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www.publish.csiro.au/journals/ajsr *Australian Journal of Soil Research*, 2003, **41**, 323–333

Leaching of copper from contaminated soil following the application of EDTA. I. Repacked soil experiments and a model

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Abstract

The EDTA-enhanced remediation of copper contaminated sandy-loam soil of volcanic origin was investigated. The soil, from an orchard, was contaminated with about 250 mg/kg of copper due to the extensive use of copper sprays. Copper-contaminated soil was packed into 100-mm-long columns, and solutions of Na_2H_2EDTA with $CaCl_2$, raised to a pH of 6.2, were applied at a flow rate of 24 mm/h. Application of an excess of 0.01 M EDTA leached about half the acid-extractable copper from the soil; most of it coming out in the first 3 liquid-filled pore volumes (PV). Also a 0.5 PV pulse of 0.001 M EDTA was applied to similar soil columns and then either leached immediately with 0.005 M $CaCl_2$, or left for periods of up to 1 month before leaching. With immediate leaching, 70% of the EDTA applied was complexed with copper in the leachate, but after a month's delay only 24% was complexed with copper in the leachate, the rest being complexed with iron. There was no evidence of EDTA retardation or adsorption.

The experimental results were simulated using the convection–dispersion equation, incorporating a source/sink term. This described 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. Reasonable simulations were achieved, mostly within errors of observation.

Additional keywords: iron, convection–dispersion equation, heavy metals.

Introduction

There are a number of reasons why the interactions between copper and EDTA in soil are of interest. Copper compounds and EDTA are widely used and are persistent chemicals in the environment. Copper is used in orchard sprays; it is applied to soil with sewage sludge; and it is used as a timber preservative, along with chromium and arsenic. The copper concentration in contaminated soils in New Zealand ranges from 100 to 1800 mg/kg, whereas the average total concentration in non-polluted soils is only 20 mg/kg (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 with micronutrients in agriculture and horticulture to increase their bioavailability. Copper and EDTA can thus inadvertently be present together in soil used for waste disposal. Also, it has been suggested that the ability of EDTA to bring heavy metals into solution be used to remediate contaminated soil. This could be done by removing the soil and leaching it with an EDTA solution off-site (Tuin and Tels 1990; Yu and Klarup 1994), or perhaps by applying EDTA to soil *in situ* to enhance metal uptake by plants (Cunningham *et al.* 1996; Blaylock *et al.* 1997; Huang *et al.* 1997; Brooks 1998; Wu *et al.* 1999; Kirkham 2000).

10.1071/SR02059 0004-9573/03/020323

EDTA-enhanced metal extraction from soil is governed by many factors, including soil type, pH, and the concentrations of EDTA and the metal (Ghestem and Bermond 1998). Once the metal is complexed with the EDTA (Me-EDTA), its mobility in soils and aquifers depends on the interactions between a series of rate-limited reactions (Davis *et al.* 2000) as well as the prevailing hydrological processes. Thus, the use EDTA-enhanced remediation techniques at copper-contaminated sites will require a good understanding of these interactions and processes.

Here we describe the transport of copper during the leaching of a contaminated soil following the application of EDTA. We also look at the effect of leaving EDTA in the soil for varying periods of time before leaching with a weak $CaCl_2$ solution. Lastly, we describe a model simulating the results of the above experiments. This mechanistic model couples the convection–dispersion equation with a source/sink term to describe the time-dependent interactions of copper and iron with free EDTA in soil.

Theory

Our aim in developing a model was to describe quantitatively the main physical and chemical processes occurring in a soil when copper and EDTA are present 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 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 data required as inputs were neither available nor readily obtainable. In terms of practical application, we believe 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), Kedziorek *et al.* (1998), and Samani *et al.* (1998). However, none of these take into account the competition between the contaminant metal and the soil's iron for EDTA. In a number of our experiments we had added a relatively small amount of EDTA, which we found had then complexed with both copper and iron from the soil. Once complexed with the more stable Fe(III), negligible interaction between EDTA and copper would be expected at the pH we used in our 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 we concluded that, while we could use some of the elements in the earlier models, in particular that of Kedziorek *et al.* (1998), it was necessary to develop our own model.

Our model aimed to describe in broad terms what happened when copper and EDTA were present in soil during leaching. Although the imposed flow was sometimes intermittent, the water content in the soil 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 contaminant present in the soil in significant quantities. So copper is the only one we considered. Our experiments showed that virtually all the copper and iron present in the soil solution was complexed with EDTA, so we assumed that it all was. Thus, solute transport for the 3 forms of EDTA of interest, as well as that of the halide tracers, was described by the convection–dispersion equation (Jury *et al.* 1991) in the form:

$$\frac{\theta R \partial C}{\partial t} = \theta D \frac{\partial^2 C}{\partial x^2} - q \frac{\partial C}{\partial x} + S \tag{1}$$

where θ is the volumetric water content (m^3/m^3), 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), t is time (s), D is the dispersion coefficient (m^2/s) accounting for hydrodynamic dispersion and molecular diffusion, x is distance in the direction of flow (m), q is the Darcy flux density (m/s), and S is a term accounting for any kinetic chemical reactions bringing that chemical species into or out of solution (mol/m^3 soil.s). Note that R 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 1 if there is no adsorption to the matrix, and is >1 if there is adsorption.

For diffusion–dispersion we assume (from Wagenet 1983):

$$D = aD_o + \lambda q/\theta \tag{2}$$

where a is a dimensionless tortuosity factor, D_o is the molecular diffusion coefficient in solution (m^2/s), and λ is the dispersivity (m). Note that in some of our experiments, and in the field situation, the soil solution remains stationary for long periods of time in between leaching events. So the first term in Eqn 2, which in our 1-D system describes longitudinal molecular diffusion, can be as significant as the second term, which describes mechanical dispersion. The latter is zero when $q = 0$.

It remains to define S. For the inert halide tracers, $S = 0$. For EDTA, we consider 3 reactions. The first 2 involve the added EDTA, which we will denote as $EDTA_o$, reacting with copper and iron in the soil to form complexes that we will denote 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 we assume 1 mole of metal ion (Cu^{2+} or Fe^{3+}) reacts with 1 mole of EDTA (Kedziorek *et al.* 1998; Brown and Elliott 1992). So we can write:

$$S_{Cu} = K_1(C_o \rho_b M_{Cu})^n - K_3(C_{Cu} \rho_b M_{Fe})^n \tag{3}$$

$$S_{Fe} = K_2(C_o \rho_b M_{Fe})^n + K_3(C_{Cu} \rho_b M_{Fe})^n \tag{4}$$

and

$$S_o = -S_{Cu} - S_{Fe} \tag{5}$$

Here in the above equations, S_o, S_{Cu}, and S_{Fe} are the source/sink terms for $EDTA_o$, $CuEDTA^{2-}$, and $Fe(III)EDTA^{-}$, respectively, n is a dimensionless constant indicating the order of the reaction, and ρ_b is the bulk density (kg/m^3). In Eqns 3 and 4, K_1 is the rate constant for the reaction between $EDTA_o$ and the extractable copper, K_2 is the rate constant for the reaction between $EDTA_o$ 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 $EDTA_o$, $CuEDTA^{2-}$ and $Fe(III)EDTA^{-}$. In Eqns 3–5, a minus sign indicates that the particular chemical species is taken out of solution. M_{Cu} is the EDTA-extractable copper concentration in the soil (mol/kg), and M_{Fe} is the EDTA-extractable iron concentration (mol/kg).

During our dynamic experiments, chemical equilibrium was not obtained, so stability equilibrium constants are not used in the model. However, Eqns 3–5 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* 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 1–5 were solved numerically, using the appropriate boundary and initial conditions. 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.

Materials and methods

The soil came from a site near Opotiki, New Zealand, in the North Island on the Bay of Plenty that had been used to grow passionfruit over 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 was Opotiki sandy loam, a Vitric Orthic Allophanic soil (Hewitt 1993). The top 100 mm had a bulk density of 0.9 Mg/m^3, with a relatively high cation exchange capacity of 22 $cmol_c/kg$ and an organic matter content of 16%. The pH of the soil in 1 : 2.5 water was 5.6. The clay mineralogy of the A horizon consists of 15% allophane plus imogolite, 25% vermiculite, 18% kandite, and 40% VG Am. SiO_2.

Two sets of leaching experiments were conducted. The soil for these experiments was collected from the top 100 mm at Opotiki. It was passed through a 2-mm nylon sieve and homogenised when it was moist. Different batches of soil were used for the 2 experiments. The acid-extractable copper content in the soil used for the first experiment was 290 mg/kg, and that for the second experiment was 248 mg/kg. Note that these values are at the high end of the range of contaminated values reported in Australian orchard soils by Merry *et al.* (1983). A depth of 100 mm of soil was packed at a bulk density of 0.65 Mg/m^3 into acrylic tubes with an internal diameter of 45 mm, with nylon mesh at the base. A peristaltic pump was used to apply the leaching solutions to the columns at about 44 mL/h. This corresponds to a Darcy flux density of about 28 mm/h. The leachate dripped from the bottom of the columns at atmospheric pressure and was collected in aliquots.

The influent $EDTA_o$ solutions used in these experiments were prepared by mixing equal molarities of EDTA and Cl^- using Na_2H_2EDTA ($C_{10}H_{14}N_2O_8Na_2.H_2O$) and $CaCl_2$. Disodium EDTA salt was used instead of the more common trisodium salt to reduce the amount of sodium added to the soil. The solutions were then brought to pH 6.2 by the addition of KOH.

The first experiment involved pre-leaching with about one liquid-filled pore volume (PV) or about 95 mL 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 $EDTA_o$.

In the second experiment, after an initial application of about 1 PV of 0.0025 M $CaCl_2$ solution, some 31 mm (0.5 PV) of 0.001 M $EDTA_o$ was added to 4 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 the same solution after a delay of 1 day; the third was leached after a 1-week delay, and the fourth after a delay of 1 month. During the delay periods the columns were wrapped in polyethylene to minimise evaporation.

At the conclusion of both experiments, the soil was extruded from each column and cut into sections. These were weighed, and their water content and copper concentration measured.

Chemical analyses

Leachate aliquots from the columns were analysed for copper, iron, and sometimes aluminium, manganese, and zinc, using a GBC 904 atomic absorption spectrophotometer. Chloride was analysed using a Dionex HPLC. In some aliquots, the dissolved organic carbon (DOC) concentration was measured using a Shimadzu TC-5000 analyzer. As the DOC concentration of the leachate prior to the EDTA addition was insignificant, the DOC data allowed the total concentration of EDTA, in all forms, to be inferred, by assuming no organic carbon came into solution during the experiments. The validity of this assumption is discussed later. The pH of the leachate was also measured. Before analysis a selection of the leachate samples was passed through Maxi-Clean IC-Chelate Cartridges. This removed any free metal ions, leaving only complexed metal ions.

All soil samples were first weighed and homogenised. Subsamples were then taken for gravimetric water content determination by drying at 105°C. This allowed the liquid-filled pore volume to be determined. Other subsamples were analysed for acid-extractable copper. To do this, about 0.2 g of sieved soil was placed in a boiling tube; 10 mL of concentrated HNO_3 was 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. To measure the EDTA-extractable copper under batch conditions, 1 g of dry soil was mixed with 25 mL of 0.01 M $EDTA_o$ solution, left in an end-over-end shaker overnight, and the copper in the solution measured.

Results and discussion

EDTA and hydraulic conductivity

There have been a number of reports of EDTA having deleterious affect on soil structure, resulting in a significant decrease in hydraulic conductivity (Kedziorek *et al.* 1998; Sun *et al.* 2001). We observed no surface ponding during infiltration, so the saturated hydraulic conductivity remained higher than 28 mm/h. In fact, the measured water contents in the columns were between 0.58 and 0.61 m^3/m^3, significantly lower than the porosity of 0.7 m^3/m^3 (calculated from the bulk density assuming a particle density of 2.5 Mg/m^3).

Chloride and EDTA

The chloride and EDTA results are shown in Figs 1*a* and 2*a* and *b*. The dimensionless concentrations are presented 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 applied in the treatment. There was no evidence of EDTA being adsorbed, as the breakthrough curves for EDTA show no retardation relative to the chloride data. This is consistent with Kedziorek *et al.* (1998), but it has not always been found to be the case. EDTA was also found to be resistant to breakdown in the soil, even after 1 month. In the second experiment, 54 µmol of EDTA exited with immediate leaching, and 53 µmol left when leaching was delayed by 30 days. Both values are close to the 50 µmol applied, with the difference attributable to either measurement error, or not all the DOC being EDTA. In Fig. 2*a* and *b*, the difference between the curves for the column leached immediately and for the column leached a month after the chloride and EDTA were applied demonstrates how over time molecular diffusion reduced the peak concentration.

Copper and iron

The effluent concentrations for copper and iron in the first experiment are shown in Fig. 1*b*. A small amount of zinc was also measured in the leachate, as discussed later. As insignificant amounts of copper, iron, and zinc were found in the leachate during the

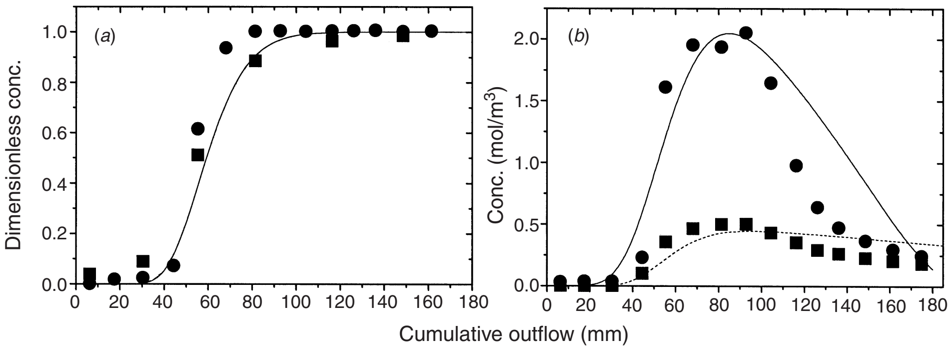

Fig. 1. Breakthrough data for the first experiment: (*a*) measured and simulated values for chloride (●, —) and EDTA (from DOC) (■, ----), (*b*) measured and simulated values for copper (●, —) and iron (■, ----). Note that in (*a*), the simulated curves for chloride and EDTA coincide, so a single curve is shown. One liquid filled pore volume equals 60 mm.

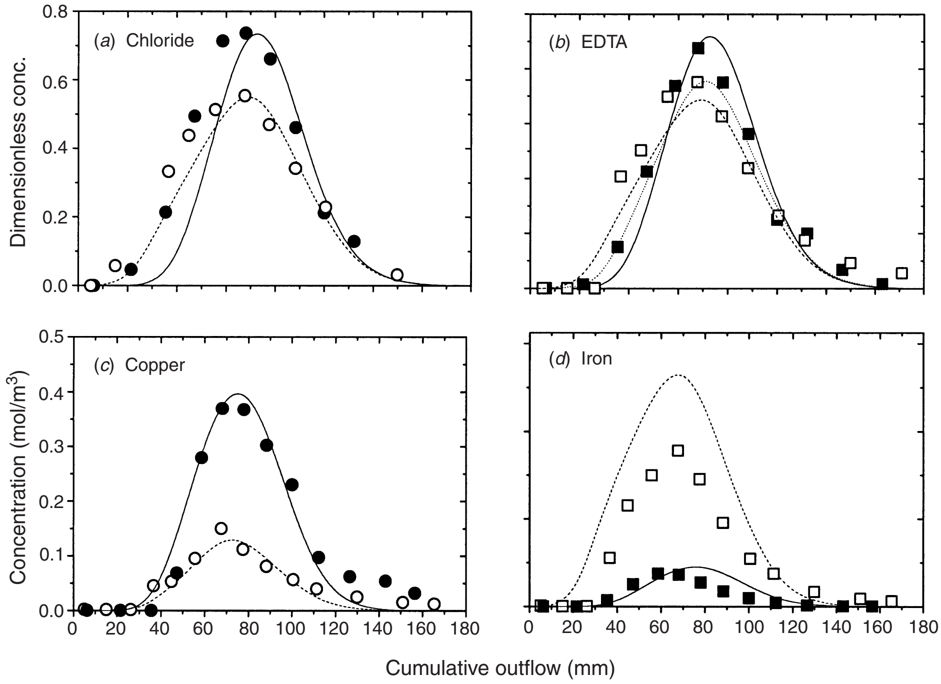

Fig. 2. Breakthrough data for the second experiment. The closed symbols and solid lines are for the column leached immediately; the open symbols and dashed lines are for the column left for a month before leaching: (*a*) chloride, (*b*) EDTA (see text for details), (*c*) copper, (*d*) iron. One liquid filled pore volume equals 60 mm.

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 a speciation analysis of the measured effluent concentration using GEOCHEM-PC (Parker *et al.* 1995) at various times during the experiment. This indicated that all of the copper, iron, and zinc would have been complexed with EDTA at the measured effluent pH of 5.3–5.6. 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 was apparently associated with calcium, as insignificant amounts of aluminium and manganese were found in the effluent.

The leachate copper concentrations shown in Fig. 1*b* increased steadily to a peak and then declined to a low value. Even though more than enough EDTA was applied to complex with all the copper present in the soil, only 57% of the soil copper was leached during the experiment. This reflects the fact that copper is adsorbed to different soil components, such as the various organic matter fractions, iron and aluminium oxides, and the clay fractions, with varying strengths. Each fraction differs in its ease of extraction (McLaren and Crawford 1973; Hong *et al.* 1999). Soil iron also varies widely in the ease and speed with which it can be extracted by agents such as EDTA (Elliott and Shastri 1999). The 9500 μmol of EDTA applied in the first experiment extracted 295, 140, and 26 μmol of copper, iron, and zinc, respectively. It is noteworthy that 80% of the copper extracted came out in the first 3 PV of leachate (180 mm), and we only found 20% in the remaining 7 PV (for which data are not shown in Fig. 1*b*). So, once the weakly adsorbed copper had been removed, the extraction process became much less efficient.

The EDTA leached the copper uniformly from throughout the column (data not shown). About 92 µg/g of copper remained in the soil. However, all but 28 µg/g of this remaining copper was extracted by shaking 1 g of the soil with 25 mL of 0.01 M $EDTA_0$ solution for 24 h at a pH of 6.2. This illustrates the greater efficiency of batch extraction compared with column extraction. We suggest that this is due mainly to the breakdown in soil structure under batch conditions, which allows the EDTA to get at strongly adsorbed copper, which is usually inaccessible (Kookana *et al.* 1994).

The second experiment was designed to find out how stable $CuEDTA^{2-}$ is in soil. Four columns were set up in which, after pre-leaching, 50 mL or 31-mm pulses of 0.001 M $EDTA_0$ were applied and left for 0, 1, 7, and 30 days, before leaching resumed with 0.0025 M $CaCl_2$. Fig. 2*c* and *d* show the effluent copper and iron concentrations for columns leached immediately, and 30 days after, the $EDTA_0$ application. Table 1 gives the amounts leached from all 4 columns. The total amount of copper leached declined markedly as the time for which the EDTA was left in the soil increased. One month's delay reduced by 66% the amount of copper leached. In contrast, the amount of iron leached increased with increasing EDTA residence time. These results are consistent with the following series of reactions occurring. Initially, the EDTA complexes with soil copper and iron to form $CuEDTA^{2-}$ and $Fe(III)EDTA^{-}$. The $CuEDTA^{2-}$ then slowly reacts with soil iron, leading to the copper being released and subsequent re-adsorption to the soil, with $Fe(III)EDTA^{-}$ coming into solution. Szecscody *et al.* (1994, 1998*a*), Jardine and Taylor (1995), Brooks *et al.* (1996), Nowack and Sigg (1997), and Davis *et al.* (2000) all report similar reactions for the transformation of heavy metal–EDTA complexes to $Fe(III)EDTA^{-}$. The effluent pH showed a difference in the second experiment. 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 1 month's delay. We attribute this to the consumption of hydrogen ions during the slow transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ (Szecsody *et al.* 1998*b*).

The resident copper concentrations in the soil at the end of leaching are shown in Fig. 3. In contrast to the first experiment, in the second experiment only in the top 20 mm was there a large reduction in copper content. This was due to the much smaller amount of EDTA added. In the column left with EDTA in it for 1 month, the copper content at the 35 mm depth increased. This we attribute to the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$, and the associated release and re-adsorption of Cu^{2+} at that depth.

Modelling

Solution of Eqns 1–5 requires that parameter values be found. These values were directly measured, obtained from the literature, or determined indirectly using the results of the experiments. The measured values were used for the Darcy flux density (q). The gravimetric water contents measured at the time of final destructive sampling of the columns, and the measured bulk density, allowed the volumetric water content (θ) in each

Table 1. The iron and copper leached (µmol) with varying EDTA residence times in the second experiment

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

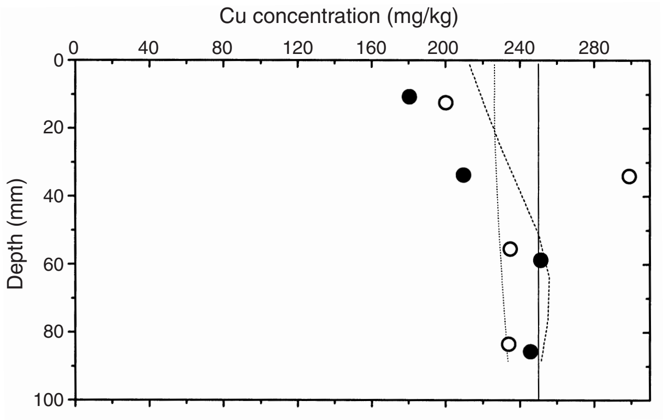

Fig. 3. The initial copper concentration (—) and the final measured and simulated copper concentrations in the soil column leached immediately (●,......), and 1 month (○, ------) after $EDTA_0$ application in the second experiment.

column at the conclusion of the experiment to be found. These values were assumed constant with time. The traditional value of 0.66 was assumed for the tortuosity factor *a* (Penman 1940), as all the soil columns were near saturation. A molecular diffusion coefficient (D_0) value of 1×10^{-9} m^2/s was used for chloride (Robinson and Stokes 1959). A molecular diffusion coefficient value for EDTA was not found in the literature, so we used the above value (Jardine *et al.* 2002). We show later that the model is fairly insensitive to any error in this assumption.

The dispersivity (λ) for the repacked soil was determined by optimising the appropriate analytical solutions of the convection–dispersion equation, for the imposed boundary and initial conditions, to the effluent chloride data. Data from the first experiment, and the immediately leached column in the second experiment, 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 2 experiments, and these are within the range of values for repacked soil given by Wagenet (1983). The average of the 2 values, 3 mm, was used for all solutes in all simulations.

The optimised values of *R* for chloride in the first experiment, and in the immediately leached column in the second experiment, gave values close to unity. This indicated that neither adsorption nor exclusion had occurred. The simulated breakthrough curves for chloride are shown in Figs 1*a* and 2*a*. The simulations of EDTA behaviour in the same experiments are shown in Figs 1*a* and 2*b*, also assuming $R = 1$. EDTA transport was modelled successfully, implying little or no adsorption occurred. Note that in Fig. 1*a* the simulated curves for chloride and EDTA coincide, so a single curve is shown.

Comparison of the chloride breakthrough with immediate leaching, and after 1 month's delay (Fig. 2*a*), shows the effect of molecular diffusion over the month. It reduced the amplitude of the pulse and spread it out more. Both the measured and simulated values show this behaviour. The EDTA-breakthrough curves show the same behaviour, but it is less pronounced. Two simulated curves are shown for EDTA with 1 month's delay in leaching. The curve with the higher peak uses the molecular diffusion coefficient for chloride, 1×10^{-9} m^2/s, and the other uses a lower value of 2.5×10^{-10} m^2/s. This is half the value given for atrazine, a similar large organic molecule, by Hu and Brusseau (1996). Note that the 2 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 1 month, all of the DOC in the leachate was in fact EDTA.

We assumed that the first experiment removed all the iron that is EDTA-extractable at the prevailing pH. The first 3 PV of the iron breakthrough curve are shown in Fig. 1*b*. We found an initial value of 1.25 mmol/kg for M_{Fe} from the area under the curve. This value is used in all the simulations. In the first experiment we also assumed that all the copper that could be removed by leaching with EDTA had been removed. So the 90 mg/kg (1.4 mmol/kg) remaining was effectively inert. Thus, the initial value of M_{Cu} was the acid-extractable value less 1.4 mmol/kg.

Kedziorek *et al.* (1998) found that metal–EDTA reactions, over a wide range of EDTA concentrations, could be described using an equation similar to our Eqn 3 with $n = 1$. This implies a first-order equation with respect to both the EDTA and the extractable metal concentrations. However, we found that $n = 0.5$ better described the way the EDTA concentration, over a 10-fold difference in concentrations, affected extraction. So we subsequently used this value in the model. Values for the rate-coefficients K_1 and K_2 were obtained by visually fitting the model predictions to the CuEDTA data in Figs 1*b* and 2*c*. We assumed that K_3 was zero during this optimisation process, as we expected little transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$ during the relatively short resident times of the first experiment. 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.

It remained then to find a value for K_3. The data from the second experiment were used. Here EDTA was left in the soil for varying periods of up to 1 month. Optimisation showed that a K_3 value of 2.2×10^{-7} s^{-1} reasonably described the decreasing amounts of $CuEDTA^{2-}$ in the leachate with increasing EDTA residence time in the soil (Table 1; Fig. 2*c*). Note that K_3 is 2 orders of magnitude lower than K_1, justifying the assumption in the previous paragraph.

With this parameter set, the model described quite successfully the copper concentration in the leachate in Figs 1*b* and 2*c*, 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 second experiment that the model did not describe well. Although the model correctly estimated the amount of copper leached immediately, with a 1-month delay it did overestimate the amounts leached after 1 day and 1 week (Table 1). Our 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 (Fig. 3).

The amount of iron in the leachate of both experiments was also quite closely simulated (Figs 1*b* and 2*d*; Table 1), except for the column with the 1-month delay before leaching. The overestimation in this case was possibly due to some degradation, or slow irreversible adsorption, of EDTA over the month.

Conclusions

Leaching with an excess of 0.01 M EDTA removed about half the copper from a contaminated soil, and most of this copper was removed in the first 3 PV. A substantial amount of iron was also leached. The soil with a pH in water of 5.6 did not adsorb any of the EDTA forms.

When a pulse of EDTA was applied to copper-contaminated soil, and left there for periods of up to a month before leaching, the amount of copper leached decreased as the delay period increased. One month's delay reduced by 66% the amount of copper leached. We explain this behaviour as Cu-EDTA^{2-} being slowly adsorbed to iron compounds in the soil, and thereby dissociating to form the more-stable Fe(III)EDTA^{-}. The latter is released back into the soil solution, whilst the Cu^{2+} is re-adsorbed.

The experimental results were successfully simulated using the convention–dispersion equation, which incorporated a source/sink term describing the competing time-dependent reactions of copper and iron with EDTA, as well as the reversion of CuEDTA^{2-} to adsorbed Cu^{2+} and Fe(III)EDTA^{-}. In the accompanying paper (Thayalakumaran *et al.* 2003) further experimental studies with different boundary conditions, different repacked soils, and intact soil cores, enable further testing and development of the model.

Acknowledgments

This work was funded by New Zealand's Foundation for Research Science and Technology through contract C06830 'Root-zone Processes and Water Resource Sustainability' and C06X0004 'Knowledge Tools for Environmental Action'. The authors would like to thank Landcare Research New Zealand Ltd (Palmerston North) for the analysis of DOC, and Dr Alan S. Palmer of Massey University for helping with soil identification.

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Manuscript received 21 May 2002, accepted 15 November 2002