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Leaching of copper from contaminated soil following the application of EDTA. II. Intact core experiments and model testing*

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Abstract

In Part I, we proposed a model for EDTA-facilitated transport of copper, and we tested the robustness of this scheme by reference to experiments with various initial and boundary conditions on a repacked soil. Now we examine a quite different repacked soil, and consider intact cores of the same soil as in Part I.

Continuous leaching of an intact core of a contaminated orchard soil of volcanic origin under unsaturated conditions with excess 0.01 M EDTA (510 mm) reduced the copper concentration from 240 down to 80 µg/g in the top 25 mm. When a 480 µmol pulse of 0.001 M EDTA was applied to similar intact cores, 126 µmol of copper came out with immediate leaching, but only 18% of that was leached out from a core that was left for 1 month before leaching. The month's delay caused an increase in the amount of iron leached from 116 to 286 µmol. An experiment in which daily pulses $CuEDTA^{2-}$ were applied to a non-contaminated soil for 3 months indicated that these changes were due to $CuEDTA^{2-}$ slowly changing to $Fe(III)EDTA^{-}$, with the re-adsorption of the Cu^{2+} released.

Application of our model from Part I indicated that different rate constants are required for the chemical reactions for different soils, and also for the same volcanic soil when the pH is lower. But by changing just the dispersivity from 3 mm to 23 mm, the model with the same chemical parameters was able to simulate both the repacked columns and the intact core experiments using the volcanic soil.

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

Introduction

In Thayalakumaran *et al.* (2003), which we will subsequently refer to as Part I, we described the transport, under near-saturated conditions, of copper in repacked columns of a contaminated soil, as well as its temporal stability in the soil solution following the application of EDTA. We described a simple mechanistic model that simulated the experimental results rather well. The usefulness of these data, and the model that we developed from them, depends on whether the scheme can be extrapolated to predict other conditions. For example, can it describe how a different soil behaves? Can it describe what happens if copper is leached from contaminated topsoil into essentially copper-free subsoil? Can it describe how EDTA behaves when it is applied to unsaturated intact soil columns?

We sought to answer these questions by conducting 7 leaching experiments. These we will denote as A–G. Experiments A and B involve an alluvial repacked soil with a quite different mineralogy, and with much less organic matter, than the soil used in Part I. Expts C–G used the same repacked volcanic soil studied in Part I. Expt C involved adding daily

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aliquots of $CuEDTA^{2-}$ for nearly 3 months, to test the model's ability to describe the slow reactions this compound undergoes in the soil. Expts D and E examined what happened when EDTA leached copper out of contaminated surface topsoil into soil below, which was essentially free of copper. This physical situation is a common field scenario. Lastly, Expts F and G involved moving another step closer to field conditions. Larger cores of intact soil were used to determine whether or not the model, parameterised using data from the repacked column experiments, could be applied to unsaturated flow in soil with natural structure. Here, there would be quite different geometric relationships between the adsorbed copper and the predominant flow pathways.

Materials and methods

The influent EDTA solutions used in all experiments, except C, were prepared by mixing Na_2H_2EDTA, and either $CaCl_2$ or $CaBr_2$, to give the same molar concentration of halide tracer as EDTA. The solutions were then brought to pH 6.2 by the addition of KOH. The 0.001 M $CuEDTA^{2-}$ solution used in Expt C was made by the stoichiometric addition of copper as $CuCl_2$, and EDTA as Na_2H_2EDTA (1:1). The mixture was equilibrated for 24 h, then $CaBr_2$ was added, and finally KOH added to raise the pH to 6.2. A summary of the leaching procedures used in all experiments is given in detail in Table 1.

The 2 soils used were both collected from the A horizon of orchards in which copper sprays were used. The volcanic soil used in Part I, Opotiki sandy loam, a Vitric Orthic Allophanic soil (Hewitt 1993), was used in all experiments, except A and B. For these 2 experiments, an alluvial soil, the Manawatu fine sandy loam, a Weathered Fluvial Recent soil (Hewitt 1993) was used. All the experiments were performed in the laboratory under similar conditions.

Repacked column experiments

The 2 different soils used for Expts A–E were passed through a 2-mm nylon sieve while moist, and then homogenised by frequent mixing, but they were not allowed to dry out. A depth of 100 mm of soil was

Table 1. Experiment procedures for repacked soil Experiments A–E

	Experiment A (1 column)	Experiment B (4 columns)	Experiment C (1 column)	Experiment D (1 column)	Experiment E (2 columns)
Soil used	Contaminated Manawatu soil	Contaminated Manawatu soil	Uncontaminated Opotiki soil	Top 30 mm—contaminated Opotiki soil Remainder— 70 mm uncontaminated Opotiki soil	Top 30 mm—contaminated Opotiki soil Remainder— 70 mm uncontaminated Opotiki soil
Pre-leaching	0.0025 M $CaCl_2$ (93 mL)	0.0025 M $CaCl_2$ (90 mL)	0.0025 M $CaCl_2$ (96 mL)	0.0025 M $CaCl_2$ (93 mL)	0.0025 M $CaCl_2$ (95 mL)
EDTA application	Excess of 0.01 M $EDTA_o$ (Na_2H_2EDTA + $CaBr_2$) (260 mL)	31 mm 0.001 M $EDTA_o$ (Na_2H_2EDTA + $CaCl_2$) (49 mL)	0.001 M $CuEDTA^{2-}$ + $CaBr_2$ (as 28-mm pulses for 83 days to give a total of 3684 mL)	Excess of 0.01 M $EDTA_o$ (Na_2H_2EDTA + $CaBr_2$) (260 mL)	31 mm 0.001 M $EDTA_o$ (Na_2H_2EDTA + $CaBr_2$) (49 mL)
Delay after EDTA application	None	Wrapped in polythene bags and kept for 0, 1, 7, or 30 days	—	none	Wrapped in polythene bags and kept for 0, 1, 7, or 30 days
Final leaching	—	0.0025 M $CaCl_2$ (190 mL)	0.0025 M $CaCl_2$ (240 mL)	—	0.0025 M $CaCl_2$ (190 mL)

packed into acrylic tubes with an internal diameter of 45 mm and with nylon mesh at the base. In Expts A and B, the Manawatu soil was packed to a bulk density of about 1.0 Mg/m^3, whereas in Expts C–E the Opotiki soil was packed to about 0.65 Mg/m^3. A peristaltic pump was used to apply the leaching solutions to all the columns at about 46 mL/h, which corresponded to a Darcy flux density of about 29 mm/h. The leachate dripped from the bottom of the columns at atmospheric pressure and was collected in aliquots.

The Manawatu soil for Expts A and B came from 2 different batches, obtained from 2 nearby locations in the same orchard. The samples had different copper and organic matter contents. The acid-extractable copper content in Expt A was 60 mg/kg and the organic matter content was 9%. In Expt B, the copper content was 21 mg/kg and the organic matter content was 5%. Expt A involved pre-leaching with about 1 liquid-filled pore volume (PV) of 0.0025 M $CaCl_2$ solution, and then continuously leaching a soil column with 163 mm (2.8 PV or 260 mL) of 0.01 M $EDTA_o$. In Expt B, after an initial application of about 1 PV of 0.0025 M $CaCl_2$ solution, some 31 mm (0.53 PV or 49 mL) of 0.001 M $EDTA_o$ was added to 4 soil columns. The first of these columns was then leached immediately with about 120 mm of 0.0025 M $CaCl_2$ solution. The second was leached with the same solution after a delay of 1 day, the third after a 1-week delay, and the fourth after a 1-month delay. During the delay periods the columns were wrapped in polyethylene to minimise evaporation.

For Expt C, the Opotiki soil was collected from the site where the soil for the experiments in Part I had been obtained; however, it was taken from an adjacent location that had not been subject to copper sprays. The soil at this location had a lower pH than the orchard soil, namely 4.5 compared with 5.6, measured in water. This difference was presumably due to the second soil not having been limed. Its copper content was 13 mg/kg, similar to other reported values for uncontaminated soil (Merry *et al.* 1983). Its organic matter content was same as that of the contaminated Opotiki soil. The column was pre-leached with 0.0025 M $CaCl_2$ for 1 PV. Then a total of 2316 mm (39 PV) of 0.001 M $CuEDTA^{2-}$ was applied as daily pulses of 28 mm (0.5 PV) over an 83-day period. By this time, the effluent concentration had reached the influent concentration. The column was then again leached with 0.0025 M $CaCl_2$.

In Expts D and E, the bottom 70 mm in each column was Opotiki soil that was uncontaminated, as used in Expt C, and the top 30 mm was contaminated Opotiki soil containing 340 mg/kg of copper. In all other respects, Expts D and E were the same as Expts A and B.

At the conclusion of Expts A–E, the soil was extruded from each column, cut into sections, and weighed, and then water content and copper concentration were measured as described in Part I.

Intact soil columns

Three soil cores were collected in close proximity to each other at the copper-contaminated Opotiki site. After the grass cover had been removed, plastic tubes 100 mm in internal diameter and 150 mm long were pressed into the soil. The cores were then retrieved by excavation and transported to the laboratory. Several smaller 35-mm-diameter soil cores were taken close to the larger diameter cores in order to measure the copper distribution in the soil profile.

An 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 a given pre-set pressure potential maintained by a bubbling tower and vacuum system. A similar porous disk and suction apparatus underneath allowed solution removal while maintaining the same pressure potential at the base. The imposed pressure potential at the top, and bottom, was –100 mm. This resulted in a flow rate of about 24 mm/h for the core used in Expt F, and 14 and 7 mm/h for the 2 cores used in Expt G. A thin layer of sand (<2 mm) was used to ensure the contact between the disk and the soil.

Each core was first pre-leached with 0.0025 M $CaSO_4$ solution for about 87 mm (1 PV or 680 mL). In Expt F the infiltrating solution was then quickly changed to 0.01 M $EDTA_o$ solution, and this was applied continuously for about 5 PV. In Expt G, 61 mm (0.7 PV) of 0.001 M $EDTA_o$ was applied to the 2 cores. After the application of $EDTA_o$ 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 it 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 and analysed for copper, iron, manganese, and aluminium as described in Part I.

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

Results and discussion

EDTA and hydraulic conductivity

The air-filled porosity, as calculated from the gravimetric water content and bulk density, assuming a particle density of 2.5 Mg/m^3, was 0.07–0.09 m^3/m^3 in the repacked Manawatu soil, and 0.10–0.15 m^3/m^3 for the repacked Opotiki soil, indicating better aeration in the latter. This reflects the less-developed structure, and lower saturated hydraulic conductivity, in the alluvial Manawatu soil, compared with the volcanic allophanic Opotiki soil.

In the repacked soil columns used in Expts A–E, we observed no ponding, except in the Expt B column with 1 month's delay between the EDTA$_0$ application and leaching it with $CaCl_2$. In this case, the Manawatu fine sandy loam soil ponded during the final leaching phase. However, similar columns kept for 1 month after applying water or $CaCl_2$ solution, but with no EDTA application, also ponded. Therefore, we suggest that 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 dissolution, or dispersion, due to the addition of EDTA or sodium (Allison 1947).

During the intact core Expts F and G using the Opotiki soil, the gravity-induced flow at –100 mm pressure head varied by <15%, except for the core in which leaching was delayed for 1 month after EDTA application. In that core, the flow rate during the final leaching dropped to 3 mm/h from 7 mm/h found during pre-leaching and EDTA application 1 month earlier. Simply removing and replacing the disk permeameter could itself induce such changes. So we conclude that the effect of the EDTA on unsaturated hydraulic conductivity was negligible, or at worst slight.

EDTA application to repacked Manawatu fine sandy loam: Expts A and B

The results for Expts A and B are shown in Figs 1 and 2. The dimensionless concentrations shown were calculated as $(C - C_1)/(C_2 - C_1)$, where C is the measured effluent concentration, C_1 is the concentration in the pre-leaching solution, and C_2 is the concentration applied in the treatment. Figs 1*a* and 2*a* and *b* show that the EDTA was not adsorbed, as the breakthrough curves for EDTA show no retardation relative to non-reactive tracer (bromide or chloride). This is consistent with the Opotiki sandy loam data in Part I.

In Expt B, where 50 μmol of EDTA was applied, there was an apparent anomaly in the mass balance. The DOC analyses suggest that 52 μmol of EDTA was lost by immediate leaching, but 64 μmol was removed when leaching was delayed by 1 month. Also for the column with 1 month's delay, the peak EDTA concentration in the leachate was twice that found with immediate leaching (Fig. 2*b*). In contrast, the month-long pause had little effect on the EDTA breakthrough curve of the second experiment in Part I, except for a slight lowering of the peak value with a 1-month delay. Presumably this was due to molecular diffusion. In the experiments of Part I, and Expt A in this paper, pre-leaching would have removed any DOC initially present in the soil solution. Also, the relatively high copper concentration in the soil solution would have inhibited microbial reactions during the experiments. Thus, almost all DOC in the effluent was probably EDTA. Loveday (1974) suggested a copper concentration in solution of 2 mol/m^3 was sufficient to inhibit the activity of most microorganisms. Our soil solutions mostly contained copper concentrations of around this value. However, as Fig. 2*c* shows, the copper concentration in the soil solution dropped to 0.005 mol/m^3 during the 1-month delay in Expt B. This apparently allowed biological activity to produce a significant amount of additional soluble

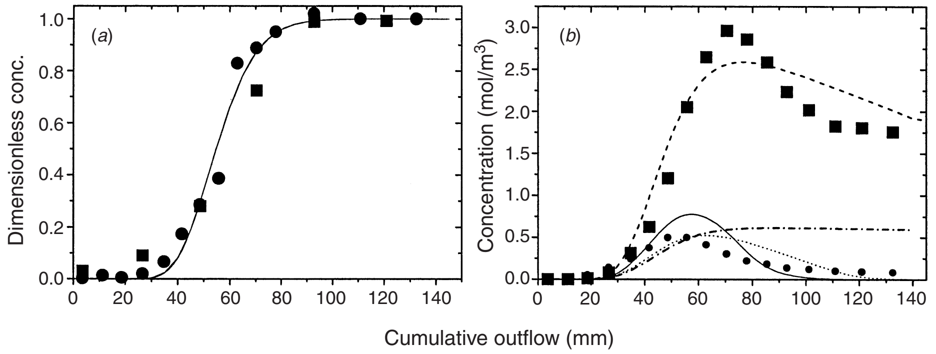

Fig. 1. Breakthrough data for the Manawatu soil column continuously leached with 0.01 M EDTA. (*a*) Measured and simulated breakthrough data for bromide (●, —) and EDTA (■, ----). Note that the simulated curves for bromide and EDTA coincide. (*b*) Measured and simulated breakthrough for copper (●, — or ....) and iron (■, ---- or –·–·–·–). Dotted and dash–dot lines indicate simulations using the kinetic rate constants of Opotiki soil and, solid and dashed lines are simulations using new rate constants of Manawatu soil. One liquid-filled pore volume equals 58 mm.

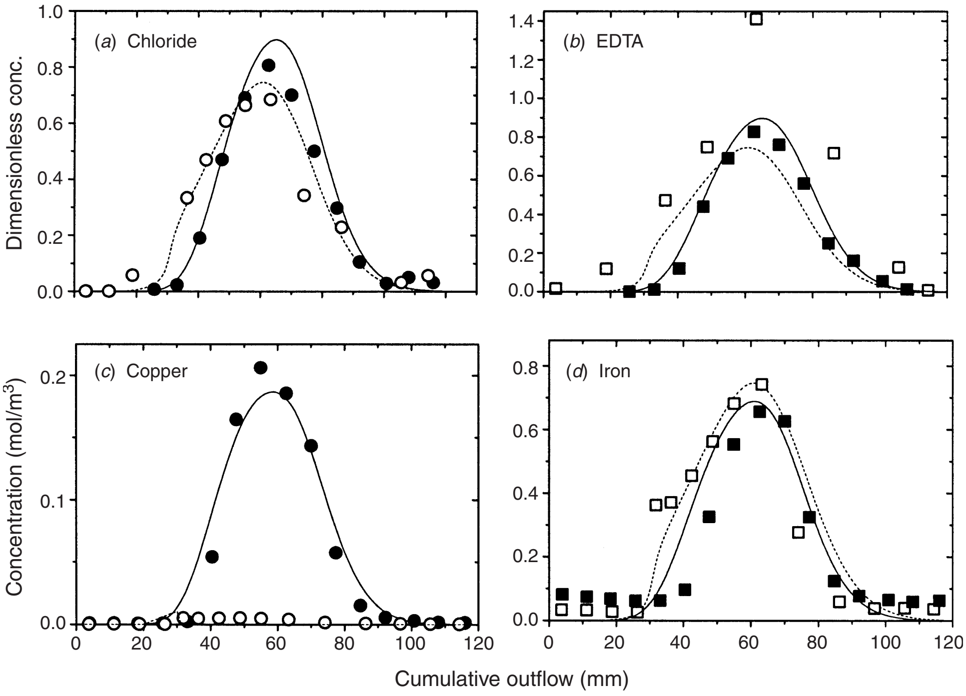

Fig. 2. Breakthrough data for Manawatu soil columns with immediate and 30-day delayed leaching. The closed symbols and solid lines are for the column leached immediately; the open symbols and dashed lines are for the column left for 1 month before leaching. (*a*) Chloride, (*b*) EDTA, (*c*) copper, (*d*) iron.

carbon, and hence showed an increase in the amount of DOC leached. So in this case the assumption of a 1:1 correspondence between DOC and EDTA is not reasonable.

The effluent concentrations for copper and iron in Expt A are shown in Fig. 1*b*. Because insignificant amounts of copper and iron were found in the leachate during pre-leaching, virtually all the copper and iron present in the leachate must have been brought into solution by complexation with EDTA. This was confirmed by a speciation analysis of the effluent chemistry using GEOCHEM-PC (Parker *et al.* 1995). EDTA that was not complexed with copper or iron apparently leached with calcium, because insignificant amounts of aluminium and manganese were found in the effluent.

The 2600 µmol of $EDTA_o$ applied in Expt A leached out 45 µmol of copper and 369 µmol of iron. Even though the amount of EDTA applied was well in excess of the amount needed to complex all the copper present in the soil, only 35% of the soil copper was leached during the experiment. About 40 mg/kg of copper was found to have remained, spread quite uniformly throughout the soil. This contrasts with the 90 mg/kg remaining after the analogous experiment using the Opotiki soil in Part I, and demonstrates how organic matter content and clay mineralogy can affect the binding strength for copper of different soils (McGrath *et al.* 1988; Barona *et al.* 2001)

Expt B was designed to find out how stable $CuEDTA^{2-}$ is in the Manawatu soil. Four columns were set up in which 50 mL (31 mm) pulses of 0.001 M $EDTA_o$ were applied and then left for different time periods before leaching was 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 application of 50 µmol of $EDTA_o$. Table 2 gives the amounts leached with the different delay times. The amount of copper leached declined markedly as the time the EDTA was left in the soil increased. With a delay of a week or more, little copper was leached. In all cases, >80% of the applied EDTA apparently left the soil complexed with iron. In contrast to Expt A, in Expt B most of the leached copper was removed from the top half of the column, due to the much smaller amount of EDTA added.

In order to use the model developed in Part I to simulate these experiments, new values for some parameters had to be found, as a different soil was used. For the Darcy flux density (q) and volumetric water content (θ), the measured values were used. The water content in the Manawatu soil ranged from 0.49 to 0.58 m^3/m^3, and in the Opotiki soil it ranged from 0.57 to 0.62 m^3/ m^3. Values for D_o, a, and n were the same as those used in Part I.

An average dispersivity (λ) of 3 mm was found by fitting the bromide data in Figs 1*a* and 2*a* to the appropriate analytical solutions of the convection–dispersion equation. This value is similar to that found for the repacked Opotiki soil in Part I. Optimisation for R in the Manawatu soil experiments gave a value close to unity, indicating that neither adsorption nor exclusion of chloride occurred. The measured and modelled bromide data in Fig. 1*a* and chloride data in Fig. 2*a* are in close agreement. This clearly demonstrates how molecular diffusion during the 1-month pause in leaching reduced the amplitude of the pulse, and spread it out.

The simulations for EDTA transport were successful (Figs 1*a*, 2*b*), except for the column with a 1-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 above. Again, as the model with $R = 1$ describes the data; little or no adsorption of EDTA occurred.

Table 2. The iron and copper leached (µmol) with varying EDTA residence times in Expt B with the Manawatu fine sandy loam

Residence time (days)	Cu leached		Fe leached	
	Experiment	Model	Experiment	Model
0	10	11	42	41
1	4.4	6	59	57
7	0.8	0.5	55	50
30	0.3	0.1	44	50

As in Part I, we assumed in Expt A that all the copper that could be removed by leaching with EDTA had been removed. So the 40 mg/kg (0.63 mmol/kg) remaining in the soil was effectively too strongly bound to be extracted. Thus, the initial value of M_{Cu} in Expt A was taken as the acid-extractable value, less 0.63 mmol/kg. However, as the soil used for Expt B was collected from a different spot, the same value for M_{Cu} could not be used here. Therefore, the copper concentration measured in the top layer of column leached immediately after the $EDTA_o$ application in Expt B was taken as the EDTA non-extractable copper. This was found to be 0.20 mmol/kg. A value for the EDTA-leachable iron of 4.2 mmol/kg was obtained from an experiment similar to Expt A. Here, enough EDTA was added to leach from the soil all iron that was EDTA extractable under the prevailing conditions. Note that this EDTA-leachable iron was 3.3 times greater than the value found for the Opotiki soil.

Simulation of the copper and iron leachate concentrations in Expt A, using the values for the rate-constants K_1, K_2, and K_3 used for the Opotiki soil in Part I, grossly underestimated the iron concentration in the leachate (Fig. 1*b*, dot–dash line), and also predicted slower leaching of copper (Fig. 1*b*, dotted line) than was observed. We attribute this to the copper and iron being adsorbed with different strengths in the Opotiki and Manawatu soils. Therefore, we looked for a factor that we could apply to these rate constants to obtain new values which would better describe the data of Expt A (Fig. 1*b*, Fe, dashed line; Cu, solid line). We found that assuming all 3 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 faster rate constants in the Manawatu soil are probably due to its lower organic matter content.

Using the parameters described above, the model simulated the copper, iron, and EDTA concentrations in the leachate reasonably well for Expt A (Fig. 1*a*, *b*). It also successfully simulated the results for copper and iron in Expt B (Fig. 2*c*, *d*; Table 2), despite the much lower concentration, and smaller amount, of EDTA applied, and the varying periods it was left in the soil. Thus, the simple model developed appears quite robust, for it is capable of predicting the results of experiments done in a quite different soil, given that the values for the key parameters are adjusted appropriately.

Leaching the repacked Opotiki soil with $CuEDTA^{2-}$: Expt C

To investigate specifically the time-dependent reaction of $CuEDTA^{2-}$ with iron, $CuEDTA^{2-}$ solution was applied to a column of Opotiki sandy loam soil obtained from an area that had not been contaminated with copper sprays. Each day for 83 days, some 28 mm of $CuEDTA^{2-}$ solution (44.5 µmol) was added. Figure 3*a* shows the average daily bromide, copper, and iron concentrations in the leachate. Of the 3685 µmol of copper applied in total, 2860 µmol was leached, and 720 µmol remained in the soil. The soil ended up with an average copper concentration of 444 µg/g. This left just 105 µmol of copper unaccounted for. The 726 µmol of iron in the leachate equalled the amount of copper staying in the soil, indicating 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. 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 1 h per day, with a 23-h break between applications, and the collection of each day's leachate in 3 aliquots, allowed the rate dependence of the chemical reactions to be observed. Fig. 3*b* shows the copper and iron

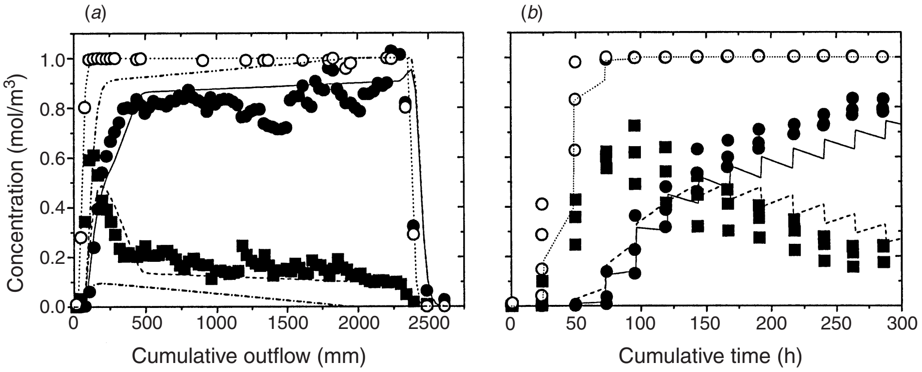

Fig. 3. Observed and simulated effluent concentrations as a function of (*a*) cumulative outflow, and (*b*) cumulative time for the column to which $CuEDTA^{2-}$ solution was applied. Bromide (○, ...) copper (●, — or – – – –), iron (■, ------- or – – – –). Dash-dot lines show simulations using the kinetic rate constants for Opotiki contaminated soil, and solid and dashed lines are simulations using new rate constants for Opotiki uncontaminated soil.

leachate concentrations in each aliquot during the first 12 days (300 h) of the experiment. As expected, there was an increase in the copper concentration in the 3 aliquots collected on each day. However, the concentration in the first aliquot on the following day was lower than in the last aliquot on the previous day. The iron concentration shows complementary behaviour, decreasing during each flow event, and then increasing immediately after non-flow periods. We attribute this behaviour to the gradual replacement of $CuEDTA^{2-}$ with $Fe(III)EDTA^{-}$ during the 23-h non-flow periods. The behaviour became less pronounced with increasing time, as the system approached equilibrium with the invading $CuEDTA^{2-}$ solution.

Figure 3*a* and *b* 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 $CaCl_2$, Fig. 3*a* 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 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. This contrasting behaviour 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 $Fe(III)EDTA^{-}$. We noted that the first effluent aliquot had a pH of 4.5, and the last, some 83 days later, had a pH of 6.2. As Brooks *et al.* (1996) showed, the higher the pH, the less likely it is that EDTA is adsorbed. So we suggest the $CuEDTA^{2-}$ that was adsorbed had gradually come back into solution as the pH rose.

In Expt C, the only significant reaction taking place was the transformation of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$. This allows us to study this aspect of the model in some detail. The model, with the values for M_{Fe}, and K_3 used for experiments in Part I and using the same Opotiki sandy loam but from a contaminated area, grossly underestimated the amount of iron leached (Fig. 3*a* dot-dash line), and so the reaction rate of the $CuEDTA^{2-}$ formed. We believe this was due to the soil's pH, which was 4.5. This is significantly lower than the 5.6 of the contaminated soil. The lower pH would have made iron in the soil more easily extracted by EDTA (Brooks *et al.* 1996), and so it would necessitate the use of a higher value for K_3 at the lower pH. 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 (Fig. 3*a*), suggests another approach. We propose 2 EDTA-extractable iron fractions: 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 2 additional terms are required in the model. One describes the reaction between EDTA$_o$ and $M_{Fe}{}^*$, and the other describes the reaction between CuEDTA^{2-} and $M_{Fe}{}^*$. Thus, Eqns 3 and 4 in Part I now become:

$$S_{Cu} = K_1(C_o \rho_b M_{Cu})^n - K_3(C_{Cu} \rho_b M_{Fe})^n - K_5(C_{Cu} \rho_b M_{Fe}{}^*)^n \tag{1}$$

$$S_{Fe} = K_2(C_o \rho_b M_{Fe})^n + K_4(C_o \rho_b M_{Fe}{}^*)^n + K_3(C_{Cu} \rho_b M_{Fe})^n + K_5(C_{Cu} \rho_b M_{Fe}{}^*)^n \tag{2}$$

Here K_4 is the rate constant for the reaction between EDTA$_o$ 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 are defined in Part I.

To use this modified model to simulate the data in Fig. 3, we need values for $M_{Fe}{}^*$ and K_5. We also need a new value for K_3, which we expect to be higher 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 for $M_{Fe}{}^*$, 1.3×10^{-6} s^{-1} for K_3, and 1.3×10^{-7} s^{-1} for K_5. We also expect some adsorption of EDTA in the soil at pH 4.5 soils, in which we assumed an *R*-value of 2, for reasons discussed below in the relation to Expt D. As in this experiment the only significant reaction taking place was the transformation of CuEDTA^{2-} to Fe(III)EDTA$^-$, values for rate constants K_2 and K_4 were not required.

The saw-tooth shape of the simulated curves in Fig. 3*b* fit the observed behaviour 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 our simple model, which divided the soil iron into just 2 fractions.

EDTA application to non-uniformly contaminated repacked Opotiki sandy loam: Expts D and E

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

For Expt D, the EDTA breakthrough curve in Fig. 4*a* shows obvious retardation compared with the non-reactive halide tracer, indicating some adsorption of EDTA by the soil. This is in contrast to findings in Part I where, in an analogous experiment, EDTA was not adsorbed. We believe that this difference is due to the low pH of 4.5 in the uncontaminated soil relative to that of the contaminated soil, which was 5.6. The pH of the effluent reflected this observed difference in soil pH. In Experiment D, it was between 4.5 and 4.6, whereas the effluent pH for the comparable experiment in Part I fell between 5.3 and 5.6. Brooks *et al.* (1996) also reported greater retardation of the cobalt complexes Co(II)EDTA^{2-} and Co(III)EDTA$^-$ through ferrihydrite when the pH was decreased.

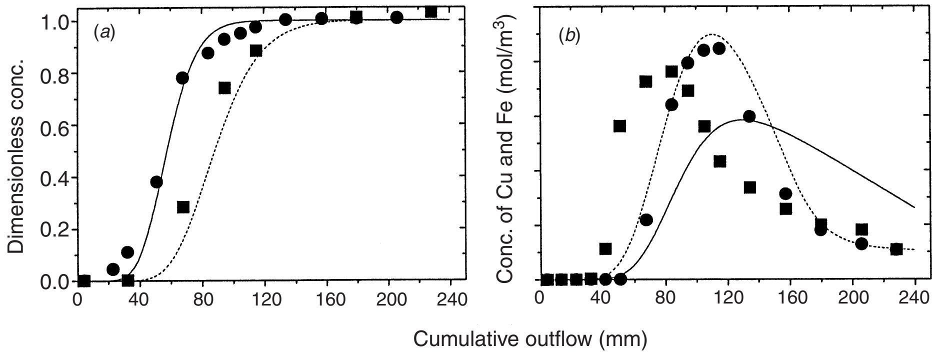

Fig. 4. Breakthrough data for the Opotiki non-uniformly contaminated column continuously leached with 0.01 M EDTA. (*a*) Measured and simulated breakthrough data for bromide (●, —) and EDTA (■, ----). (*b*) Measured and simulated breakthrough for copper (●, —) and iron (■, ----).

Due to the smaller amount of copper in the soil compared with the first experiment in Part I, much less copper was leached, namely 110 μmol compared with 295 μmol. The copper concentration in the soil at the end of leaching (data not shown) showed that little, or none, of the copper removed from the top 30 mm was re-adsorbed in the almost copper-free soil below. We attribute this to the short residence time of the $CuEDTA^{2-}$ in the soil, and the relative slowness of the reaction involved.

Figure 5 shows the results of Expt E where 50-mL (31 mm) pulses of 0.001 M $EDTA_0$ (50 μmol) were left in soil columns for 0 and 30 days 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 column leached immediately, but virtually none from the column with 1 month's delay.

To apply the model to Expts D and E, we need to take into account the greater availability of the iron at the lower pH in the soil used in the bottom 70 mm of the columns. As discussed above, in relation to Expt C, soil iron becomes more reactive as the pH decreases. So we now assume that the values for K_2 and K_4 changed with pH in the same way as we assumed earlier for K_3 and K_5. Thus, for both Expts D and E, we took K_2 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 Part I.

As discussed above, in Expt 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 (Fig. 4*a*). This value was also assumed in the lower pH soil used in Expts C and E.

In Expt D, the observed copper breakthrough was more peaked than the simulated curve, and further the iron came out somewhat earlier (Fig. 4*b*). This could perhaps be due $CuEDTA^{2-}$ 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.

In the immediately leached column of Expt E, although the observed exiting pulse of EDTA from the column had the roughly expected retardation, its amplitude was about half that of the simulation (Fig. 5*b*). This suggests more adsorption of EDTA than implied by our assumed R value of 2. Our simple model implies a linear adsorption isotherm, whereas

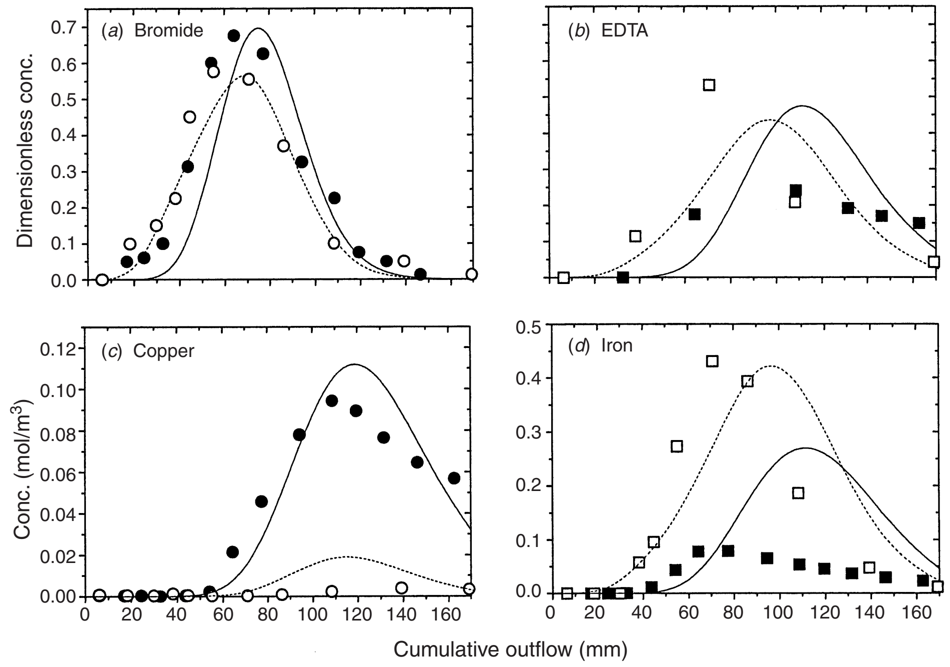

Fig. 5. Breakthrough data for Opotiki non-uniformly contaminated columns with immediate and 30-day delayed leaching. The closed symbols and solid lines are for the column leached immediately; the open symbols and dashed lines are for the column left for a month before leaching. (*a*) Bromide, (*b*) EDTA, (*c*) copper, (*d*) iron.

isotherms are usually non-linear. This non-linearity is consistent with the *R* value derived for 0.01 M EDTA underestimating the adsorption of 0.001 M EDTA.

In contrast to the immediately leached column, in Fig. 5*b* the peak EDTA concentration was greater than the simulated value for the column in which leaching was delayed for a month. We suggest the predictions are too high due to the presence of organic compounds other than EDTA affecting the DOC analyses, as discussed above.

Figure 5*c* shows that the concentrations of copper in the leachate from the immediately leached column in Expt E were closely simulated by the model, but not the column with delayed leaching, where it was overestimated. At these lower concentrations it seems the model underestimated the rate of conversion of $CuEDTA^{2-}$ to $Fe(III)EDTA^{-}$. In contrast, Fig. 5*d* 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 our procedure 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 sensitive to this rate constant.

EDTA application to intact soil cores of Opotiki sandy loam: Expts F and G

Experiments F and G again involved the same treatments as Expts A and B, but they entailed intact-soil cores of Opotiki sandy loam, rather than repacked soil columns. We first need to describe how we handled the problem of getting the initial copper concentration with depth, as we had no way of non-destructively measuring the initial copper distribution. We did take several smaller cores adjacent to each large core and measured the copper distribution in them. But due to soil variability, this need not necessarily give an accurate

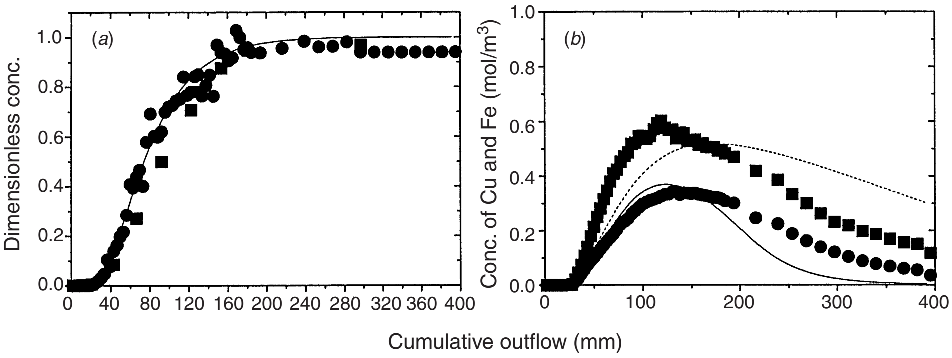

Fig. 6. Breakthrough data for the intact Opotiki soil core leached continuously with 0.01 M EDTA. (*a*) Measured and simulated breakthrough data for bromide (●, —) and EDTA (■, ----). (*b*) Measured and simulated breakthrough for copper (●, —) and iron (■, ----). One liquid-filled pore volume equals 87 mm.

indication of the profiles in the large cores. However, by adding the amount of copper leached to that left in the soil after leaching, we found the total amount of copper that must have been initially present in each of the 3 large soil cores. We then used these total values, in conjunction with the shape of the distribution measured in the smaller soil cores taken adjacent to the large cores, to infer an initial copper distribution for each large core.

Figure 6*a* 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 Fig. 4*a*, the EDTA data are only slightly retarded relative to the bromide, indicating little or no EDTA adsorption. This is probably due to the soil pH in the lower part of the intact soil core being higher than in Expt D (a pH of 5.0, compared with 4.5)

The 40 mmol of EDTA applied in Expt F only extracted 641 μmol of copper, 75 μmol of zinc (data not shown), and 1076 μmol of iron in a cumulative volume of about 7 PV of leachate (Fig. 6*b*). The 641 μmol of copper was 54% of that present in the soil.

The EDTA application brought the copper concentration down from 240 mg/kg to 75 mg/kg in the top 30 mm of soil. In the first experiment in Part I using the same soil, but with a repacked column, the same treatment reduced the copper concentration to a similar value of 90 mg/kg. We were surprised at how effective the EDTA was in removing copper from the intact soil, given the highly non-uniform flow pathways usually found there. We believe this was due to the permeable nature of this soil, and to the flow being under non-ponding flow conditions. If the soil had been less permeable, and if ponding had occurred, we would have expected the flow to be highly preferential, and much less effective in removing the copper.

Figure 7*a* and *c* show bromide, EDTA, copper, and iron effluent concentrations as a function of cumulative outflow for the column leached immediately after the $EDTA_0$ application. Figure 7*b* and *d* show the comparable data for the column with 1 month's delay before leaching. The calculated percentages of the applied bromide recovered in the leachate were 115% with immediate leaching and 94% for the 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 (Fig. 7*a*). This indicates some adsorption of EDTA by the soil. This behaviour is less evident for the column in which leaching was delayed for 1 month (Fig. 7*b*). Likely reasons for this are given below.

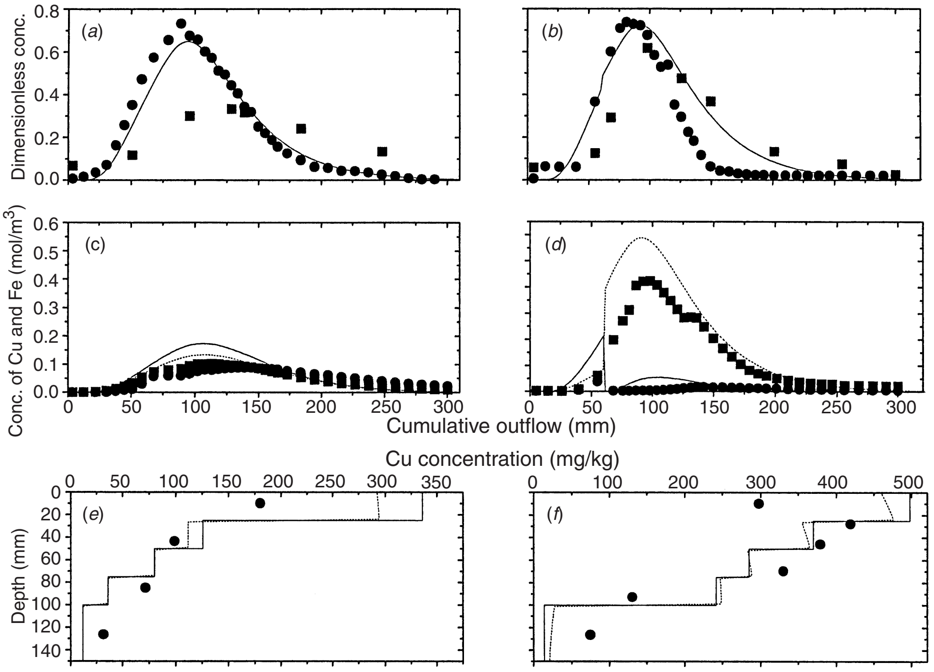

Fig. 7. Results of immediate and delayed leaching of Opotiki soil intact cores; (*a*), (*c*), and (*e*) show results for immediate leaching; (*b*), (*d*), and (*f*) show results with 1 month's delay before leaching; (*a*) and (*b*) show measured and simulated breakthrough data for bromide (●, —) and EDTA (■, ----); (*c*) and (*d*) show measured and simulated breakthrough data for copper (●, —) and iron (■, ----); (*e*) and (*f*) show the initial copper distribution (●) and the final measured (—) and simulated (----) copper concentrations in the soil cores.

While the 1-month pause in leaching, when the cumulative outflow was 61 mm, did not cause any noticeable discontinuity in the bromide concentration (Fig. 7*b*), the pause induced a pronounced drop when leaching resumed in the copper concentration, and a large increase in the iron concentration (Fig. 7*d*). These changes reflect the time-dependent chemical reaction of CuEDTA^{2-}. 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 factor in our experiment. Hence, the discontinuity in the copper and iron concentrations was due to the slow chemical reactions described above.

Leaving the 480 μmol of EDTA$_0$ pulse in the soil for 1 month caused a decrease from 126 μmol, to 23 μmol, in the amount of copper leached. The associated increase in the iron leached was from 116 μmol to 286 μmol.

Figure 7*e* and *f* show the distributions of copper in the soil after immediate and delayed leaching. Figure 7*e* 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 330 mg/kg to 180 mg/kg. In the delayed leaching experiment (Fig. 7*f*), except in the top 20 mm, the final copper concentration was greater than that initially present. Following the application of the 61 mm EDTA$_0$ pulse, some copper, after complexing with the EDTA, would have travelled to the end of the column, given the high dispersivity of 23 mm. The presence of some EDTA and copper in the first 61 mm of leachate confirms this. Hence, in contrast to the second experiment in Part I using repacked soil, where most of the copper was re-adsorbed in a narrow band at a depth of 35 mm, Fig. 7*d* shows that in the intact soil, the copper was re-adsorbed over the whole 150 mm column depth.

One of the aims of the study was to see if the model that we developed for the repacked soil could be applied to intact soil. To simulate the intact soil core data from Expt F, the parameters derived from experiments in Part I were used, as the soil used was the same. The only exception was the quite different soil structure, and so flow pathways; hence we expected a very different dispersivity (λ). The bromide breakthrough data in Fig. 6*a* yielded a fitted value of 23 mm, an order of magnitude greater than the value for the repacked soil. The simulated curve obtained using this value is shown in Fig. 6*a*. The same curve, which assumes negligible adsorption ($R = 1$), simulated the EDTA breakthrough. The observed EDTA data for Expt F show only a slight retardation relative to the bromide data, much less than in Fig. 4*a*, indicating little adsorption. This was expected, as the intact soil pH was much closer to that of the repacked soil used in Part I than that used in Expt D.

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

For the immediately leached column in Expt G, Fig. 7*a* 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 Expt E (Fig. 5*a*). It is interesting, however, that the second experiment in Part I showed no EDTA adsorption. We surmise this result was due to the higher soil pH.

For the immediately leached column, there was only 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 (Figs 7*c*, *e*). 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 Fig. 7*a*. Also, in the early leachate, the iron concentration was higher than the copper concentration, while the simulation predicted the opposite. We attribute this 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 Expt B, the month's delay in leaching, 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 being higher in Fig. 7*b* than in Fig. 7*a* might be an artefact. 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 (Fig. 7*d*). The drop in the leachate copper concentration, and the sudden increase in iron concentration following the month-long pause, was simulated reasonably well.

The simulated, final copper concentrations shown in Fig. 7*e* and *f* 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 value for K_1 was too low.

Conclusions

Prolonged leaching with 0.01 M EDTA reduced the copper concentration in a repacked column of Manawatu fine sandy loam from 60 to 40 µg/g. It also reduced the copper concentration in the top 25 mm of an intact core of contaminated Opotiki sandy loam from 240 to 80 µg/g. A substantial amount of iron was also leached in both cases.

When a pulse of EDTA was applied to copper-contaminated soil, and left there for up to 1 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. A month's delay reduced, to a negligible amount, the copper leached in both the repacked Manawatu soil and the intact Opotiki sandy loam cores. Associated with this reduction was an increase in the amount of iron leached. An experiment in which daily pulses $CuEDTA^{2-}$ were applied to a low-copper soil for 3 months showed that this reduction in copper mobilisation was due to $CuEDTA^{2-}$ slowly changing to $Fe(III)EDTA^{-}$, and the re-adsorption of the Cu^{2+} released.

The features of the experimental results were generally well simulated using the model developed in Part I, but the kinetic rate coefficients were different for the 2 soils, and for the Opotiki soil when the pH was lower. The repacked-soil model was able to simulate reasonably successfully the intact soil core experiments by simply changing the dispersivity from 3 mm to 23 mm. We see the main value of the model as providing a vehicle for discussing the experimental results in terms of the interacting physical and chemical processes involved. However, our simplified model is only appropriate for aerobic soils in which copper is the only heavy metal present in significant amounts. It would not be applicable to soils or sediments under anaerobic conditions and those that have multiple metals as contaminants. In such cases several other metal–EDTA reactions and their interactions would need to be taken into account.

The results presented here, and in Part I, show that off-site leaching with an EDTA solution could remove most of the copper from contaminated soil. The copper could then be extracted from the leachate and the EDTA recycled. Whether it is feasible technically and economically remains to be seen. The prospects for using *in situ* application of EDTA to enhance phytoremediation do not seem good. In a week or so, nearly all the copper initially brought into solution is likely to have been re-adsorbed, leaving only a brief window for enhanced uptake by plants. On the other hand, leaching with EDTA could perhaps be used in some situations to reduce an undesirably high copper concentration in the surface soil, distributing much of that copper throughout the soil profile at a much lower concentration. This would require that the residence time of soil water moving through the profile to the water table to be in excess of a month. Furthermore, the soil would need to contain a reasonable amount of EDTA-extractable iron. Otherwise groundwater contamination is likely.

Acknowledgments

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References

Allison LE (1947) Effect of micro-organisms on permeability of soil under prolonged submergence. *Soil Science* **63**, 439–450.

Barona A, Aranguiz I, Elias A (2001) Metal associations in soils before and after EDTA extractive decontamination: implications for the effectiveness of further clean-up procedures. *Environmental Pollution* **113**, 79–85.

Brooks SC, Taylor DL, Jardine PM (1996) Reactive transport of EDTA-complexed cobalt in the presence of ferrihydrite. *Geochimica et Cosmochimica Acta* **60**, 1899–1908.

Brusseau ML, Rao PSC, Jessup RE, Davidson JM (1989) Flow interruption: A method for investigating sorption nonequilibrium. *Journal of Contaminant Hydrology* **4**, 223–240.

Hewitt AE (1993) 'New Zealand soil classification.' Landcare Research Science Series No. 1. (Manaaki-Whenua Press: Lincoln, NZ)

Loveday J (1974) 'Methods for analysis of irrigated soils.' (CAB International: Wallingford, UK)

Magesan GN, Vogeler I, Scotter DR, Clothier BE (1995) Solute movement through two unsaturated soils. *Australian Journal of Soil Research* **33**, 585–596.

McGrath SP, Sanders JR, Shalaby MH (1988) The effects of organic matter levels on soil solution concentrations and extractabilities of manganese, zinc and copper. *Geoderma* **42**, 177–188.

Merry RH, Tiller KG, Alston AM (1983) Accumulation of copper, lead and arsenic in some Australian orchard soils. *Australian Journal of Soil Research* **21**, 549–561.

Murali V, Aylmore LAG (1980) No-flow equilibrium and adsorption dynamics during ionic transport in soils. *Nature* **283**, 467–469.

Parker DR, Norvell WA, Chaney RL (1995) GEOCHEM-PC: A chemical speciation program for IBM and compatible personal computers. In 'Chemical equilibrium and reaction models'. (Eds RH Loeppert, PA Schwab, S Goldberg) SSSA Special Publication No. 42. pp. 253–269. (Soil Science Society of America: Madison, WI)

Thayalakumaran T, Vogeler I, Scotter DR, Percival HJ, Robinson BH, Clothier BE (2003) Leaching of copper from contaminated soil following the application of EDTA. I. Repacked soil experiments and a model. *Australian Journal of Soil Research* **41**, 323–333.

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