_0$ in the Opotiki soil.

By changing just the dispersivity from 3 mm to 23 mm, the model, with the same chemical parameters derived from the repacked Opotiki soil column experiments, was able to simulate the intact soil experiments reasonably well. In particular the leachate copper concentration, and the sudden increase in iron concentration following the month-long pause, were simulated reasonably well. This implies that the chemistry was the same in the repacked and intact soil, and that the change in the dispersivity, a physical property, took account of the effects of the different flow patterns in the repacked and intact soil.

The model describing the EDTA-enhanced transport of copper was developed further to simulate the plant uptake of copper. To do this transient water movement and water and solute uptake by the plant were included. The observed copper exclusion by the roots was described in either of two ways: a constant ratio between the copper concentration in the water entering the plant and the soil solution of 0.0006 was set; or a critical concentration C_{crit} was introduced to limit the uptake at higher concentrations. Although the model simulated the copper concentration profile in the soil after the final leaching, neither uptake description could simulate the plant copper uptake correctly, nor could they predict the differences in copper uptake by grass grown on repacked and intact soil. The failure of the model to predict this difference could be due to heterogenity in the location of copper adsorption sites, and in the differences in the local root distribution that reduced the accessibility of the copper to the plants in the intact soil.

The main value of developing the model in this study was to provide a vehicle for discussing the experimental results in terms of the interacting physical and chemical processes involved. A secondary value of the model is that it allows extrapolation of the experimental results to a wide range of conditions. This has been illustrated by simulating the amounts of copper and iron removed if a pulse of EDTA had been applied and leached at a wide range of flow rate.

7.6 Practical implications

The results from this work show that off-site leaching with an EDTA solution could remove most of the copper from contaminated soil. This option is more suitable for cleaning a copper polluted sawdust pile, or an industrial waste site where small volumes of copper contaminated material are involved, or for soils that are highly contaminated.

The leachate would be collected, the copper and EDTA extracted from it, and the EDTA recycled. Whether this would be economically feasible would need to be assessed.

The off-site washing method of remediation is not practically or economically feasible for large areas of agricultural land, and hence *in situ* methods need to be considered. One of the crucial factors for the success of any phytoremediation technology is the time required for eventual site decontamination. The time requirements for clean-up of the Opotiki soil investigated in this study can be roughly estimated as follows. The maximum copper concentration measured in the *A.tenuis* grown on the Opotiki repacked soil was 300 mg kg^{-1} (0.3 kg t^{-1}) and the dry matter production was 4.2 t h^{-1}. If similar behavior were to occur under the field conditions a crop of *A. tenuis* grown over a hectare of Opotiki soil might be expected to remove 1.3 kg h^{-1} of copper in a single harvest each year. Copper contamination in the Opotiki soil was mostly found in the surface 8 cm. If the top 8 cm of soil is considered for remediation, assuming a bulk density of 1100 kg m^{-3}, the weight of the soil is 8.8×10^5 kg per hectare. The copper concentration varied with depth and space, however assuming a 400 mg kg^{-1} of concentration was assumed throughout the 8 cm depth, the time required for a four fold reduction to 100 mg kg^{-1} in copper concentration would be 209 years. If two harvests were possible in a year, then the same reduction in copper concentration could be achieved in 104 years. Based solely on the long time requirement calculated, the prospects for using *in situ* application of EDTA to enhance phytoremediation of copper do not seem good with *A.tenuis*.

The feasibility of EDTA-enhanced phytoremediation can be further evaluated using the highest recorded metal concentrations in plant tissue from the literature data. As discussed in Chapter 5, Dearam *et al.* (2000) reported an uptake up to 7500 $\mu g\ g^{-1}$ copper in *Arrhenatherum elatius* species with a yield of 4.2 t h^{-1} per harvest. Remediating the Opotiki soil using *A. elatius* would take only 8 years with one harvest per year and 4 years with two harvests per year. This is probably a reasonable period of time for remediation. These calculations show that EDTA-enhanced remediation using *A. elatius* may be a feasible option for the moderately copper polluted soils. But the probability for leaching of copper to the groundwater also needs to be considered, and makes this approach less attractive.

Whatever plant species is used for phytoremediation, a strategy for managing leaching losses needs to be an important part of any plan for EDTA-enhanced phytoremediation. In order to reduce the downward leaching of copper in soil, growing a copper-tolerant grass species (e.g. *A. elatius*) together with deep-rooted trees such as poplars or willows might be an option. With such a system the grass could accumulate the copper from the highly contaminated surface soil, while water extraction by the deep-rooted plants could reduce the downward leaching of copper. This approach could be most beneficial in places where there is a water deficit during summer, allowing the trees to dry out the deep subsoil.

Alternatively, *in situ* leaching with EDTA could perhaps be used in some situations to reduce an undesirably high copper concentration in the surface soil, redistributing most of that copper lower down the soil profile at a much lower concentration. This is discussed below by considering the Opotiki site as an example.

Opotiki has average annual rainfall of 1394 mm, and a reference crop evaporation of 950 mm per year, so drainage of 440 mm is expected in a typical year. If plug flow is assumed, 440 mm of drainage in a soil with a field capacity of 0.5 m^3 m^{-3} would move the copper down 880 mm per year. With the water table 2 m deep at the Opotiki site, it would be about three years after application before the EDTA reached the groundwater. However it would be less than three years where the water table is shallower than 2 m. Better control of the copper leaching would be possible if the EDTA were applied to a dry soil in summer and leached by irrigation rather than by natural rainfall.

Based on the leaching experiments on the intact Opotiki soil, the following scenarios of the *in situ* method of remediation for redistributing the soil copper can be evaluated. Addition of 60 mm of 0.001 *M* EDTA to soil with a copper concentration of 300 mg kg^{-1} in the top 100 mm could reduce the concentration to 180 mg kg^{-1} if 350 mm irrigation were done within a day or two of the EDTA application. Irrigating the soil quickly after the EDTA application reduces the possibility of the copper being re-adsorbed by the soil at the same depth as it was before. However, it would also require that the residence time of the soil water containing the CuEDTA in the soil above the water table was in excess of a month, otherwise the probability of copper reaching the groundwater with the EDTA is higher. Extrapolation of experimental results in Chapter 6 suggests that a suitable flow rate for irrigating the soil after the EDTA application in the above treatment would be 12 mm h^{-1} both for reducing the topsoil copper, and redistributing it in the subsoil. However, any flow rate between 1 and 20 mm h^{-1} would be satisfactory.

Restrictions are needed therefore on the application of EDTA and other chelating agents to soils containing heavy metals, as they can cause groundwater pollution by copper and other metals under some circumstances. Further, repeated additions of EDTA might be destructive to the structure of the soil.

A cheaper and less risky solution for a copper contaminated surface soil is to redistribute the copper simply by cultivation. In order to bring the copper concentration from 400 mg kg^{-1} in the surface 80 mm down to 100 mg kg^{-1} the soil needs be mixed to a depth of 320 mm, assuming there is negligible copper below 80 mm depth.

Of course redistributing the copper is a technique that can only be used once. For a long-term solution, the copper addition to the soil needs to cease as well. In the case of Opotiki, this would mean finding an alternative to the use of copper fungicide sprays.

Future work is required to find an efficient yet a biodegradable chelate to complex with copper so that the groundwater pollution by any metal-chelate at longer times is minimised.

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Appendix

Program 1

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'NUMERICAL SOLUTION OF CDE TO SIMULATE THE EDTA-ENHANCED
TRANSPORT OF COPPER FROM A CONTAMINATED SOIL-Continuous leaching
‘units mm, h, µmol

‘INITIAL SECTION
Dim n As Integer: Dim j As Integer
‘Mcl = total chloride concentration, Mch = total EDTA concentration
‘Mcu = EDTA extractable copper in soil, Mfe = EDTA extractable iron concentration in soil
‘Mcuch = total CuEDTA concentration, Mfech = total Fe(III)EDTA concentration
‘fcl = flux concentration of chloride, fch = flux concentration of EDTA
‘fcuch = flux concentration of CuEDTA, ffech = flux concentration of Fe(III)EDTA
‘dsink1 = term for the reaction between Cu and EDTA
‘df1sink = term for the reaction between Fe and EDTA

Dim Mcl(100), Mcu(100), Mch(100), Mcuch(100), fcl(100), fch(100), fcuch(100), Mfech(100),
ffech(100), Mfe(100)

‘PARAMETERS
‘nn = number of compartments, qw = water flux density, theta = volumetric moisture content
‘bulkd = bulkdensity of soil, colarea = area of the soil column, lamda = dispersivity
‘k1 = rate coefficient for the reaction between copper and EDTA
‘k2 = rate coefficient for the reaction between iron and EDTA

theta = 0.61: qw = 28.6: bulkd = 0.65 * 1000: colarea = 1590.4
dz = 2.5: tmax = 16.5: dt = 0.05 / qw
lambda = 3
elambda = lambda - (dz - qw * dt) / 2: If elambda < 0 Then Stop
nn = 45: k1 = 0.00004 * 3600: k2 = 0.000009 * 3600
For n = 1 To nn
    Mcu (n) = 135 / 1000 / 63.55: Mfe(n) = 48 / 1000 / 55.8: Mch(n) = 0: Mcuch(n) = 0:
    Mfech(n) = 0: Mcl(n) = 0.0025 * theta
Next n
```

```
maxcount = 100: j = 0: t = 0
counter = maxcount: MCuleached = 0: MFeleached = 0: EDTAleached = 0

'DYNAMIC SECTION
Do Until t >= tmax + dt
    fch(0) = 0.01 * qw: fcuch(0) = 0: ffech(0) = 0: fcl(0) = 0.01 * qw
    If t >= 16.5 Then fch(0) = 0: fcl(0) = 0
    disp = elambda * qw / theta
  For n = 1 To nn - 1
      fch(n) = -disp * theta * (Mch(n + 1) - Mch(n)) / theta / dz + Mch(n) / theta * qw
      fcuch(n) = -disp * theta * (Mcuch(n + 1) - Mcuch(n)) / theta / dz + Mcuch(n) / theta *
      qw
      ffech(n) = -disp * theta * (Mfech(n + 1) - Mfech(n)) / theta / dz + Mfech(n) / theta * qw
      fcl(n) = -disp * theta * (Mcl(n + 1) - Mcl(n)) / theta / dz + Mcl(n) / theta * qw
  Next n
       fch(nn) = Mch(nn) / theta * qw: fcuch(nn) = Mcuch(nn) / theta * qw
       ffech(nn) = Mfech(nn) / theta * qw: fcl(nn) = Mcl(nn) / theta * qw
       totMcu = 0: totMfe=0
  For n = 1 To nn
      dsink1 = 0: dflsink = 0
      If Mch(n) >0 And Mcu (n) > 0 Then dsink1 = k1 * Sqr(Mch(n) / theta * Mcu(n)) * dt
      If Mch(n) > 0 And Mfe (n) > 0 Then dflsink = k2 * Sqr(Mch(n) / theta * Mfe(n)) * dt
      Mcu(n) = Mcu(n) - dsink1
      Mfe(n) = Mfe(n) - dflsink
      Mch(n) = Mch(n) + (fch(n - 1) - fch(n)) * dt / dz - dsink1 - dflsink
      Mcuch(n) = Mcuch(n) + (fcuch(n - 1) - fcuch(n)) * dt / dz + dsink1
      Mfech(n) = Mfech(n) + (ffech(n - 1) - ffech(n)) * dt / dz + dflsink
      Mcl(n) = Mcl(n) + (fcl(n - 1) - fcl(n)) * dt / dz
  Next n
  For n = 1 To nn - 5
      totMfe = totMfe + (Mfe(n) + Mfech(n)) * dz
      totMcu = totMcu + (Mcu(n) + Mcuch(n)) * dz
      MEDTA = MEDTA + (Mch(n) + Mcuch(n) + Mfech(n)) * dz
  Next n
  MCuleached = MCuleached + fcuch(40) * dt
  MFeleached = MFeleached + ffech(40) * dt
  EDTAleached = MEDTA + (fch(40) + fcuch(40) + ffech(40)) * dt
```

```
    counter = counter + 1
    If counter >= maxcount Then
        j = j + 1
        counter = 0
        I = t * qw

'OUTPUT SECTION (FLUX CONCENTRATIONS)
'I = cumulative outflow, Mculeached = total amount of copper leached,
'Mfeleached = total amount of iron leached

            Worksheets("*****").Cells(j + 4, 29).Value = I
            Worksheets("*****").Cells(j + 4, 30).Value = fch(40) / qw * 1000
            Worksheets("*****").Cells(j + 4, 31).Value = fcuch(40) / qw * 1000
            Worksheets("*****").Cells(j + 4, 32).Value = (fch(40) + fcuch(40) + ffech(40)) / qw
            * 1000
            Worksheets("*****").Cells(j + 4, 33).Value = ffech(40) / qw * 1000
            Worksheets("*****").Cells(j + 4, 34).Value = fcl(40) / qw * 1000
    End If
    t = t + dt
Loop
'OUTPUT SECTION (SOIL COPPER CONCENTRATION)
For n = 1 To 40
            Worksheets("****").Cells(*, *).Value = n * dz - dz / 2
            Worksheets("****").Cells(*, *).Value = ((Mcu(n) + Mcuch(n)) * 63.55 *
            1000000 / bulkd)
Next n
            Worksheets("*****").Cells(*, *).Value = MCuleached * colarea
            Worksheets("*****").Cells(*, *).Value = MFeleached * colarea
End Sub
```

Program 2

```
'NUMERICAL SOLUTION OF CDE TO SIMULATE THE EDTA-ENHANCED
TRANSPORT OF COPPER FROM A CONTAMINATED SOIL- Delayed pulse experiment
‘units mm, h, µmol

‘INITIAL SECTION
Dim n As Integer: Dim j As Integer
‘Mcl = total chloride concentration, Mch = total EDTA concentration
‘Mcu = EDTA extractable copper in soil, Mfe = EDTA extractable iron concentration in soil
‘Mcuch = total CuEDTA concentration, Mfech = total Fe(III)EDTA concentration
‘fcl = flux concentration of chloride, fch = flux concentration of EDTA
‘fcuch = flux concentration of CuEDTA, ffech = flux concentration of Fe(III)EDTA
‘dsink1 = term for the reaction between soil copper and EDTA,  df1sink = term for the reaction
 between readily available iron, Mfe and EDTA,
 ‘dsource1 = term explaining the reaction between CuEDTA and Mfe


Dim Mcl(100), Mcu(100), Mch(100), Mcuch(100), fcl(100), fch(100), fcuch(100), Mfech(100),
ffech(100), Mfe(100)

‘PARAMETERS
‘nn = number of compartments, qw = water flux density, theta = volumetric moisture content
‘bulkd = bulkdensity of soil, colarea = area of the soil column, lamda = dispersivity
‘k1 = rate coefficient for the reaction between copper and EDTA
‘k2 = rate coefficient for the reaction between iron (Mfe) and EDTA
‘k3 = rate coeffcient for the reaction between CuEDTA and Mfe
theta = 0.61: qw = 28.6: bulkd = 0.69 * 1000: colarea = 1590.4
dz = 2.5: tmax = 5.5: dt = 0.05 / qw: tpause = 0
lambda = 3
elambda = lambda - (dz - qw * dt) / 2: If elambda < 0 Then Stop
nn = 45: k1 = 0.00004 * 3600: k2 = 0.000009 * 3600: k3 = 0.00000022 * 3600
totMcui = Mcui * dz * (nn - 5)
For n = 1 To nn
    Mcu (n) = 143 / 1000 / 63.55: Mfe(n) = 48 / 1000 / 55.8: Mch(n) = 0: Mcuch(n) = 0:
    Mfech(n) = 0: Mcl(n) = 0.005 * theta
```

```
Next n
maxcount = 100: j = 0: t = 0
counter = maxcount: MCuleached = 0: MFeleached = 0: EDTAleached = 0

'DYNAMIC SECTION
Do Until t >= tmax + dt
     fch(0) = 0.001 * qw: fcuch(0) = 0: ffech(0) = 0: fcl(0) = 0.001 * qw
     teff = t
     If t >= 1.18 Then fch(0) = 0: qw = 0: fcl(0) = 0
     If t >= 1.18 + tpause Then qw = qww: teff = t - tpause: fcl(0) = 0.005 * qw
     disp = elambda * qw / theta + (2.8 * theta * theta * 3.6)
  For n = 1 To nn - 1
        fch(n) = -disp * theta * (Mch(n + 1) - Mch(n)) / theta / dz + Mch(n) / theta * qw
        fcuch(n) = -disp * theta * (Mcuch(n + 1) - Mcuch(n)) / theta / dz + Mcuch(n) / theta *
        qw
        ffech(n) = -disp * theta * (Mfech(n + 1) - Mfech(n)) / theta / dz + Mfech(n) / theta * qw
        fcl(n) = -disp * theta * (Mcl(n + 1) - Mcl(n)) / theta / dz + Mcl(n) / theta * qw
  Next n
  fch(nn) = Mch(nn) / theta * qw: fcuch(nn) = Mcuch(nn) / theta * qw:
  ffech(nn) = Mfech(nn) / theta * qw: fcl(nn) = Mcl(nn) / theta * qw
  totMcu = 0: totMfe=0
  For n = 1 To nn
        dsink1 = 0: df1sink = 0: df2sink = 0: dsource1 = 0:
        If Mch(n) >0 And Mcu(n) > 0 Then dsink1 = k1 * Sqr(Mch(n) / theta * Mcu(n)) * dt
        If Mcuch(n) > 0 And Mfe(n) > 0 Then dsource1 = k3 * Sqr(Mcuch(n) / theta *
        Mfe(n)) * dt
        If Mch(n) > 0 And Mfe(n) > 0 Then df1sink = k2 * Sqr(Mch(n) / theta * Mfe(n)) *
        dt
        Mcu(n) = Mcu(n) - dsink1 + dsource1
        Mfe(n) = Mfe(n) - df1sink - dsource1
        Mch(n) = Mch(n) + (fch(n - 1) - fch(n)) * dt / dz - dsink1 - df1sink
        Mcuch(n) = Mcuch(n) + (fcuch(n - 1) - fcuch(n)) * dt / dz + dsink1 - dsource1
        Mfech(n) = Mfech(n) + (ffech(n - 1) - ffech(n)) * dt / dz + df1sink + dsource1
        Mcl(n) = Mcl(n) + (fcl(n - 1) - fcl(n)) * dt / dz
 Next n
  For n = 1 To nn - 5
       totMfe = totMfe + (Mfe(n) + Mfech(n)) * dz
```

```
      totMcu = totMcu + (Mcu(n) + Mcuch(n)) * dz
      MEDTA = MEDTA + (Mch(n) + Mcuch(n) + Mfech(n)) * dz
  Next n
      MCuleached = MCuleached + fcuch(40) * dt
      MFeleached = MFeleached + ffech(40) * dt
      EDTAleached = MEDTA + (fch(40) + fcuch(40) + ffech(40)) * dt
      counter = counter + 1
  If counter >= maxcount Then
      j = j + 1
      counter = 0
      I = teff * qw

‘OUTPUT SECTION (FLUX CONCENTRATIONS)
‘I = cumulative outflow, Mculeached = total amount of copper leached
‘Mfeleached = total amount of iron leached

      Worksheets("*****").Cells(*, *).Value = I
      Worksheets("*****").Cells(*, *).Value = fch(40) / qw * 1000
      Worksheets("*****").Cells(*, *).Value = fcuch(40) / qw * 1000
      Worksheets("*****").Cells(*, *).Value = (fch(40) + fcuch(40) + ffech(40)) / qw * 1000
      Worksheets("*****").Cells(*, *).Value = ffech(40) / qw * 1000
      Worksheets("*****").Cells(*, *).Value = fcl(40) / qw * 1000
  End If
  t = t + dt
Loop
‘OUTPUT SECTION (SOIL COPPER CONCENTRATION)
For n = 1 To 40
    Worksheets("*****").Cells(*, *).Value = n * dz - dz / 2
    Worksheets("*****").Cells(*, *).Value = ((Mcu(n) + Mcuch(n)) * 63.55 *
     1000000 / bulkd)
Next n
    Worksheets("*****").Cells(*, *).Value = MCuleached * colarea
    Worksheets("*****").Cells(*, *).Value = MFeleached * colarea
End Sub
```

Program 3

```
'NUMERICAL SOLUTION OF CDE WITH EDTA-CuEDTA leaching experiment
units mm, h, µmol

‘INTITIAL SECTION
Dim n As Integer: Dim j As Integer: Dim ii As Integer
‘Mbr = total bromide concentration, Mch = total EDTA concentration
‘Mfe1= EDTA extractable rapidly reacting iron in soil,
‘Mfe2 = EDTA extractable slowly reacting iron concentration in soil
‘Mcuch = total CuEDTA concentration, Mfech = total Fe(III)EDTA concentration
‘fbr = flux concentration of bromide, fch = flux concentration of EDTA
‘fcuch = flux concentration of CuEDTA, ffech = flux concentration of Fe(III)EDTA
‘dsource1 = term explaining the reaction between CuEDTA and Mfe1
‘dsource2 = term explaining the reaction between CuEDTA and Mfe2

Dim Mcu(100), Mfe1(100), Mfe2(100), Mch(100), Mcuch(100), MBr(100), fch(100),
fcuch(100), Mfech(100), ffech(100), fBr(100), cufac(100)

'PARAMETERS
‘nn = number of compartments, qw = water flux density, theta = volumetric moisture content,
‘bulkd = bulkdensity of soil, colarea = area of the soil column, lamda = dispersivity
‘k3 = rate coeffcient for the reaction between CuEDTA and Mfe1
‘k5 = rate coeffcient for the reaction between CuEDTA and Mfe2
‘cufac = retardation due to adsorption

theta = 0.62: qww = 28:  bulkd = 0.63 * 1000: colarea = 1590.4
dz = 2.5: tmax = 2004: dtt = 0.2 / qww:
lambda = 3
elambda = lambda - (dz - qww * dt) / 2: If elambda < 0 Then Stop
nn = 45
k3 = 0.005: k5 = kad / 10
For n = 1 To nn
     Mcu(n) = 10/1000/63.55: Mfe1(n) = 44 / 1000 / 55.8: Mfe2(n) = 221 / 1000 / 55.8:
     Mch(n) = 0: Mbr(n) = 0: Mcuch(n) = 0: Mfech(n) = 0: cufac(n) = 2
Next n
maxcount = 140: j = 0: t = 0
```

```
counter = maxcount: MCuleached = 0: Mfeleached = 0: EDTAleached = 0

'DYNAMIC SECTION
Do Until t >= tmax + dt
    If (t / 24#) >= Int(t / 24#) And (t / 24#) < Int(t / 24#) + 1 / 24 Then
      qw = qww
      fcuch(0) = 0.001 * qw: fBr(0) = 0.001 * qw: ffech(0) = 0: dt = dtt
    Else: fcuch(0) = 0: fbr(0) = 0: qw = 0: dt = dtt * 10
    End If
    If t >= 1992 Then qw = qww: dt = dtt: fcuch(0) = 0
       disp = elambda * qw / theta + (0.66 * theta * theta * 3.8)
        i = i + (dtt * qw)
 For n = 1 To nn - 1
    fcuch(n) = (-disp * theta * (Mcuch(n + 1) - Mcuch(n)) / theta / dz + Mcuch(n) / theta *
    qw) / cufac(n)
    ffech(n) = (-disp * theta * (Mfech(n + 1) - Mfech(n)) / theta / dz + Mfech(n) / theta *
    qw) / cufac(n)
    fBr(n) = -disp * theta * (MBr(n + 1) - MBr(n)) / theta / dz + MBr(n) / theta * qw
 Next n
    fcuch(nn) = (Mcuch(nn) / theta * qw) / cufac(nn): ffech(nn) = (Mfech(nn) / theta * qw) /
    cufac(nn): fbr(nn) = Mbr(nn) / theta * qw
    totMcu = 0: totMfe = 0: MEDTA = 0
 For n = 1 To nn
    dsource1 = 0: dsource2 = 0
    If Mcuch(n) > 0 And Mfe1(n) > 0 Then dsource1 = k3 * Sqr(Mcuch(n) / theta *
    Mfe1 (n)) * dt
    If Mcuch(n) > 0 And Mfe2(n) > 0 Then dsource2 = k5 * Sqr(Mcuch(n) / theta *
    Mfe2(n)) * dt
    Mfe1(n) = Mfe1(n) - dsource1
    Mfe2(n) = Mfe2(n) - dsource2
    Mcu(n) = Mcu(n) + dsource1 + dsource2
    Mcuch(n) = Mcuch(n) + (fcuch(n - 1) - fcuch(n)) * dt / dz - dsource1 - dsource2
    Mfech(n) = Mfech(n) + (ffech(n - 1) - ffech(n)) * dt / dz + dsource1 + dsource2
    Mbr(n) = MBr(n) + (fbr(n - 1) - fbr(n)) * dt / dz
 Next n
 For n = 1 To nn - 5
    totMfe = totMfe + (Mfe1(n) + Mfe2(n) + Mfech(n)) * dz
```

```
        totMcu = totMcu + (Mcu(n) + Mcuch(n)) * dz
    Next n
        MCuleached = MCuleached + fcuch(40) * dt
        Mfeleached = Mfeleached + ffech(40) * dt
        counter = counter + 1
    If counter >= maxcount And qw > 0 Then
        j = j + 1
        counter = 0
 'OUTPUT SECTION (FLUX CONCENTRATIONS)
'i = cumulative outflow, Mculeached = total amount of copper leached,
'Mfeleached = total amount of iron leached

        Worksheets("*****").Cells(*, *).Value = i
        Worksheets("*****").Cells(*, *).Value = t
        Worksheets("*****").Cells(*, *).Value = fch(40) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = fcuch(40) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = (fch(40) + fcuch(40) + ffech(40)) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = ffech(40) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = fcl(40) / qw * 1000
    End If
    t = t + dt
Loop
'OUTPUT SECTION (SOIL COPPER)
For n = 1 To 40
      Worksheets("*****").Cells(*, *).Value = n * dz - dz / 2
      Worksheets("*****").Cells(*, *).Value = ((Mcu(n) + Mcuch(n)) * 63.55 *
       1000000 / bulkd)
Next n
       Worksheets("*****").Cells(*, *).Value = MCuleached * colarea
       Worksheets("*****").Cells(*, *).Value = MFeleached * colarea
End Sub
```

Program 4

```
Sub EDTA1()
'NUMERICAL SOLUTION OF CDE WITH EDTA-Pulse experiment on intact core
units mm,h,mumol

‘INITIAL SECTION
Dim n As Integer: Dim j As Integer
‘Mbr = total chloride concentration, Mch = total EDTA concentration
‘Mcu = total copper in soil, Mcu1 = EDTA extractable copper in soil
‘Mfe1= EDTA extractable rapidly reacting iron in soil,
‘Mfe2 = EDTA extractable slowly reacting iron concentration in soil
‘Mcuch = total CuEDTA concentration, Mfech = total Fe(III)EDTA concentration
‘fbr = flux concentration of bromide, fch = flux concentration of EDTA
‘fcuch = flux concentration of CuEDTA, ffech = flux concentration of Fe(III)EDTA
‘dsink1 = sink term for the reaction between EDTA extractable soil copper and EDTA
‘df1sink = term for the reaction between EDTA and Mfe1
‘df2sink = term for the reaction between EDTA and Mfe2
‘dsource1 = term explaining the reaction between CuEDTA and Mfe1
‘dsource2 = term explaining the reaction between CuEDTA and Mfe2

Dim Mcu(100), Mcu1(100), Mcu2(100), Mfe1(100), Mfe2(100), Mbr(100), Mch(100),
Mcuch(100), fch(100), fbr(100), fcuch(100), Mfech(100), ffech(100), cufac(100), k1(100),
k2(100), k3(100), k4(100), k5(100)

'PARAMETERS
‘nn = number of compartments, qw = water flux density, theta = volumetric moisture content,
‘bulkd = bulkdensity of soil, colarea = area of the soil column, lamda = dispersivity,
‘k1 = rate coefficient for the reaction between copper and EDTA,
‘k2 = rate coefficient for the reaction between Mfe1 and EDTA,
‘k3 = rate coeffcient for the reaction between CuEDTA and Mfe1
‘k4 = rate coefficient for the reaction between Mfe2 and EDTA
‘k5 = rate coeffcient for the reaction between CuEDTA and Mfe2
‘cufac = retardation of EDTA due to adsorption

theta = 0.54: qww = 14: qw = qww: bulkd = 0.924 * 1000: colarea = 7857
dz = 2.5: tmax = 28: dt = 0.02 / qw: tpause = 0
```

```
lambda = 23
elambda = lambda - (dz - qw * dt) / 2: If elambda < 0 Then Stop
nn = 65: Mcu2max = 83 / 1000 / 63.55: k1 = 0.00004 * 3600:
For n = 1 To 10
        Mcu(n) = 309 / 1000 / 63.55: k2(n) = 0.000009 * 3600: k4(n) = k2(n) / 10000: k3(n) = 0.00000022 * 3600: k5(n) = k3(n) / 10000: cufac(n) = 1
Next n
For n = 11 To 20
        Mcu(n) = 116 / 1000 / 63.55: k2(n) = 0.000009 * 3600: k4(n) = k2(n) / 10000: k3(n) = 0.00000022 * 3600: k5(n) = k3(n) / 10000: cufac(n) = 1
Next n
For n = 21 To 30
        Mcu(n) = 74 / 1000 / 63.55: k2(n) = 0.000009 * 3600: k4(n) = k2(n) / 10000: k3(n) = 0.00000022 * 3600: k5(n) = k3(n) / 10000: cufac(n) = 1
Next n
For n = 31 To 40
        Mcu(n) = 33 / 1000 / 63.55: k2(n) = 0.000009 * 3600: k4(n) = k2(n) / 10000: k3(n) = 0.00000022 * 3600: k5(n) = k3(n) / 10000: cufac(n) = 1
Next n
For n = 41 To 50
        Mcu(n) = 11 / 1000 / 63.55: k2(n) = 0.000009 * 3600: k4(n) = k2(n) / 10000: k3(n) = 0.00000022 * 3600: k5(n) = k3(n) / 10000: cufac(n) = 1
Next n
For n = 51 To 65
        Mcu(n) = 11 / 1000 / 63.55: k2(n) = 0.000009 * 3600: k4(n) = k2(n) / 10000: k3(n) = 0.00000022 * 3600: k5(n) = k3(n) / 10000: cufac(n) = 1
Next n
For n = 1 To nn
        If Mcu(n) > Mcu2max Then
                Mcu1(n) = Mcu(n) - Mcu2max: Mcu2(n) = Mcu2max
        Else: Mcu1(n) = 0: Mcu2(n) = Mcu(n)
        End If
        Mfe1(n) = 65 / 1000 / 55.85: Mfe2(n) = 323 / 1000 / 55.8: Mch(n) = 0:
        Mcuch(n) = 0: Mfech(n) = 0
Next n
        maxcount = 100: j = 0: t = 0
        counter = maxcount
```

```
'DYNAMIC SECTION
Do Until t >= tmax + dt
        fch(0) = 0.001 * qw: fcuch(0) = 0: ffech(0) = 0: fbr(0) = 0.001 * qw
         teff = t
        If t >= 4.5 Then fch(0) = 0: qw = 0: fbr(0) = 0
        If t >= 4.5 + tpause Then qw = qww: teff = t - tpause
        disp = elambda * qw / theta + (0.66 * theta * theta * 3.6)
  For n = 1 To nn - 1
        fch(n) = -disp * theta * (Mch(n + 1) - Mch(n)) / theta / dz + Mch(n) / theta * qw
        fcuch(n) = (-disp * theta * (Mcuch(n + 1) - Mcuch(n)) / theta / dz + Mcuch(n) / theta * qw)
        ffech(n) = -disp * theta * (Mfech(n + 1) - Mfech(n)) / theta / dz + Mfech(n) / theta * qw
        fbr(n) = -disp * theta * (Mbr(n + 1) - Mbr(n)) / theta / dz + Mbr(n) / theta * qw
  Next n
        fch(nn) = Mch(nn) / theta * qw: fcuch(nn) = (Mcuch(nn) / theta * qw)
        ffech(nn) = Mfech(nn) / theta * qw: fbr(nn) = Mbr(nn) / theta * qw
        totMcu = 0
  For n = 1 To nn
        dsink1 = 0: dsink2 = 0: df1sink = 0: df2sink = 0: dsource1 = 0: dsource2 = 0
        If Mch(n) > 0 And Mcu1(n) > 0 Then dsink1 = k1 * Sqr(Mch(n) / theta * Mcu1(n)) * dt
        If Mcuch(n) > 0 And Mfe1(n) > 0 Then dsource1 = k3(n) * Sqr(Mcuch(n) / theta * Mfe1(n)) * dt
        If Mcuch(n) > 0 And Mfe2(n) > 0 Then dsource2 = k5(n) * Sqr(Mcuch(n) / theta * Mfe2(n)) * dt
        If Mch(n) > 0 And Mfe1(n) > 0 Then df1sink = k2(n) * Sqr(Mch(n) / theta * Mfe1(n)) * dt
        If Mch(n) > 0 Then df2sink = k4(n) * Sqr(Mch(n) / theta * Mfe2(n)) * dt
        If Mcu2(n) < Mcu2max Then
                Mcu1(n) = Mcu1(n) - dsink1: Mcu2(n) = Mcu2(n) - dsink2 + dsource1 + dsource2
        Else: Mcu1(n) = Mcu1(n) - dsink1 + dsource1 + dsource2: Mcu2(n) = Mcu2(n) - dsink2
        End If
        Mfe1(n) = Mfe1(n) - df1sink - dsource1
        Mfe2(n) = Mfe2(n) - df2sink - dsource2
        Mch(n) = Mch(n) + (fch(n - 1) - fch(n)) * dt / dz - dsink1 - dsink2 - df1sink - df2sink
        Mcuch(n) = Mcuch(n) + (fcuch(n - 1) - fcuch(n)) * dt / dz + dsink1 + dsink2 - dsource1 - dsource2
```

```
        Mfech(n) = Mfech(n) + (ffech(n - 1) - ffech(n)) * dt / dz + df1sink + df2sink + dsource1
        + dsource2
        Mbr(n) = Mbr(n) + (fbr(n - 1) - fbr(n)) * dt / dz
    Next n
    For n = 1 To nn - 5
         totMfe1 = totMfe1 + (Mfe1(n) + Mfech(n)) * dz
        totMcu = totMcu + (Mcu1(n) + Mcu2(n) + Mcuch(n)) * dz
        MEDTA = MEDTA + (Mch(n) + Mcuch(n) + Mfech(n)) * dz
    Next n
        MCuleached = MCuleached + fcuch(60) * dt
        Mfeleached = Mfeleached + ffech(60) * dt
        Mbrleached = Mbrleached + fbr(60) * dt
        EDTAleached = MEDTA + (fch(60) + fcuch(60) + ffech(60)) * dt
        counter = counter + 1
    If counter >= maxcount And qw > 0 Then
        j = j + 1
        counter = 0
        I = teff * qw

'OUTPUT SECTION (FLUX CONCENTRATIONS)
'I = cumulative outflow, Mculeached = total amount of copper leached,
'Mfeleached = total amount of iron leached

        Worksheets("*****").Cells(*, *).Value = I
        Worksheets("*****").Cells(*, *).Value = fbr(60) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = fch(60) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = fcuch(60) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = (fch(60) + fcuch(60) + ffech(60)) / qw * 1000
        Worksheets("*****").Cells(*, *).Value = ffech(60) / qw * 1000
 End If
        t = t + dt
Loop
'OUTPUT SECTION (SOIL COPPER CONCENTRATION)
For n = 1 To 40
        Worksheets("*****").Cells(*, *).Value = n * dz - dz / 2
        Worksheets("*****").Cells(*, *).Value = ((Mcu1(n) + Mcu2(n)+Mcuch(n)) * 63.55 *
        1000000 / bulkd)
```

```
Next n
        Worksheets("*****").Cells(*, *).Value = MCuleached * colarea
        Worksheets("*****").Cells(*, *).Value = MFeleached * colarea
End Sub
```

Program 5

```
Sub GrassEDTA()
'NUMERICAL SOLUTION OF CDE WITH EDTA-Copper uptake by grass grown on repacked column
units mm, h, μmol

'INITIAL SECTION
Dim n As Integer: Dim j As Integer
‘Mch = total EDTA concentration, Mcu = total copper in soil
‘Mcu1 = EDTA extractable copper in soil
‘Mcu2 = non EDTA extractable copper in soil
‘Mfe1= EDTA extractable rapidly reacting iron in soil
‘Mfe2 = EDTA extractable slowly reacting iron concentration in soil
‘Mcuch = total CuEDTA concentration, Mfech = total Fe(III)EDTA concentration
‘fbr = flux concentration of bromide, fch = flux concentration of EDTA
‘fcuch = flux concentration of CuEDTA, ffech = flux concentration of Fe(III)EDTA
‘dsink1 = sink term for the reaction between EDTA extractable soil copper and EDTA
‘df1sink = term for the reaction between EDTA and Mfe1
‘df2sink = term for the reaction between EDTA and Mfe2
‘dsource1 = term explaining the reaction between CuEDTA and Mfe1
‘dsource2 = term explaining the reaction between CuEDTA and Mfe2
‘sink = water uptake
‘uptake = copper uptake by grass

Dim Mcu1(100), Mcu2(100), Mfe1(100), Mfe2(100), Mcl(100), Mch(100), Mcuch(100), fch(100), fcuch(100), Mfech(100), ffech(100), fcl(100), sink(100), qw(100), theta(100), uptake(100)

'PARAMETERS
‘nn = number of compartments, qw = water flux density,
‘qww = water flux density during leaching, theta = volumetric moisture content,
‘thetafc = volumetric moisture content at column capacity
‘bulkd = bulkdensity of soil, colarea = area of the soil column, lamda = dispersivity
‘k3 = rate coeffcient for the reaction between CuEDTA and Mfe1
‘k5 = rate coeffcient for the reaction between CuEDTA and Mfe2
‘cufac = retardation due to adsorption
```

```
‘k1 = rate coefficient for the reaction between copper and EDTA,
‘k2 = rate coefficient for the reaction between Mfe1 and EDTA
‘k4 =  rate coefficient for the reaction between Mfe2 and EDTA

thetafc = 0.587: qw2 = 18: qww = 6: bulkd = 0.75 * 1000: colarea = 7854.4: factor = 1:
maxMcuch = 0.000004
dz = 2.5: tmax = 896: dtt = 0.05 / qww: dt = dtt
lambda = 3
elambda = lambda - dz / 2: If elambda < 0 Then Stop
evap = 11.4 / 24
nn = 60: Mcui = 170 / 1000 / 63.55: k1 = 0.00004 * 3600:
k2 = 0.000009 * 3600: k4 = 0: k3 = 0.0008: k5 = 0: fcuch(0) = 0: ffech(0) = 0
For n = 1 To nn
        Mcu2(n) = 68 / 1000 / 63.55: Mcu1(n) = Mcui - Mcu2(n): Mfe1(n) = 51 / 1000 / 55.8:
        Mfe2(n) = 350 * bulk / 1000 / 55.8: Mch(n) = 0:
        Mcuch(n) = 0: Mfech(n) = 0:
        sink(n) = evap / 150 * ((nn - n - 0.5) / (nn / 2)): theta(n) = thetafc - 11.4 / 150
Next n
maxcount = 100: j = 0: t = 0
counter = maxcount: MCuleached = 0: Mfeleached = 0: EDTAleached = 0:
totuptake = 0

‘DYNAMIC SECTION
Do Until t >= tmax + dt
        If (t / 24#) >= Int(t / 24#) And (t / 24#) < Int(t / 24#) + 1.9 / 24
                Then qw(0) = qww: dt = dtt
        Else: qw(0) = 0: dt = dtt * 20
        End If
        If (t / 432#) >= Int(t / 432#) And (t / 432#) < Int(t / 432#) + 1.9 / 432 Then
                fch(0) = 0.007 * qw(0): fcl(0) = 0.001 * qw(0)
        Else: fch(0) = 0: fcl(0) = 0
        End If
        If t >= 863 Then qw(0) = qw2: dt = dtt: fch(0) = 0: sink(n) = 0
        I = I + (dtt * qw(60))
  For n = 1 To nn
        If theta(n) > thetafc Then qw(n) = (theta(n) - thetafc) * dz / dt Else qw(n) = 0
        theta(n) = theta(n) + ((qw(n - 1) - qw(n)) * dt / dz) - (sink(n) * dt)
```

```
Next n
For n = 1 To nn - 1
    disp = elambda * qw(n) / theta(n) + (0.66 * theta(n) * theta(n) * 3.8)
    fch(n) = -disp * theta(n) * (Mch(n + 1) - Mch(n)) / theta(n) / dz + Mch(n) / theta(n) * qw(n)
    fcuch(n) = -disp * theta(n) * (Mcuch(n + 1) - Mcuch(n)) / theta(n) / dz + Mcuch(n) / theta(n) * qw(n)
    ffech(n) = -disp * theta(n) * (Mfech(n + 1) - Mfech(n)) / theta(n) / dz + Mfech(n) / theta(n) * qw(n)
    fcl(n) = -disp * theta(n) * (Mcl(n + 1) - Mcl(n)) / theta(n) / dz + Mcl(n) / theta(n) * qw(n)
Next n
fch(nn) = Mch(nn) / theta(nn) * qw(nn): fcuch(nn) = Mcuch(nn) / theta(nn) * qw(nn):
ffech(nn) = Mfech(nn) / theta(nn) * qw(nn): fcl(nn) = Mcl(nn) / theta(nn) * qw(nn)
totMcu = 0: totMfe1 = 0: MEDTA = 0
For n = 1 To nn
    dsink1 = 0: df1sink = 0: df2sink = 0: dsource1 = 0: dsource2 = 0
    If Mch(n) > 0 And Mcu1(n) > 0 Then dsink1 = k1 * Sqr(Mch(n) / theta(n) * Mcu1(n)) * dt
    If Mcuch(n) > 0 And Mfe1(n) > 0 Then dsource1 = k3 * Sqr(Mcuch(n) / theta(n) * Mfe1(n)) * dt
    If Mcuch(n) > 0 And Mfe2(n) > 0 Then dsource2 = k5 * Sqr(Mcuch(n) / theta(n) * Mfe2(n)) * dt
    If Mch(n) > 0 And Mfe1(n) > 0 Then df1sink = k2 * Sqr(Mch(n) / theta(n) * Mfe1(n)) * dt
    If Mch(n) > 0 Then df2sink = k4 * (Mch(n) / theta(n) * Mfe2(n)) ^ 0.5 * dt
    If Mcuch(n) / theta(n) <= maxMcuch / factor Then
            uptake(n) = sink(n) * Mcuch(n) / theta(n) * dt
    Else: uptake(n) = sink(n) * maxMcuch * dt
    Mcu1(n) = Mcu1(n) - dsink1 + dsource1
    Mfe1(n) = Mfe1(n) - df1sink - dsource1
    Mfe2(n) = Mfe2(n) - df2sink - dsource2
    Mch(n) = Mch(n) + (fch(n - 1) - fch(n)) * dt / dz - dsink1 - df1sink - df2sink
    Mcuch(n) = Mcuch(n) + (fcuch(n - 1) - fcuch(n)) * dt / dz + dsink1 - dsource1 - dsource2 - uptake(n)
    Mfech(n) = Mfech(n) + (ffech(n - 1) - ffech(n)) * dt / dz + df1sink + df2sink + dsource1 + dsource2
```

```
        Mcl(n) = Mcl(n) + (fcl(n - 1) - fcl(n)) * dt / dz
    Next n
    For n = 1 To nn
        totMfe1 = totMfe1 + (Mfe1(n) + Mfech(n)) * dz
        totMcu = totMcu + (Mcu1(n) + Mcuch(n)) * dz
        MEDTA = MEDTA + (Mch(n) + Mcuch(n) + Mfech(n)) * dz
        totuptake = totuptake + uptake(n) * dz
    Next n
        MCuleached = MCuleached + fcuch(60) * dt
        Mfeleached = Mfeleached + ffech(60) * dt
        EDTAleached = MEDTA + (fch(60) + fcuch(60) + ffech(60)) * dt
        counter = counter + 1
    If counter >= maxcount And qw(60) > 0 Then
      j = j + 1
      counter = 0

'OUTPUT SECTION (FLUX CONCENTRATION)
      Worksheets("****").Cells(*,*).Value = I
      Worksheets("****").Cells(*,*).Value = t
      Worksheets("****").Cells(*,*).Value = fch(60) / qw(60) * 1000
      Worksheets("****").Cells(*,*).Value = fcuch(60) / qw(60) * 1000
      Worksheets("****").Cells(*,*).Value = (fch(60) + fcuch(60) + ffech(60)) / qw(60) * 1000
      Worksheets("****").Cells(*,*).Value = ffech(60) / qw(60) * 1000
      Worksheets("****").Cells(*,*).Value = (totMcu1 + totMu2 + MCuleached) * bulkd
      Worksheets("****").Cells(*,*).Value = theta(60)
      Worksheets("****").Cells(*,*).Value = qw(60)
      Worksheets("****").Cells(*,*).Value = totuptake
    End If
    t = t + dt
Loop

'OUTPUT SECTION (RESIDENT CONCENTRATION)
For n = 1 To 60 Step 5
      Worksheets("****").Cells(*,*).Value = n * dz - dz / 2
      Worksheets("****").Cells(*,*).Value = ((Mcu1(n) + Mcu2(n) + Mcuch(n)) * 63.55 *
      1000000 / bulkd)
      Worksheets("****").Cells(*,*).Value = theta(n)
```

```
Next n
        Worksheets("****").Cells(*,*).Value = MCuleached * colarea
         Worksheets("****").Cells(*,*).Value = Mfeleached * colarea
         Worksheets("****").Cells(*,*).Value = EDTAleached * colarea
         Worksheets("****").Cells(*,*).Value = totuptake * colarea
End Sub
```