Citation for published version:

López-Periago, J.E., Arias-Estévez, M., Nóvoa-Muñoz, J.C., Fernández-Calviño, D., Soto, B., Pèrez-Novo, C. and Simal-Gándara, J. (2008), Copper Retention Kinetics in Acid Soils. Soil Sci. Soc. Am. J., 72: 63-72. https://doi.org/10.2136/sssaj2006.0079

Peer reviewed version

Link to published version: https://doi.org/10.2136/sssaj2006.0079

1 # Copper retention kinetics in acid soils

2

3 José Eugenio López-Periago, Manuel Arias-Estévez, Juan Carlos Nóvoa-Muñoz,

4 David Fernández-Calviño, Benedicto Soto, Cristina Pérez-Novo, Jesús Simal-Gándara

5

6 Faculty Sciences, University of Vigo, As Lagoas Ourense, Ourense 32004, SPAIN.

7

14 **ABSTRACT**

15 Retention and release kinetics of copper on four acid Typic haplumbrepts

16 developed on two different types of parent rock material (granite and amphibolite)

17 was studied with a stirred-flow chamber (SFC) method. The granitic soils were lower

18 in organic material and lower in Fe and Al oxides than the soils formed in

19 amphibolite.

20 The kinetic parameters were assessed in four consecutive copper retention–release

21 cycles by alternately applying pulses of solutions with and without copper. Granite

22 soils showed lower total Cu retention (7 - 12 mmol kg^{-1}) than amphibolite soils (16 -

23 21 mmol kg^{-1}) after one single pulse application of 0.0787 mmol Cu L^{-1} at pH 5.5,

24 which may be due to differences in their organic and oxides compositions. The

25 amount of Cu retained diminished to 40-25 % in the third retention cycle relative to

26 the first, suggesting that the soils´ Cu retention depends on the previous metal loading.

27 Conversely, the released Cu was approximately 20 % of that retained in the first cycle,

28 but the amounts released were similar for all cycles and all soils. The results obtained

1 were fitted using a first-order equation for both retention and release of copper. In the

2 first cycle, first order rate coefficients of retention ranged from 0.084 to 0.56 min^{-1},

3 and increased by about a factor of two in the next cycle. Release rate coefficients were

4 more than ten times lower than those of retention, and less dependent on the previous

5 metal loading. The process of retention and release of copper was found to be

6 hysteretic, which suggest that the desorption mechanism or path is not an exact

7 opposite of the adsorption mechanism or path.

8

9

10 **Abbreviations:** SFC, stirred-flow chamber; BTC, breakthrough curve; CV, chamber

11 volume; LDF, linear driving force.

INTRODUCTION

The copper concentration in soil depends on the nature of its parent material and is especially high in soils developed on mafic and intermediate rocks (Kabata-Pendias and Pendias, 2001). In recent years, the Cu content of surface horizons in agricultural soils in the vicinity of some industries has risen significantly world wide. The increased levels of Cu have resulted largely from the use of organic and inorganic fertilizers, nearness to metal processing industries and repeated application of copper-based pesticides (Kabata-Pendias and Pendias, 2001).

The increased levels of Cu in soils have promoted studies on the way the metal partitions between soil compartments (Shuman, 1991; Arias et al., 2004). Most studies have revealed that the copper is strongly bound to the organic fraction or to amorphous inorganic oxides. The adsorption and desorption of Cu in soils depend primarily on soil pH and organic matter (McLaren et al., 1983; Msaky and Calvet, 1990; Harter, 1992; Silveira, 2002).

The retention and release of copper in soil can be time-dependent if its kinetics is slow enough relative to water motion. Therefore, studying the retention kinetics of this metal may help elucidate its dynamics in soil. Kinetic methods can also be useful to examine the interaction of Cu with soil. For example, Harter and Lehman (1983) successfully resolved diffusion and ion exchange of Cu via kinetic experiments in soil horizons of a Typic Paleudult and a Typic Fragiochrept. Also in the same soils, Lehman and Harter (1984) used the copper release kinetics to discriminate retention energies for this metal, and Harter (1991, 1992) examined its competition with other metals. Other studies on the adsorption kinetics of Cu on different soil types (Mattigod et al., 1981; Sposito, 1982) and Histosols (Aringheri et al., 1985) have revealed that the process involves a rapid initial step by which the metal is adsorbed at readily accessed sites and a second, slower step typical of adsorption on modified surfaces, coprecipitation reactions and diffusion into inner surfaces.

1   Much research on reaction kinetics in soils has relied on batch techniques, the

2   efficiency of which is limited by the slowness of phase separation processes, or on

3   miscible displacement in soil columns, which is diffusion-controlled. The stirred-flow

4   chamber (SFC) technique (Heyse et al., 1997) alleviates the shortcomings of batch

5   method by virtue of the adsorbate being continuously injected, which avoids the

6   problems posed by a decreased concentration in the liquid phase in batch processes.

7   Also, during the desorption phase the metal released into the liquid phase is removed

8   from the chamber, which accelerates further desorption, especially if the flow rate is

9   fast enough to preclude readsorption of the released metal. The advantage of SFC with

10   respect to the column experiments is that the film diffusion resistance that can be the

11   rate limiting step in the sorption kinetics can be more effectively reduced by the

12   stirring of the soil suspension. These features, favor the SFC technique which allows

13   one to examine the kinetics of the retention process over a short time scale.

14   Desorption of metals in soils can often be much slower than adsorption, and

15   sorption reactions are often pseudo-irreversible (Strawn and Sparks, 1999). Due to

16   slow desorption, successive Cu loads may take place before reaching equilibrium with

17   the soil, causing the sorption to become dependent on the metal loading history. This

18   may be a reason for the commonly observed hysteresis in adsorption isotherms

19   (Verburg and Baveye, 1994).

20   It was assumed that the history of copper application can also affect sorption

21   dynamics. Therefore, when copper is repeatedly applied to soil, its previous retention-

22   release history may influence future copper dynamics. Understanding the dynamics of

23   Cu in soil should consider its Cu loading history. The purpose of this work was to

24   examine the behavior of Cu retention and release on the minute scale with a view to

25   identifying and quantifying the effects of successive adsorption–desorption cycles on

26   the dynamics of Cu retention by acid soils.

27

MATERIAL AND METHODS

Soils

3   Four soil samples were collected from two different locations in Galicia (NW

4   Spain). Two of the soils (Amph1 and Amph2) developed from amphibolite and the

5   other two (Gra1 and Gra2) from granite; all four were Typic haplumbrepts (Soil

6   Survey Staff, 1997). The major minerals in the amphibolite soils were halloysite,

7   allophane and gibbsite (Macías and Calvo, 1992). The granite soils had lower Fe

8   contents and a coarser texture than the amphibolite soils. The clay fraction in the

9   surface horizons of the granite soils was dominated by mica strongly weathered to

10   vermiculite and contained abundant hydroxyl-Al interlayers (Macías and Calvo,

11   1992). The studied soil samples were collected from the A horizon, air-dried and

12   sieved through a 2 mm screen. The < 2 mm fraction was then used for characterization

13   analyses.

14   Soil particle density was measured by water picnometry (Blake and Hartge,

15   1986). Soil texture was determined by using the standard pipette method following

16   sieving (Gee and Bauder, 1986), and organic carbon on a Finnigan Flash EA-1113-NC

17   catalyzed dry combustion analyzer from Thermo Electron Corp. (Waltham, MA). Soil

18   pH was measured in H_2O and 0.1 M KCl, using a 1:2.5 soil/solution ratio.

19   Exchangeable Al was determined by displacement with 1M KCl by atomic absorption

20   spectrophotometry. Effective cation exchange capacity (CEC_e) was determined as the

21   sum of bases (Na, K, Ca and Mg) extracted with 0.2 M NH_4Cl and exchangeable Al

22   (Bertsch and Bloom, 1996). All samples were extracted for Fe and Al (Fe-OX, Fe-PP,

23   Al-OX, and Al-PP) with ammonium oxalate (Blakemore, 1978) and sodium

24   pyrophosphate (Bascomb, 1968). Dithionite–citrate extractable Fe and Al (Fe-DC and

25   Al-DC) (Holmgren, 1967) were also determined. The pyrophosphate reagent is an

26   effective extractant for humus complexes of Al and Fe, while the oxalate reagent

27   additionally extracts non-crystalline Fe and Al hydrous oxides, allophane, imogolite

28   and allophane-like constituents. Exchangeable cations were extracted with 1 M

29   ammonium acetate and determined by atomic absorption (Ca and Mg) or atomic

1 emission spectrophotometry (Na and K). Table 1 summarizes the properties of the

2 soils.

3

4 **Batch experiments**

5   In order to determine the maximum number of adsorption sites at equilibrium,

6 the four soils were also subjected to batch isotherm tests. To this end, 1 g of soil was

7 pre-equilibrated in a 0.01 M Ca(NO$_3$)$_2$ background solution at pH 5.5 for 24 h in each

8 run. pH of 5.5 was chosen because at lower (more acid) pH values, the soil buffering

9 capacity would facilitate the release of Al to the solution, thus critically affecting the

10 reactions of copper with soil. The pH 5.5 is a usual value for acid soils and ensures

11 mostly that complexation effects will be kept constant.

12 In order to account for the time required to reach equilibrium, Cu adsorption was

13 measured at five different incubation times (*viz.* 1, 4, 6, 24 and 48 h) for Amph1 and

14 Gra1 soils.

15   For the batch tests, each sample 1 g of soil was suspended in 5 mL of each of

16 the following Cu(NO$_3$)$_2$ solutions (*viz.* 0.16, 0.32, 0.79, 1.2, 1.6, 2.4, 3.2 mM). The pH

17 sample was adjusted to pH 5.5 following addition of the Cu solution and re-adjusted

18 after 24 h. The solid concentration in the samples after the addition of water was 100 g

19 L^{-1}. Samples were incubated on an end-over-end shaker at 18 rpm for 48 h and then

20 centrifuged at 800 g for 15 min. The supernatant thus obtained was filtered and diluted

21 with 1 M HNO$_3$ to determine total Cu by atomic absorption spectrometry with an error

22 of only 2%.

23   The Cu adsorption results were used to determine the parameters of the

24 Langmuir equation:

25

1   $$q = \frac{C \times qL_{\max} \times k_L}{1 + C \times k_L} \quad (1)$$

2   where q is the adsorbed concentration of Cu at equilibrium (mmol kg^{-1}), C the

3   solution concentration (mmol L^{-1}), k_L the Langmuir adsorption constant (L kg^{-1}) and

4   $qL_{\max}$ the maximum adsorbed concentration at equilibrium (mmol L^{-1}).

5

6

7

8   **Kinetic tests**

9   Reactor and operating conditions:

10 The SFC (Fig. 1) was made of polypropylene and had an inlet side port at the bottom

11 and a cover with an outlet port at the top. Two PTFE filters 10 mm in diameter and

12 0.45 μm in pore size were fitted immediately below the outlet port and over the inlet

13 port in order to retain soil samples in the chamber. The chamber volume was 1.2 cm^3.

14 Both the influent and effluent were carried through 0.5 mm i.d. PTFE tubing

15 connected to a Gilson Minipuls 3 peristaltic pump (Gilson S.A.S., Villiers Le Bel,

16 France). The temperature was kept at 25 ± 0.1 ºC by placing the reactor chamber in a

17 thermostated cell connected to a circulating water bath. The flow rate was monitored

18 throughout and found to oscillate by less than 3%. Stirring was provided by a PTFE-

19 coated magnetic bar that was spun at 400 rpm. Effluent fractions were collected into

20 1.5 mL polypropylene Eppendorf vials by using a Gilson FC 203 G automatic

21 fraction collector.

22   Two unbuffered solutions containing no copper and another two containing

23 different Cu concentrations were used. The former two were 0.0787 and 0.157 mM

24 Ca(NO$_3$)$_2$, respectively, and the latter 0.0787 and 0.157 mM Cu(NO$_3$)$_2$, respectively.

25 All were adjusted to pH 5.5 with HNO$_3$. Stirred-flow tests were conducted on the soil

26 fraction finer than 0.5 mm. To this end, an amount of *ca.* 0.2 g of soil was placed

27 together with a magnetic stirring bar in the reaction chamber, which was then filled up

28 with Ca(NO$_3$)$_2$ solution and carefully closed to avoid bubble formation. The Ca(NO$_3$)$_2$

1   solution was circulated at a flow rate (J_w) of 0.35 mL min^{-1}. The copper concentration

2   and pH of the effluent were measured on a periodic basis.

3   Once the pH leveled off at 5.4–5.6 and no native Cu was detected in the

4   effluent, the system was deemed ready for application of Cu pulses. In the retention

5   step, a solution of $Cu(NO_3)$ was circulated by using a Rheodyne 5001 switching valve

6   (Rheodyne Europe GmbH, Bensheim, Germany) to select the mobile phase; for the

7   release step, the valve was actuated in the opposite direction in order to circulate

8     $Ca(NO_3)_2$ solution again.

9   The copper concentrations in the different fractions obtained during each kinetic

10   run were used to construct breakthrough curves (BTCs) in order to examine the

11   variation of copper retention and release.

12   The adsorption of Cu by the chamber walls was checked in a experiment where

13   there was an absence of soil in the chamber using a 200 min pulse of 0.0787 mM Cu

14   at J_w = 0.56 mL min^{-1}.

15   To determine if the retention and release were limited by the rate of adsorption

16   instead of transport in the SFC, two tests proposed by Bar-Tal et al. (1990) were used.

17   The former test, involving altering the flow rate, was performed at 0.35, 0.56 and 0.7

18   mL min^{-1} using a copper concentration of 0.0787 mM and a soil-loaded chamber. The

19   latter, involving stopping the flow, was performed at the same Cu concentration at a

20   flow rate of 0.56 mL min^{-1}; following application of 23–27 mL (20–23 chamber

21   volumes, CV).

22

23   Retention-release tests:

24   The kinetics of retention and release were studied in consecutive copper retention–

25   release cycles that were established by alternately applying pulses of solutions

26   containing and excluding copper at a flow rate of 0.56 mL min^{-1}. The two steps were

27   repeated four times at each Cu concentration (0.0787 and 0.157 mM).

1   The amount of copper retained or released in the retention tests was calculated

2   from the concentrations in the effluent fractions from the reactor obtained in two tests

3   (with and without soil in the reactor), using the equation of Yin et al. (1997):

4

5    $$q(i) = \left\{ \sum_{j=1}^{i} \left[\frac{(C_1(j) - C_2(j))\Delta t \, J_w}{Ve} \right] + \left[C_1(i+1) - C_2(i+1) \right] \right\} \frac{Ve}{m} \qquad (2)$$

6   where $q(i)$ (mmol kg^{-1}) is the concentration of copper retained by the soil over the

7   discrete interval i —which denotes the position in the sequence of the effluent fraction

8   from the start of the run—; $C(i)$, the Cu concentration in the effluent fraction (mmol

9   mL^{-1}) at time step i; and $C(i+1)$, the concentration in the chamber, which was assumed

10   to coincide with that in the next effluent fraction ($i+1$) and is approximately 0.9-1 CV.

11   Subscripts 1 and 2 in the equation denote the concentrations in the effluent fractions

12   corresponding to the absence and presence of soil in the chamber, respectively; Δt is

13   the time difference between each effluent fraction; J_w is flow rate; V_e is the effective

14   solution volume in the chamber (L); and m the mass of soil placed in it (kg).

15   Parameter V_e was estimated by fitting the expression $c(t) = c_{in} \left[1 - \exp(-Jw \, t / V_e) \right]$

16   to match the BTC resulting from the application of a pulse of Cu with an influent

17   concentration (c_{in}) containing 0.0787 mmol Cu(NO$_3$)$_2$ at Jw = 56 mL min^{-1} SFC

18   without soil.

19

20   Modeling kinetic data:

21   The equation used for the rate of retention or release in a SFC, which was proposed by

22   Bar-Tal et al. (1990), was as follows:

23

24   $$\frac{dC}{dt} = \left[(C_{in} - C_{out}) \times \frac{Jw}{Ve} \right] - \left(\frac{m}{Ve} \times \frac{dq}{dt} \right) \qquad (3)$$

25   where C is the copper concentration in the chamber (mol L^{-1}), t time (min), C_{out} the

26   copper concentration leaving the chamber (mol L^{-1}) and q the amount of Cu adsorbed

1   in it (mol kg^{-1}). Since the solution was well mixed in the chamber, $C = C_{out}$. All other

2   variables in the equation were defined above. The term dq/dt describes the kinetics of

3   copper retention or release by the soil; therefore eq. (3) is in fact a system of ordinary

4   differential equations that allow the Cu concentrations retained and released by the

5   soil to be calculated with provision for Cu dilution in the chamber.

6   Breakthrough curves were constructed by numerically solving eq. (3) and the

7   kinetic law, using the Runge-Kutta explicit formula (Dormand and Prince, 1980) as

8   implemented in the ODE45 routine of MatLab v. 6.5.0R14 (Mathworks, Inc., Natick,

9   MA). The initial conditions for the SFC were set at dC/dt = dq/dt = C = q = 0. The

10   initial boundary condition was $C_{in} = Ci(t)$, where $Ci(t)$ is the function describing the

11   application of a Cu pulse to the influent. In the retention step t = (0–200) min, $Ci(t)$

12   equaled the concentration in the Cu solution; in the release step, $Ci(t)$ = 0 at t = (200–

13   400) min. The kinetic variables in the Equation [3] were optimized by using a

14   nonlinear fitting subroutine which provided the best fit in terms of r^2 and the root

15   mean square error statistic as corrected for the number of data pairs and variables:

16   RMSE = $[rss/(n – p)]^{0.5}$, where rss is the summation of residuals (*viz.* the differences

17   between the measured and estimated concentrations in each time interval) squared, n

18   the number of data pairs and p that of parameters.

19

20   **RESULTS AND DISCUSSION**

21   **Batch experiments**

22   Kinetics of Cu adsorption on two soils (Amph1 and Gra1) at the added

23   concentration of 0.787 mM is shown in Figure 2. After 24 h, 99% and 86% of the Cu

24   initially added to the suspension had been removed in Amph1 and Gra1 respectively.

25   Since no significant changes in Cu retention occurred between 24 to 48 h of

26   incubation, 24 h was long enough to ensure equilibrium in both soils.

27   Figure 3 illustrates the adsorption of copper by the studied soils after 24 h of

28   incubation. As it can be seen, the four soils exhibited a typical L-shaped sorption

29   isotherm (Sparks, 1989). When added at low concentrations, most Cu was retained by

1   the soils. This indicates a strong affinity for this metal. As the amount of adsorbed Cu

2   increased, the slope of the sorption isotherm tended to level off, which suggests that

3   the soil was approaching its maximum adsorption capacity. Table 2 shows the results

4   obtained by nonlinear least squares regression fitting the adsorption data to the

5   equation for the Langmuir isotherm [eq. (1)], minimizing r^2 between the observed and

6   predicted data (Schulthess and Dey, 1995). The calculated isotherms are shown as

7   lines in Fig. 3. Fits were acceptable for all soils; therefore, the Langmuir model

8   provides an accurate description of Cu adsorption after 24 h of incubation.

9   Based on K_L and qL_{max} values (Table 2), the amphibolite soils exhibited

10   higher Cu adsorption capacity than did the granite soils. This may be a result of higher

11   contents in organic carbon, clay, extractable Fe and Al, and also increased CEC_e, in

12   the amphibolite soils. These soil parameters play a key role in Cu adsorption by acid

13   soils (Arias et al., 2004). The two amphibolite soils differed little in their organic C

14   concentrations, so the greater K_L and qL_{max} values for Amph1 may be a result of it

15   containing a higher concentration of Fe oxides (Table 1). With the granite soils, Gra2

16   had an increased qL_{max} value relative to Gra1, presumably due to the higher

17   concentrations of organic C and Fe oxides in the former. Although K_L for Gra2 was

18   the half of Gra1, its difference in terms of Cu interaction energy with colloidal soil

19   particles was smaller with respect to the amphibolite soils.

20

21   **SFC: flow rate and stopped flow experiments**

22

23   Variable flow rate and stopped-flow tests were conducted in order to check

24   whether the reactor operating conditions were appropriate for studying the copper

25   retention kinetics. In addition, these tests can help to elucidate the mechanisms

26   controlling the retention process.

27   The X-shaped symbols in Fig. 4a represent the observed Cu concentration in

28   the outflow without soil (J_w 0.56 mL min^{-1}), while the line represents a theoretical

1   nonadsorbing tracer. Based on the mass balance obtained in the absence of soil, the

2   mass of copper retained by the chamber fell within the range of experimental error

3   (*ca.* 2%). During the retention step in Amph1 (J_w 0.56 mL min^{-1}) the pH in the

4   outflow fractions decreased from 5.5 to 4.4 when CV<20. This decrease of pH was

5   due to a reduction in Ca release rate (Figure 4b) from soil samples which were

6   previously treated with $Ca(NO_3)_2$. Then at CV higher than 20, pH values increase

7   slowly to 5.0 (Figure 4b); this increase of pH suggests that Cu retention mechanisms

8   are related to proton release.

9

10   Flow rate:

11   Tests with soil in the chamber showed that the increase in Cu concentration in the

12   outflow was delayed relative to the theoretical tracer. With soil Amph1 at $J_w = 0.56$

13   mL min^{-1}, no Cu was detected in solution until 20 chamber volumes (CV) were

14   circulated (Figure 4c). This suggests that retention was faster than the mass flux of Cu

15   entering the chamber. The amount of Cu initially retained during this period

16   accounted for 18 mmol kg^{-1} (65% of that retained throughout the test). At $J_w = 0.7$ mL

17   min^{-1}, however, it accounted for less than 2% of the total amount of Cu retained,

18   showing that increasing mass flux of Cu exceed the retention rate. These results were

19   similar for all soils —albeit less marked in the granite soils as shown in Fig. 4d—.

20

21   Comparing Cu concentration in experiments with soil against without soil

22   (Figure 4a, c and d), it was observed a slower increase in Cu concentration for all

23   studied flow rates was observed when the experiment was carried out with soil. For a

24   flow rate of 0.56 mL min^{-1}, the increase in Cu concentration at the effluent took place

25   approximately after 18 CV, whereas for 0.35 mL min^{-1} this increase was observed

26   after 50 CV (Fig. 4c). Following Strawn and Sparks (2000), this behavior can have

1   two different origins: one is the effect of a gradual decrease in the number of readily

2   available adsorption sites, and the other the simultaneous occurrence of secondary

3   slower retention mechanisms that might gain prominence once the faster process has

4   finished. It is possible that both mechanisms can occur simultaneously, however we

5   cannot confirm either of these two possibilities.

6   The retention rates for the granite soils (Fig. 4d) were lower than those for the

7   amphibolite soils. In the release step, Cu concentration decreased with increasing

8   flow-rate. Accordingly, Cu release must also be influenced by the rate of the process.
9

10   Stopped flow:

11   Figure 5 shows the effect of stopping the flow at $J_w = 0.56$ mL min^{-1} through soils

12   Amph1 and Gra1. With Amph1, halting the flow during the retention step decreased

13   the Cu concentration in the effluent from 0.039 to 0.031 mM (*i.e.* by 20.5%). With

14   Gra1, halting the flow after circulating 20 CV reduced the Cu concentration from

15   0.075 to 0.061 mM (18.7%). The decrease of dissolved Cu concentration in the

16   chamber was detected after the flow was resumed, indicating that the retention

17   continued when the flow was stopped. In the release step (data not shown), the flow

18   was stopped for 15 min following passage of 23 mL (20 CV). Restarting the flow

19   caused the Cu concentration in soil Amph1 to rise from 0.0205 to 0.0239 mM

20   (16.6%), and in Gra1 from 0.0120 to 0.0195 mM (62.5%). The effects of stopping the

21   flow or altering the flow rate were similar for all soils and allow one to conclude that,

22   at $J_w = 0.56$ mL min^{-1}, retention and release of copper in both soils are time-

23   dependent processes.

24   The BTCs in Fig. 6 compare the results for the retention step following

25   application of a pulse of 0.0787 mM Cu at $J_w = 0.56$ mL min^{-1} to all soils. Based on

26   the calculated mass balance after the retention step (80 CV), the amounts of Cu

27   retained by soils Amph1, Amph2, Gra1 and Gra2 were 20.6, 12.2, 6.3 and 8.3 mmol

1   kg^{-1}, respectively. These concentrations can tentatively be ascribed to the ability of

2   soil organic matter to form strong complexes with Cu, in which respect the granite

3   soils depart from the amphibolite soils. Additionally, the greater concentration of

4   extractable Fe oxides in Amph1 may have also caused the granite soil to retain more

5   Cu than the Amph2 soil. There was good consistency with their respective K_L and

6   qL$_{max}$ values as calculated from the adsorption isotherms. As regards the granite soils,

7   Gra1 retained less Cu than did Gra2.

8

9   Retention cycles:

10   Figure 7 shows the first BTCs for each retention step as obtained in an experiment

11   involving four consecutive retention–release cycles on soil Amph2. Each cycle

12   includes a pulse application of Cu and metal releases with background electrolyte. The

13   results for cycle 4 are not shown because they overlapped with those for cycle 3. As it

14   can be seen, the curve shift decreased and the Cu concentration in the outflow

15   increased with increasing number of cycles. An identical behavior was observed in all

16   soils. This indicates that the retention rate depends on the previous history of

17   retention–release cycles. In other words, the soil retention capacity and the retention

18   rate are adversely influenced by the previous incomplete release of Cu. The

19   incomplete release of Cu affects the adsorption of new Cu ions. The proportions of Cu

20   retained by soil Amph2 in each cycle with respect to the amount of Cu circulated

21   through the chamber were 62, 56, 52 and 50%, respectively. The difference between

22   cycles 3 and 4 was within the range of experimental error. Figure 8 shows the amount

23   of Cu retained as function of CV for all soils as calculated from eq. (2), and Table 3

24   summarizes the amounts retained by the soils in each retention cycle.

1   No curve shifts were observed during the release steps in any soil (see release

2   BTCs for Amph2 in Fig. 9), which indicates that the release rate decreased from the

3   start of the experiment. The amount of Cu released in each step was smaller than that

4   retained in the corresponding retention step. Therefore, a fraction of Cu was retained

5   by the soil. The amount of Cu released increased after each cycle (*viz.* from 2.65 to

6   3.04 to 3.43 to 3.57 mmol kg^{-1}, after each pulse of [Cu] = 0.0787 mM). Similar results

7   were found using [Cu] = 0.159 mM (*viz.* 3.68 to 3.84 to 4.43 to 5.02 mmol kg^{-1}).

8   Increasing the release with cycling suggests that the sorption was not at equilibrium in

9   low reversible sites. These sites should be progressively occupied as the number of Cu

10   pulses passed by the chamber.

11   Based on the high slope of the sorption isotherm at low equilibrium

12   concentrations, there should be long tails in the release process, especially if Cu

13   release from the soil is slow. Since the desorption behavior departs markedly from the

14   sorption behavior, and the desorption BTCs are nearly identical, one can conclude that

15   the kinetics of the slow desorption process is too slow to be measured with the stirred-

16   flow reactor at flow rates around 0.56 mL min^{-1}.

17

18   **SFC: Kinetic models**

19   The retention and release of Cu in soils are two complex processes because soil

20   is heterogeneous in nature. The rates of these processes in acid soils involve species

21   that may be influenced by both transport and chemical reactions. In the SFC

22   experiments, the transport in the bulk solution and the transport across the liquid film

23   at the solid-liquid interface is favored by stirring. However, surface diffusion as

24   defined in Aharoni and Sparks (1991) and the transport into intraparticle voids can

25   still be the rate determining steps.

26   Retention–release rates, dq/dt, have been described in terms of various models

27   for first-, *pseudo*-first and fractional-order reactions (Amacher et al., 1988; Selim et

28   al., 1990; Amacher, 1991), *pseudo*-second order reactions (Bhattacharyya and Gupta,

1   2005), and second-order kinetic exchange reactions with competition from protons

2   (Shi et al., 2005).

3   The simplest kinetic retention model most accurately describing Cu retention

4   and release in all studied soils was found to be the following first-order function:

5

$$6 \quad \frac{dq}{dt} = k_1 \times \left(q_{max} - q\right) - k_{-1} \times q_f \tag{4}$$

7   where k_1 and k_{-1} are the retention and release rate constant, respectively; q_{max}, the

8   retained concentration at infinite time; and q_f, the retained concentration that can be

9   fast released. This equation is first-order in available sites $(q_{max} - q)$ for retention and

10   first-order in available fast desorbing Cu for release. Expressions similar to the first

11   term on the right side of eq. (4) have been used to describe chemical kinetics (Strawn

12   and Sparks, 2000). This expression is the same as the linear driving force LDF model

13   of sorption kinetics that, because of its simplicity, it is frequently used in the

14   mathematical simulations of diffusion into a spherical adsorbing particle (Sircar and

15   Hufton, 2000), as well as the mass transfer between the solid and solution phase

16   (Parker   and   Jardine,   1986).   Mathematically   the   LDF   approximation   is

17   indistinguishable from first order adsorption kinetics.

18   The parameters of the release term in eq (4) (second on the right-hand side)

19   were modeled by using the release data. For most of the experiments, the flux

20   controlling solution residence time into the chamber volume (J_w/V_e) was more than

21   two times higher than the retention coefficient of copper in the soil suspension (k_1).

22   This means that the stirred flow system was measuring the sorption rates.

23   Assuming that the retention rate was negligible during the release step, the first

24   term on the right-hand side of eq. (4) was zero. The boundary condition for eq. (3)

25   was $C_{in} = 0$. At $t > 0$, eq. (4) simplified to

26

1
$$\frac{dq}{dt} = -k_{-1} \times q_f \tag{5}$$

2   With the initial conditions, $dq/dt = 0$ and $q_f = q_0$ (where q_0 is the initial Cu

3   concentration in the soil as calculated from the total mass released in the

4   corresponding release step). Note that q_f is the fraction of Cu that is rapidly desorbed.

5   Therefore, eq. (5) only describes those release processes that are fast enough to be

6   measured within the time frame of the experiments.

7   The curves in Figs 4–7 are the BTCs calculated from the system of equations (3)

8   and (4). As it can be seen, the model fits the experimental curves, the differences in

9   shape possibly being the result of experimental errors, particularly of partial clogging

10   of the filters or imperfect mixing in the chamber.

11   Initially, the calculated retention rate exceeded that of Cu in the influent and

12   caused a shift in the BTCs. The retention rate of Cu decreased and its concentration in

13   the effluent increased as q was raised (*i.e.* as the amount of available adsorption sites,

14     $q_{max} - q$, becomes smaller).

15   The parameter values used ($k_1 = 0.08 \pm 0.04$ and $q_{max} = 28 \pm 7$ for Amph1, and

16     $k_1 = 0.247 \pm 0.05$ and $q_{max} = 6.5 \pm 0.4$ for Gra1) allowed the BTCs to be simulated at

17   variable flow rates (see lines in Figs. 4c and 4d). Table 4 shows the parameter values

18   for the first-order kinetic model (eq. 4) in all retention experiments. The range of rate

19   constants was much wider than the millisecond time scale typical of ion exchange

20   kinetics in oxide surfaces (Sparks, 2001), and falls into the range of sorption on humic

21   acids (Bunzl et al., 1976) which suggests that both complexation reactions and

22   transport can be the rate limiting steps.

23   The optimized values for q_{max} in the first retention cycle equaled the simulated

24   equilibrium concentration in the isotherms for all soils. In consecutive cycles, better

25   fits were found by gradually reducing q_{max} at the start of each cycle (q_{max} values in

26   Table 4). These reductions of q_{max} decreased the theoretical maximum adsorption rate

27   at the start of each cycle [*viz.* $(dq/dt)_{max} = k_1 \times q_{max}$] due to a progressive decrease of

28   vacant adsorption sites.

The k_1 estimates were subject to large standard errors. This suggests that mass transfer is diffusion controlled because it is more strongly dependent on fluctuations in the SFC system. The k_1 estimates increased with increasing number of cycles. Since eq. (4) represents an "average" retention process, this suggests that faster processes prevail after a number of cycles. Thus, the sites with the lowest adsorption rates could also be those with the lowest desorption rates. On the other hand, the sites exhibiting faster retention of copper also showed faster desorption rates. The fitted k_{-1} values (see Fig. 10 and Table 5) were similar in all cases, which suggest that Cu was released via the same mechanism in the four soils studied. In addition, the small differences in released mass (q_0) between cycles suggest that the fast release was not dependent on the previous metal additions. We believe that the amount of Cu released may result from exchange with Ca^{2+}. The ratio of q_0 to CEC_e (expressed as a percentage of $cmol_c$ kg^{-1}) was 45, 45, 20 and 22 % for Gra1, Gra2, Amph1 and Amph2, respectively. These values show that only a fraction of the effective cation exchange capacity is related to the fast desorbed Cu, and that it is twice greater for the granite soils than for the amphibolite soils. We believe that the amphibolite soils can take more Cu from exchange sites to form slowly reversible bonds than can the granite soils. The amphibolite soils contain more reactive surfaces forming complexes with Cu, presumably inner sphere complexes (McBride, 1989), than do the granite soils. On the other hand, the granite soils contain more permanently charged clay minerals where Cu is preferably bound to silanol groups of the lattice face resulting in weak bonds (McBride, 1989). Instead, in amphibolite soils with dominant variable charge, Cu mainly interact with aluminol groups forming stronger bonds.

The fraction $f_{hys} = [(q_{max_1} - q_{max_4})/q_{max_1}]$, where 1 and 4 denote cycle number (see Table 4), provides an approximation to the ratio of Cu retained by highly hysteretic retention relative to the total sorption capacity as estimated from the first-order kinetics. f_{hys} values ranged from 0.60 to 0.73, which suggests that the fraction of tightly adsorbed forms of Cu was similar in all soils.

1   These results show that the history of Cu loading can affect the

2 experimental determination of kinetic parameters when desorption is not complete.

3 The hysteretic behavior can be explained by incomplete desorption. Therefore, it

4 affects the determination of kinetic coefficients in soil sorption experiments. In view

5 of these findings, slow desorption release rates should be considered in further SFC

6 experiments.

7   The heterogeneity of the binding sites in soils can result in both q_{max} and the

8 sorption rate coefficient being affected by competing cations, pH and Cu

9 concentration in feed solution loading. Using buffered soil suspensions facilitates the

10 study of the chemistry of adsorption with proton exchange. However, we chose to

11 perform tests under conditions closer to those prevailing in the field and allow the soil

12 buffering mechanism to act freely.

13   Our tests were performed only at pH of 5.5, which is the most usual value for

14 acid soils. At lower (more acid) pH values, the soil buffering capacity would facilitate

15 the release of Al to the solution, thus critically affecting the behavior of copper. Under

16 these experimental conditions, one cannot ascertain whether the effect on copper is

17 due to the solution pH or to dissolution of cations in order to keep the soil pH

18 constant. On the other hand, at higher (more alkaline) pH levels, part of the soil

19 organic matter is dissolved, which also alters the behavior of copper. Again, this

20 precludes distinguishing between the effects of pH and dissolved organic matter

21 (DOM) on copper (Shi *et al.* 2005), but the pH fixed to 5.5 ensures mostly that

22 complexation effects will be kept constant.

23   The amphibolite soils possess a higher total retention capacity and exhibit more

24 hysteretic retention. In this respect, the disparate behavior of the granite and

25 amphibolite soils can be ascribed to the increased organic carbon contents in the latter.

26 On the other hand, the greater contents in extractable Fe oxides of Amph1 may have

27 also caused it to retain more Cu than Amph2 did. Despite the differences in their

28 respective properties, the effect of slow desorption acts in the same way in all the soils

29 studied.

1

CONCLUSIONS

3   Kinetic retention and release tests conducted in a stirred-flow chamber (SFC)

4 revealed that Cu retention–release dynamics in the studied acid soils is hysteretic.

5 Based on the experimental time-frame used for each cycle in the retention–release

6 cycling tests (170 min), a fraction of the sorption sites exhibit less hysteretic dynamics

7 in the overall sorption process. The retention step is reproduced by a first-order

8 kinetics in available adsorption sites. The factor most strongly influencing the

9 retention kinetics is the previous metal addition. Based on the SFC release tests, the

10 fast release process is less hysteretic than the overall sorption process.

11   The capacity of the soils for copper retention depends on previous metal

12 addition cycles whereas its fast release do not. This is consistent with hysteretic

13 behavior of a fraction of the adsorbing copper. The history of Cu loading can affect

14 the experimental determination of the kinetic parameters when desorption is not

15 complete. Hysteretic behavior can be explained by incomplete desorption. Therefore,

16 the slow desorption release mechanisms should be modeled on further SFC studies.

17

REFERENCES

Aharoni, C. and Sparks, D.L. 1991. Kinetics of soil chemical reactions-A theoretical treatment. pp.1-18 *in* D.L. Sparks and D.L. Suárez (ed.) Rates of soil chemical processes. Vol. 27. ASA and SSSA, Madison, WI.

Amacher, M.C. 1991. Methods of obtaining and analyzing kinetic data. pp 19–59 *in* D.L. Sparks and D.L. Suárez (ed.) Rates of soil chemical processes. Vol. 27. ASA and SSSA, Madison, WI.

Amacher M.C., H.M. Selim, and I.K. Iskandar. 1988. Kinetics of chromium(VI) and cadmium retention in soils; a nonlinear multireaction model. Soil Sci. Soc. Am. J. 52:398–407.

Arias, M., E. López-Periago, D. Fernández, and B. Soto. 2004. Copper distribution and dynamics in acid vineyard soils. Soil Sci. 169:796–805.

Aringhieri, R., P. Carrai, and G. Petruzzelli. 1985. Kinetics of Cu^{2+} and Cd^{2+} adsorption by an Italian soil. Soil Sci. 139:197–204.

Bar-Tal, A., D.L. Sparks, J.D. Peseck, and S. Feigenbaum. 1990. Analyses of adsorption kinetics using a stirred-flow chamber: II theory and critical tests. Soil Sci. Soc. Am. J. 54:1273–1278.

Bascomb, C.L. 1968. Distribution of pyrophosphate extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19:251–256.

Bertsch, P.M., and P.R. Bloom. 1996. Aluminum. pp 517-550 *in* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Series:5. SSSA and ASA, Madison, WI.

1

2 Bhattacharyya, K.G., and S.S. Gupta. 2005. Kaolinite, montmorillonite, and their

3 modified derivatives as adsorbents for removal of Cu(II) from aqueous solution. Sep.

4 Purif. Technol. 50:388–397.

5 Blake, G.R., and K.H. Hartge. 1986. Particle density. pp 377–382 *in* A. Klute (ed)

6 Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. 2nd edn. ASA

7 and SSSA, Madison, WI.

8 Blakemore, L.D. 1978. Exchange complex dominated by amorphous material. pp 21–

9 22 *in* G.D. Smith (ed.) The Andisol Proposal. New Zealand Soil Bureau. New

10 Zealand.

11 Bunzl, K., W. Schmidt, and B. Sansoni. 1976. Kinetics of ion exchange in soil organic

12 matter. IV. Adsorption and desorption of Pb^{+2}, Cu^{+2}, Cd^{+2}, Zn^{+2} and Ca^{+2} by peat. Soil

13 Sci. 27: 32-41.

14 Dormand, J.R., and P.J. Prince. 1980. A family of embedded Runge–Kutta formulae.

15 J. Comput. Appl. Math. 6:19–26.

16 Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. pp 383-411 *in* A. Klute

17 (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd edition.

18 SSSA Book Series:5. ASA and SSSA, Madison, WI.

19 Harter, R.D. 1991. Kinetics of sorption/desorption processes in soil. pp 135–149 *in*

20 D.L. Sparks and D.L. Suárez (ed.) Rates of soil chemical processes. Vol. 27. ASA and

21 SSSA, Madison, WI.

1   Harter, R.D. 1992. Competitive sorption of cobalt, copper, and nickel ions by a

2   calcium saturated soil. Soil Sci. Soc. Am. J. 56:444–449.

3   Harter, R.D., and R.G. Lehmann. 1983. Use of kinetics for the study of exchange-

4   reactions in soils. Soil Sci. Soc. Am. J. 47:666–669.

5   Heyse, E., D. Dai, P.S.C. Rao, and J.J. Delfino. 1997. Development of a continuously

6   stirred flow cell for investigating sorption mass transfer. J. Contam. Hydrol. 25:337–

7   355.

8   Holmgren, G.G. 1967. A rapid citrate–dithionite extractable iron procedure. Soil Sci.

9   Soc. Am. Proc. 31:210–211.

10   Kabata-Pendias A., and H. Pendias. 2001. Trace Elements in Soils and Plants. 3rd edn.

11   CRC Press, Boca Raton, FL.

12   Verburg K., and P. Baveye. 1994. Hysteresis in the binary exchange of cations on 2:1

13   clay minerals: a critical review. Clays and Clay Minerals 42:207-220.

14   Lehmann, R.G., and R.D. Harter. 1984. Assessment of copper–soil bond strength by

15   desorption kinetics. Soil Sci. Soc. Am. J. 48:769–772.

16   Macías, F., and R. Calvo. 1992. Pedogeochemical characterisation of the soils of

17   Galicia (NW Spain) with respect to lithological variations. Evidence of a transitional

18   environment between temperate and subtropical humid domains. *C. R. Acad. Sci.*

19   *Paris* 315:1803–1810.

20   Mattigod S.V., A.L. Gibaldi, and A.L. Page. 1981. Factors affecting the solubilities of

21   trace metals in soils. pp 203–221 *in* R.H. Dowdy, J.A. Ryan, V.V. Volk, D.E. Baker

(eds) Chemistry in the Soil Environment. Publication no. 40 ASA and SSSA, Madison, WI.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. Adv. Soil Sci. 10: 1-56.

McLaren, R.G., J.G. Williams, and R.S. Swift. 1983. Some observations on the desorption and distribution behavior of copper with soil components. J. Soil Sci. 34:325–331.

Msaky, J.J., and R. Calvet. 1990. Adsorption behavior of copper and zinc in soils – influence of pH on adsorption characteristics. Soil Sci. 159:513–522.

Parker, J.C., and P.M. Jardine. 1986. Effect of heterogeneous adsorption behavior on ion transport. Water Resour. Res. 22:1334—1340.

Schulthess, C.P., and D. K. Dey. 1996. Estimation of Langmuir constants using linear and nonlinear least squares regression analysis. J. Soil Sci. Soc. Am. J. 60:433-442.

Selim, H.M., M.C. Amacher, and I.K. Iskandar. 1990. Modeling the transport of heavy metals in soils. CRREL-Monogr. 90-2. U.S. Army Corps of Engineers, Hanover, NH.

Shi, Z., D.M. Di Toro, H.E. Allen, and A.A. Ponizovsky. 2005. Modeling kinetics of Cu and Zn release from soils. Environ. Sci. Technol. 39:4562–4568.

Shuman, L.M. 1991. Chemical forms of micronutrients in soils. pp 113–144 *in* J.J. Mortvedt, F.R. Cox, L.M. Shuman, R.M. Welch (ed.) Micronutrients in Agriculture, 2nd edn. Book Series no. 4. ASA and SSSA, Madison, WI.

1 Sircar, S., and J. R. Hufton. 2000. Intraparticle adsorbate concentration profile for

2 linear driving force model. AIChE Journal 46:659-660.

3 Silveira, M.L.A. 2002. Copper adsorption in oxidic soils after removal of organic

4 matter and iron oxides. Commun. Soil Sci. Plant Anal. 33:3581–3592.

5 Soil Survey Staff. 1997. Keys to soil taxonomy. Pocahontas Press, Blacksburg, VA.

6 Sparks, D.L. 1989. Kinetics of Soil Chemical Processes. Academic Press, New York.

7 Sparks, D.L. 2001. Elucidating the fundamental chemistry of soils: Past and recent

8 achievements and future frontiers. Geoderma 100:303-319.

9 Sposito, G. 1982. On the use of the Langmuir equation in the interpretation of

10 adsorption phenomena. II. The 2-surface Langmuir equation. Soil Sci. Soc. Am. J.

11 46:1147–1152.

12 Strawn D.G., and D.L. Sparks. 1999. Sorption kinetics of trace elements in soils and

13 soil materials. pp. 1–28 *in* H.M. Selim and K.I. Iskandar (ed.) Fate and Transport of

14 Heavy Metals in the Vadose Zone. Lewis Publishers, Boca Raton, FL, USA.

15 Strawn, D.G., and D.L Sparks. 2000. Effects of soil organic matter on the kinetics and

16 mechanisms of Pb(II) sorption and desorption in soil. Soil Sci. Soc. Am. J. 64:144–

17 156.

18 Yin, Y., H.E. Allen, C.P. Huang, D.L. Sparks, and P.F. Sanders. 1997. Kinetics of

19 mercury(II) adsorption and desorption on Soil. Environ. Sci. Technol. 31:496–503.

20

2

3 Figure 1. Schematic depiction of the stirred-flow chamber.

4

5 Figure 2. Kinetics of Cu adsorption on soils at an added concentration of 0.787mM.

6 Soils: (A) Amph1, (B) Gra1.

7

8 Figure 3. Equilibrium adsorption isotherms. Symbols represent experimental data and

9 the line the Langmuir model. Soils: (A) Amph1, (B) Amph2, (C) Gra1, (D) Gra2.

10

11 Figure 4. Results of the retention tests in the SFC. Observed BTCs (symbols)

12 obtained: *(a)* with no soil; *(b)* displacement of Ca^{+2} and pH variation during Cu^{+2}

13 retention in Amph1; and (c) and (d), respectively, Amph1 and Gra1 at a variable flow

14 rate under the same conditions. Lines represent the BTCs calculated by using the first-

15 order model.
16

17 Figure 5. BTCs obtained in the stopped-flow tests. $J_w = 0.56$ mL min^{-1}. The symbols

18 represent observed data and lines the concentrations calculated from eq. (4).

19

20 Figure 6. BTCs for the four studied soils after one retention cycle. $J_w = 0.56$ mL min^{-}

21 ^{1}. $C_{in} = 0.0787$ mM. Symbols represent experimental data and lines the first-order

22 model.
23

24 Figure 7. Experimental BTCs (symbols) obtained following application of three

25 successive pulses to soil Amph2 in the retention step. $J_w = 0.56$ mL min^{-1}. $C_{in} =$

26 0.0787 mM. Lines represent the first-order model. The BTC for the fourth pulse has

27 been omitted for clarity as it overlapped with that for the third.
28

1 Figure 8. Copper concentration retained over three (A, C and D) and four (B)

2 consecutive retention–release cycles in soils Amph1 (A), Amph2 (B), Gra1 (C) and

3 Gra2 (D). Symbols represent data calculated from eq. (2) and lines the first-order

4 kinetic model. J_w = 0.56 mL min^{-1}. C_{in} = 0.0787 mM.

5

6 Figure 9. BTCs for Cu release from soil Amph2 in four successive cycles (1–4). J_w =

7 0.56 mL min^{-1}. C_{in} = 0.

8

9 Figure 10. Copper concentration retained over three (A, C and D) and four (B)

10 consecutive release cycles in soils Amph1 (A), Amph2 (B), Gra1 (C) and Gra2 (D).

11 Symbols represent data calculated from eq. (2) and lines the first-order kinetic model.
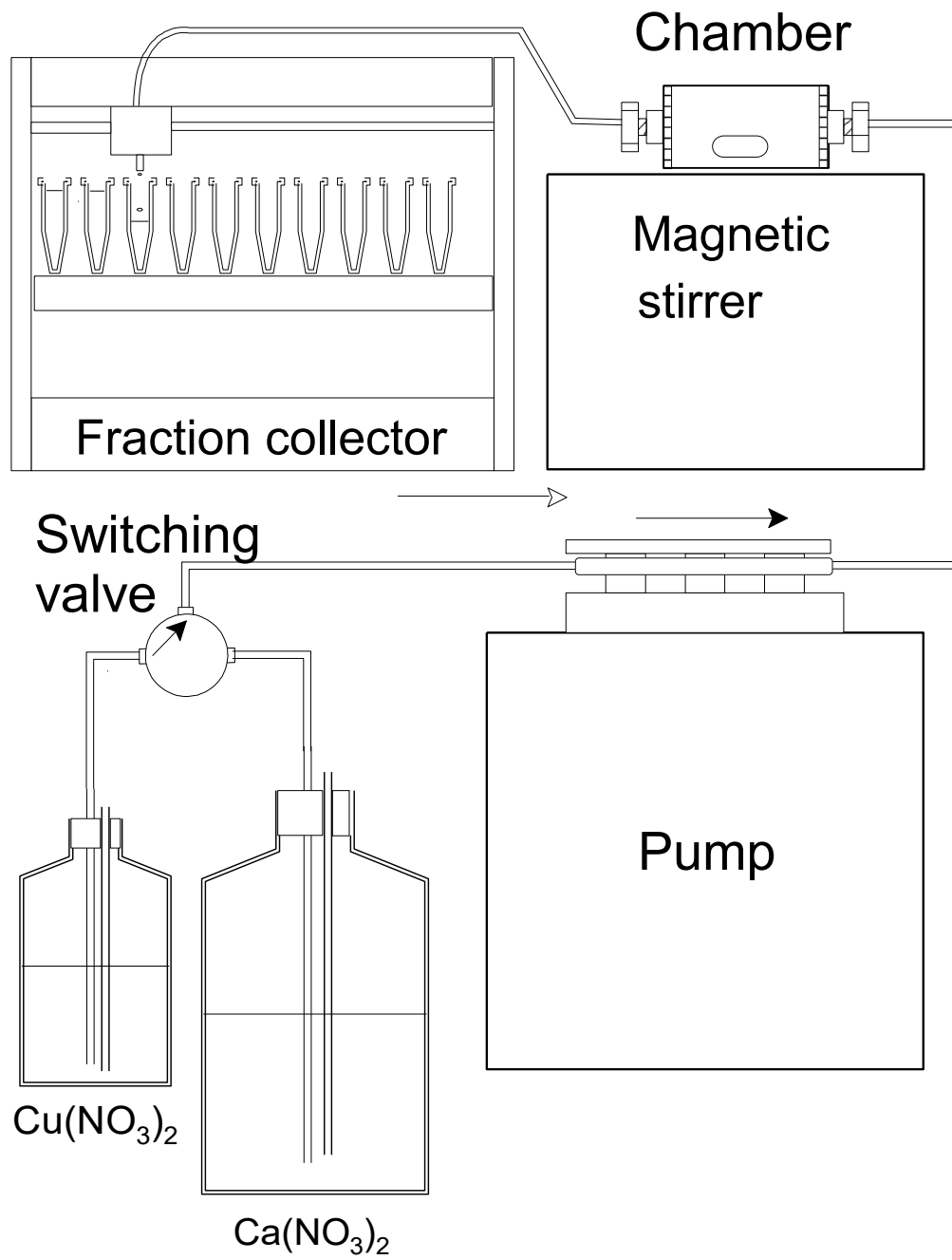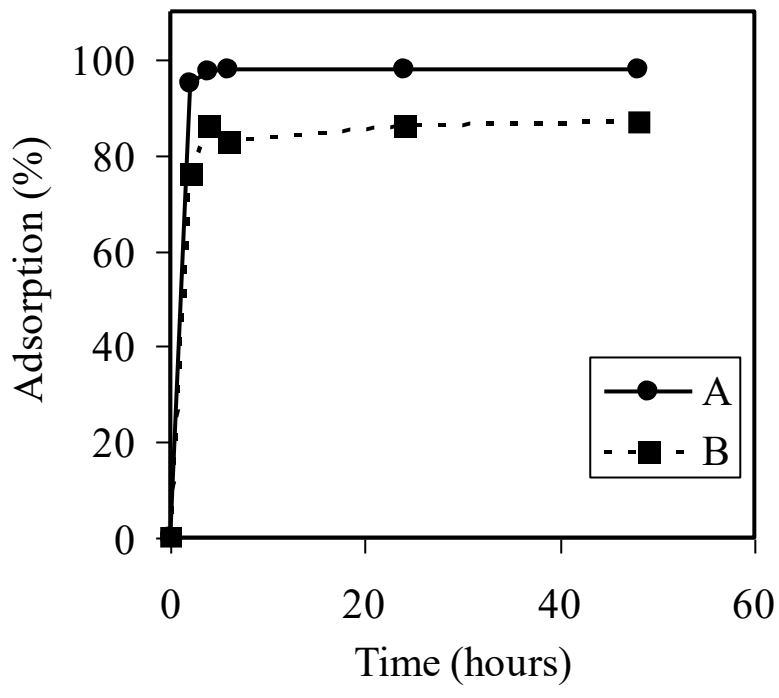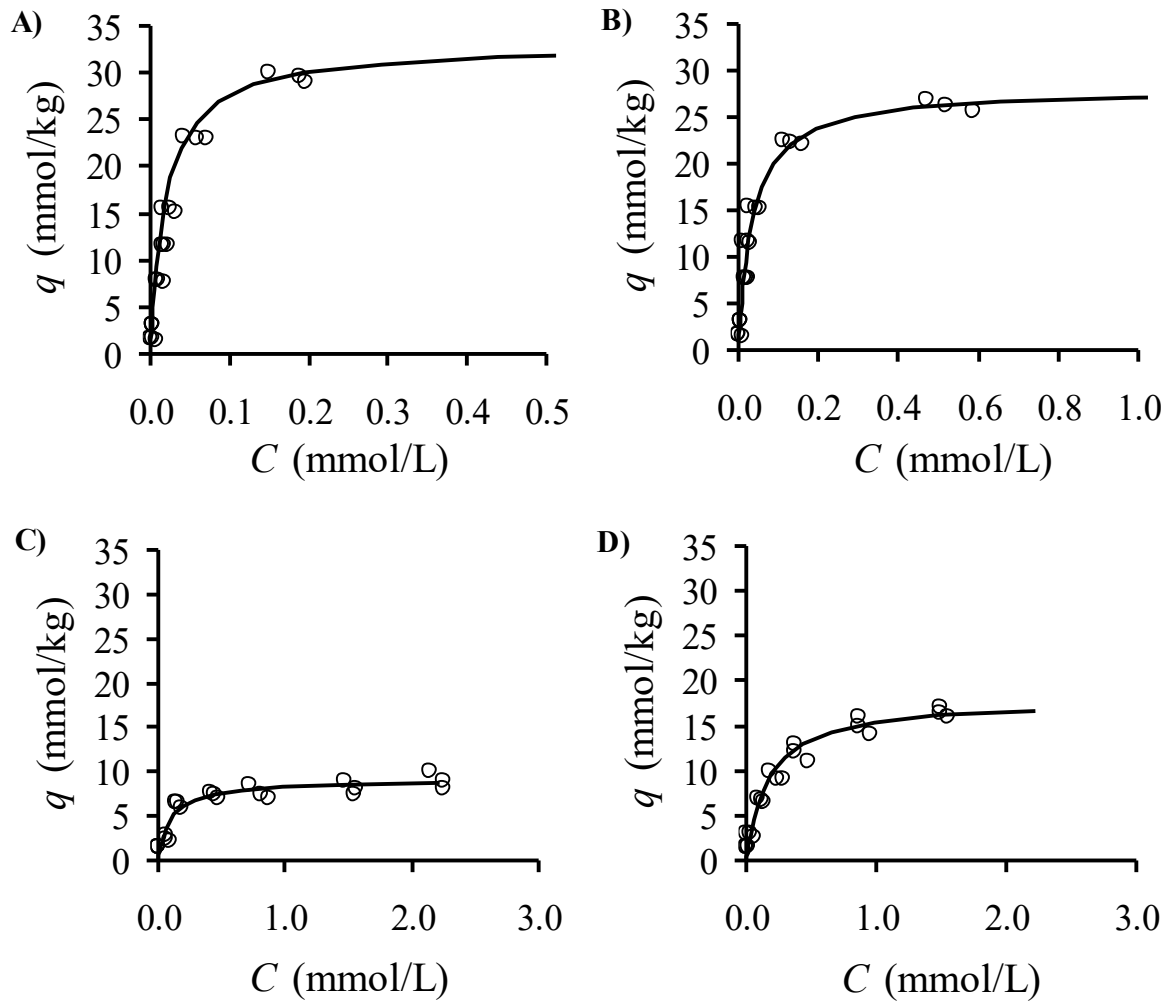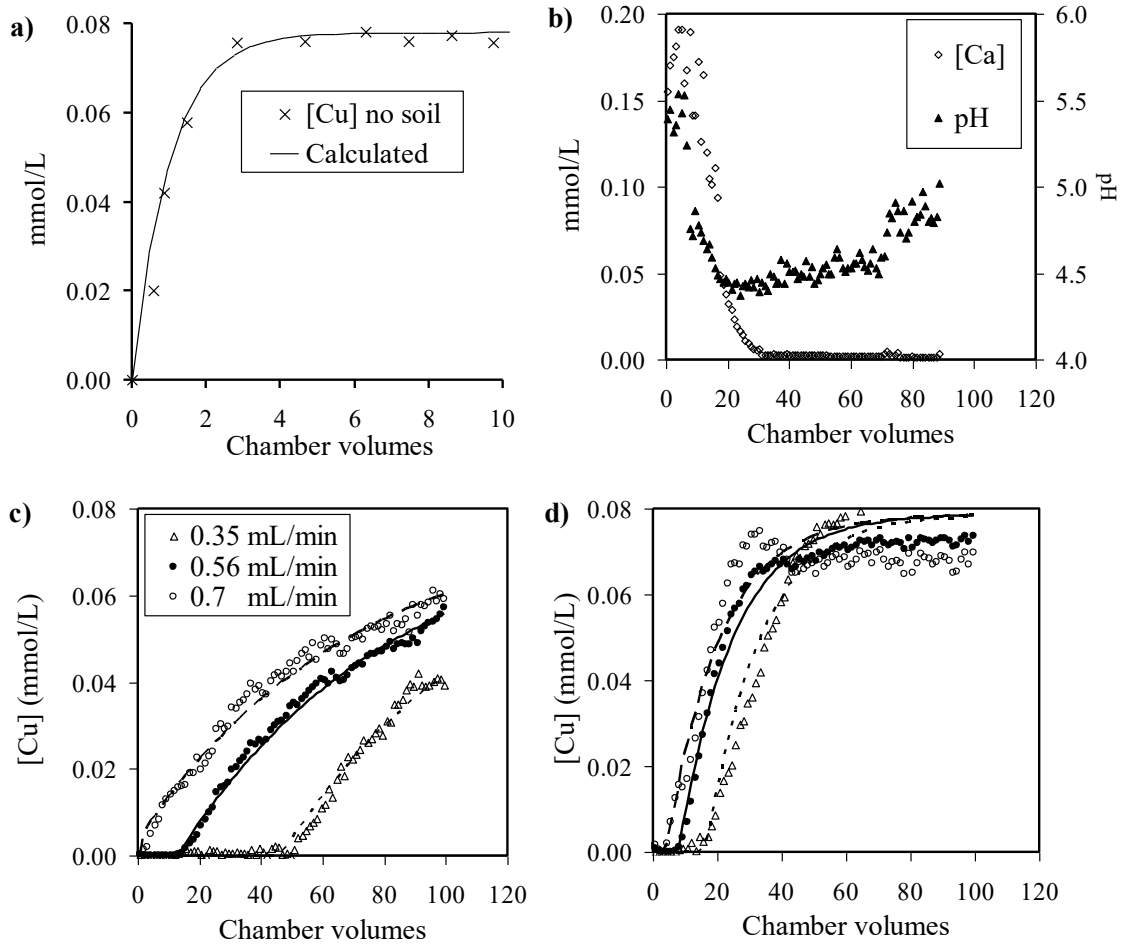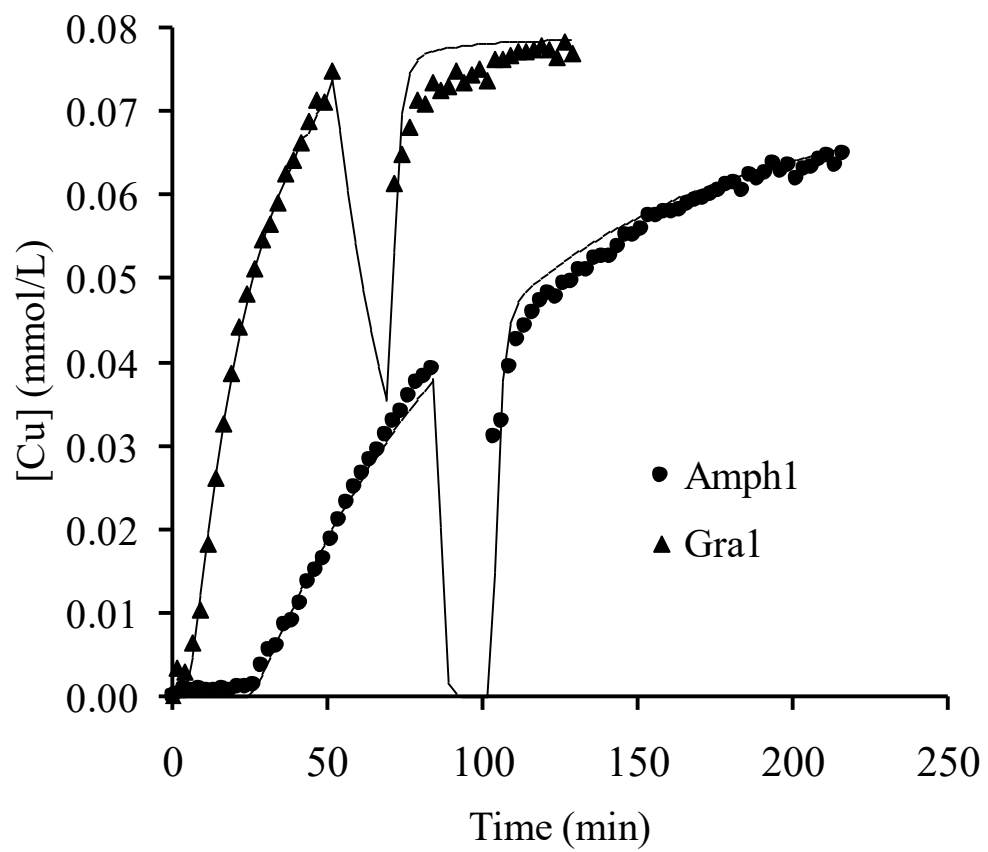
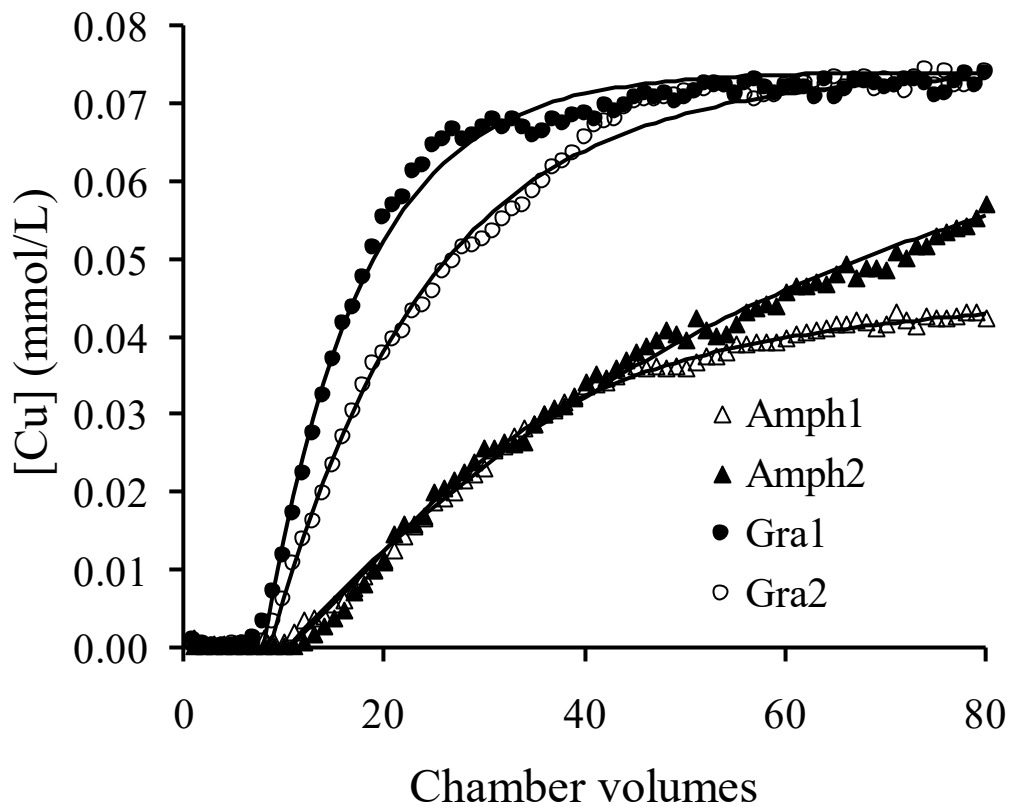12 J_w = 0.56 mL min^{-1}. C_{in} = 0.0787 mM.
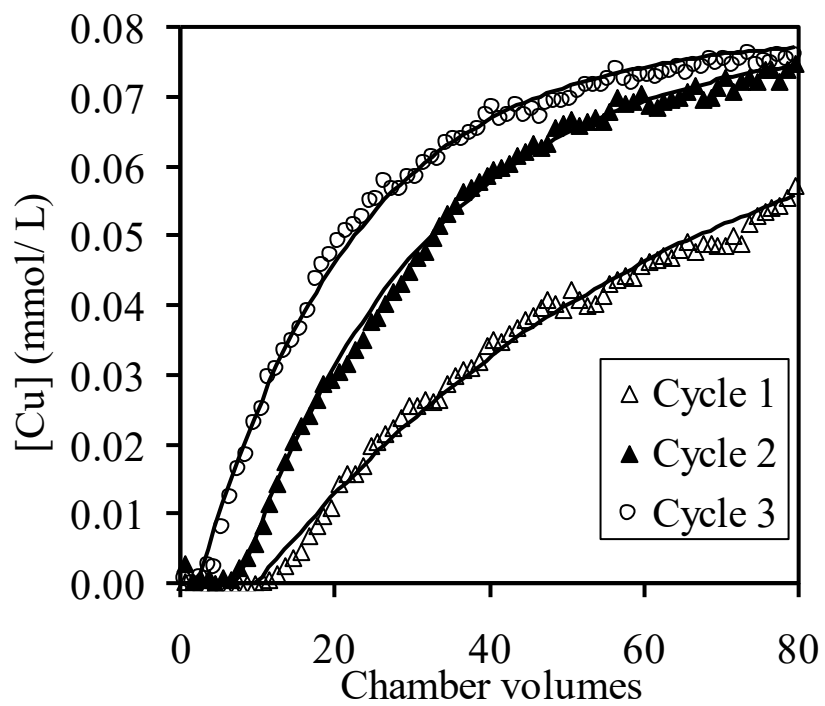
Fig. 1

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.
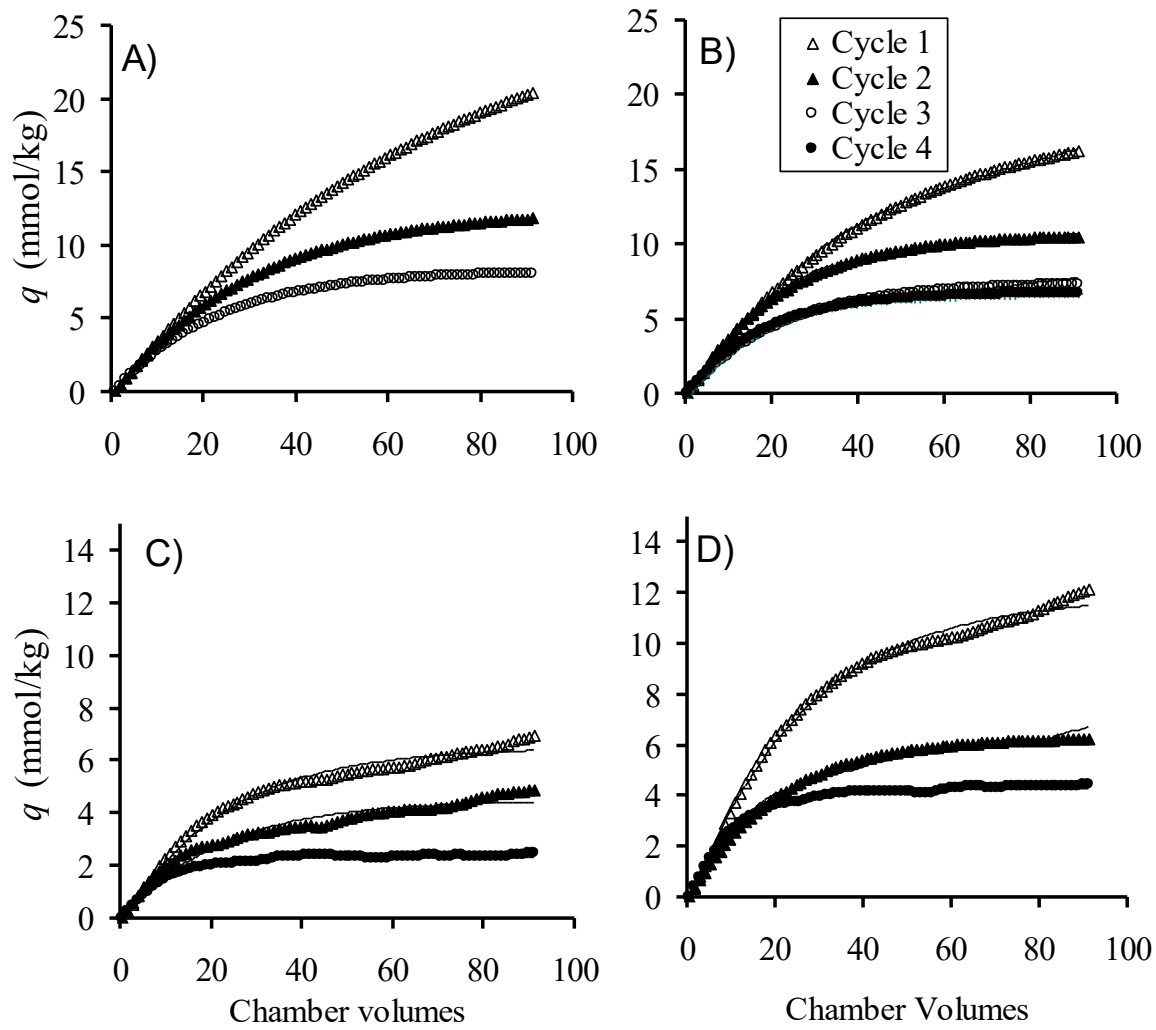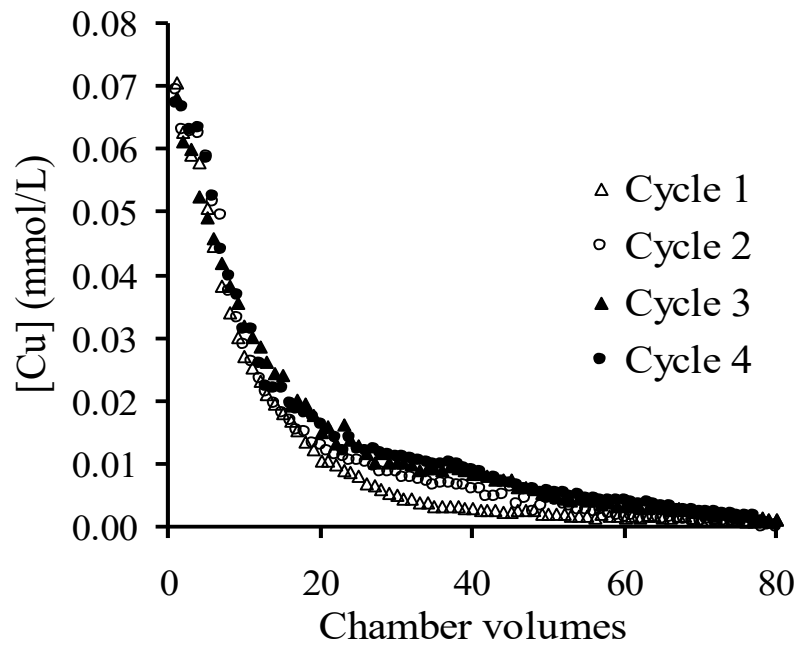
Fig. 9.
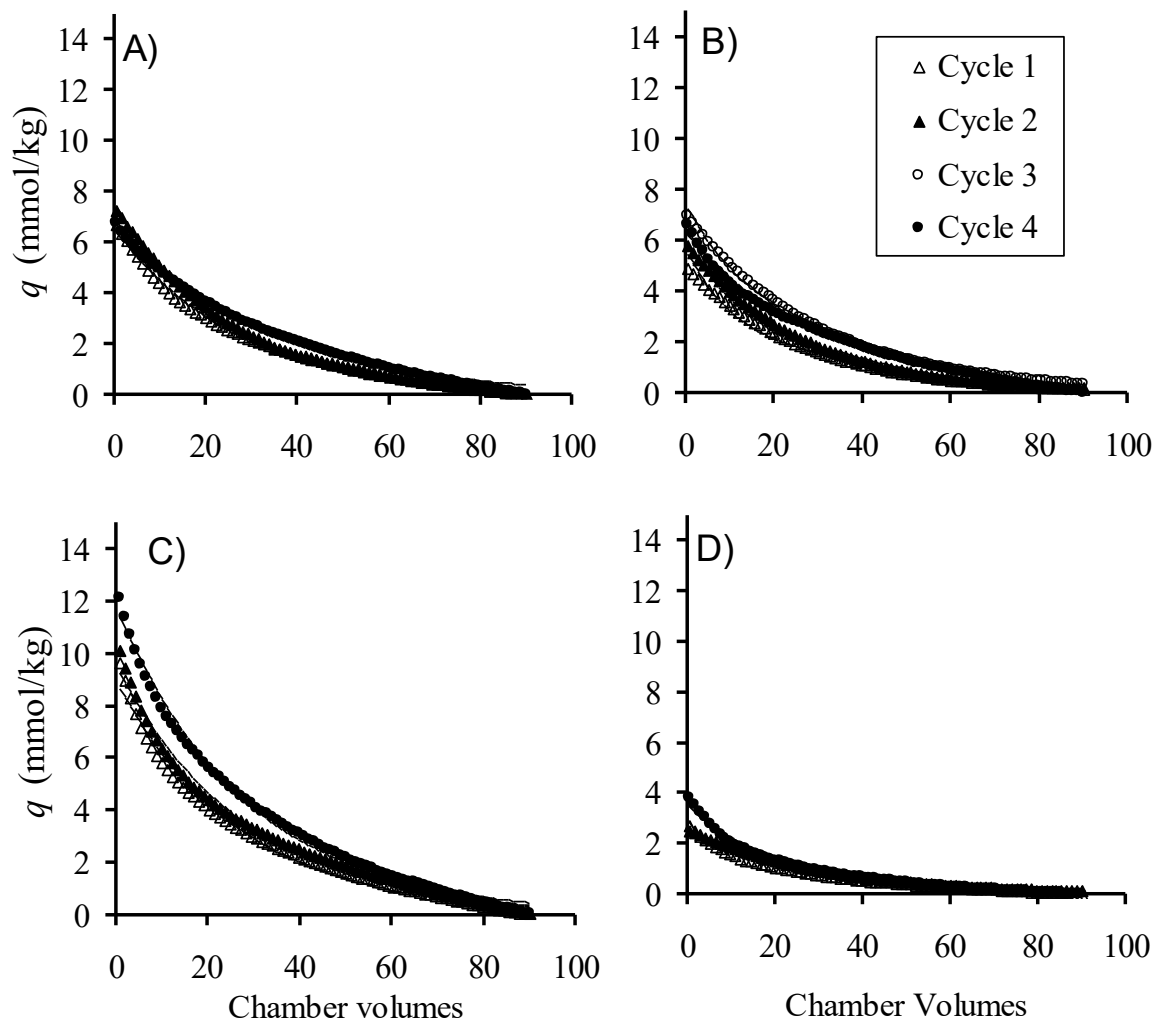
Fig. 10.

TABLES

Table 1. Selected physical and chemical properties of the soils

Property	Units	Soil			
		Gra1	Gra2	Amph1	Amph2
Particle density (ρ_p)	Kg dm^{-3}	2.54	2.53	2.48	2.48
Organic carbon	%	3.0	3.3	6.6	6.8
Sand	%	73.4	80.6	38.3	33.6
Silt	%	16.1	10.4	36.0	38.2
Clay	%	10.4	8.9	25.7	28.3
pH H$_2$O		4.4	4.1	5.4	5.8
pH KCl 0.1 M		3.7	3.6	4.6	4.4
Exchangeable Al	cmol$_c$ kg^{-1}	0.8	1.2	0.2	0.6
CEC$_e$	cmol$_c$ kg^{-1}	4.4	4.4	6.8	5.5
Al-DC	g kg^{-1}	1.4	1.9	11.7	9.8
Al-OX	g kg^{-1}	1.1	1.7	10.3	8.7
Al-PP	g kg^{-1}	1.1	1.9	7.5	6.4
Fe-DC	g kg^{-1}	1.8	3.5	52.0	44.0
Fe-OX	g kg^{-1}	1.0	2.3	11.0	8.9
Fe-PP	g kg^{-1}	0.8	1.9	5.9	5.0

Fe-OX, Al-OX, Fe-PP, Al-PP, Al-DC, Fe-DC denote oxalate, pyrophosphate and dithionite–citrate extractable Fe and Al respectively.

Table 2. Parameters fitted to the Langmuir equation (eq. 1) and q estimates obtained at equilibrium with the Cu solutions used in the SFC tests. r^2 is the degree of correlation between the observed and calculated q values for the batch experiments.

Soil	K_L	qL_{max}	$q^\dagger$	$q^\ddagger$	r^2
	L kg^{-1}	mmol kg^{-1}	mmol kg^{-1}		
Amph1	52 ±7	33 ±5	27	29	0.971
Amph2	29 ±5	28 ±3	19	23	0.994
Gra1	11 ±3	9 ±4	8	10	0.970
Gra2	6 ±2	18 ±2	6	9	0.996

†at equilibrium with [Cu] = 0.078 mmol L^{-1} in solution.
‡at equilibrium with [Cu] = 0.157 mmol L^{-1}.

Table 3. Amount of Cu retained by the soil (mmol kg^{-1}) after each retention

cycle during the SFC tests with pulses of [Cu] = 0.0787 mM.

Soil	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Amph1	20.6	11.9	8.3	8.3
Amph2	16.4	10.7	7.8	6.8
Gra1	6.9	6.3	4.9	2.5
Gra2	12.2	11.7	6.7	4.4

Table 4. Fitting of the results to a first-order retention model.

Cycle	q_{max} (mmol kg^{-1})	k_1 (min^{-1})	r2‡	RMSE†	q_{max} (mmol kg^{-1})	k_1 (min^{-1})	r2‡	RMSE†
				Influent [Cu]=0.0787 mM				
		Amph1				Gra 1		
1	27.8±7.7	0.084±0.0379	0.9998	0.0006	6.5±0.4	0.247±0.0481	0.9835	0.0049
2	12.4±1.1	0.193±0.0449	0.9990	0.0015	5.9±0.3	0.279±0.0516	0.9848	0.0045
3	8.3±0.5	0.247±0.0477	0.9966	0.0022	4.5±0.3	0.261±0.0465	0.9546	0.0081
4	8.2±0.3	0.245±0.0477	0.9966	0.0022	2.4±0.1	0.559±0.0825	0.9920	0.0024
		Amph2				Gra2		
1	18.4±2.6	0.136±0.0407	0.9992	0.0014	6.3±0.3	0.282±0.0496	0.9828	0.0049
2	10.7±0.6	0.262±0.0511	0.9972	0.0021	4.3±0.1	0.514±0.0768	0.9939	0.0021
3	7.4±0.4	0.257±0.0482	0.9871	0.0043	1.9±0.9	0.213±0.0459	0.9938	0.0032
4	7.4±0.4	0.254±0.0482	0.9871	0.0043	1.7±0.9	0.197±0.0439	0.9962	0.0025
				Influent[Cu]=0.157 mM				
		Amph1				Gra1		
1	32.1±3.5	0.084±0.0219	0.9957	0.0033	7.1±0.3	0.153±0.0243	0.9199	0.0101
2	18.9±1.4	0.109±0.0226	0.9976	0.0020	6.1±0.2	0.176±0.0278	0.9365	0.0083
3	16.5±0.9	0.138±0.0257	0.9995	0.0008	3.1±0.1	0.653±0.1846	0.9818	0.0204
4	13.1±0.6	0.156±0.0269	0.9963	0.0021	3.1±0.1	0.633±0.1464	0.9317	0.0203
		Amph2				Gra2		
1	25.8±2.6	0.085±0.0210	0.9934	0.0035	17.9±2.0	0.076±0.0193	0.9881	0.0055
2	17. 8±1.3	0.109±0.0222	0.9742	0.0065	18.2±2.7	0.064±0.0188	0.9925	0.0047
3	11.2±0.4	0.219±0.0349	0.9718	0.0051	6.0±0.2	0.176±0.0268	0.9778	0.0053
4	10.6±0.4	0.181±0.0290	0.9728	0.0054	5.4±0.1	0.313±0.0464	0.9548	0.0056

† Root mean square error.

‡ r^2 correlation between the observed and calculated q values for SFC experiments.

Table 5. Fitting of the results to a first-order release model.

Cycle	q_0 (mmol kg^{-1})	k_{-1} (min^{-1})	r^2‡	RMSE†	q_0 (mmol kg^{-1})	k_{-1} (min^{-1})	r^2‡	RMSE†
				Influent [Cu]=0.0787 mM				
		Amph1				Gra1		
1	6.4±0.7	0.016±0.0025	0.9957	0.0067	8.7±0.9	0.0165±0.0024	0.9898	0.0100
2	7.4±0.8	0.017±0.0027	0.9990	0.0037	9.9±1.0	0.0152±0.0022	0.9943	0.0072
3	6.7±0.7	0.014±0.0020	0.9941	0.0073	9.2±0.9	0.0158±0.0023	0.9903	0.0090
4	6.8±0.8	0.014±0.0020	0.9948	0.0069	11.4±1.2	0.0157±0.0023	0.9948	0.0070
		Amph2				Gra2		
1	4.9±0.5	0.016±0.0025	0.9860	0.0120	8.7±0.9	0.0178±0.0027	0.9897	0.0107
2	5.8±0.6	0.017±0.0026	0.9889	0.0110	9.9±1.0	0.0167±0.0025	0.9893	0.0104
3	6.9±0.7	0.015±0.0022	0.9945	0.0071	9.2±0.9	0.0153±0.0022	0.9899	0.0094
4	6.2±0.6	0.014±0.0022	0.9921	0.0084	11.4±1.2	0.0202±0.0032	0.9882	0.0120
				Influent[Cu]=0.159 mM				
		Amph1				Gra1		
1	2.7±0.4	0.041±0.0078	0.9987	0.0086	3.2±0.4	0.0349±0.0061	0.9624	0.0344
2	2.8±0.3	0.013±0.0020	0.9911	0.0086	3.5±0.4	0.0212±0.0033	0.9599	0.0242
3	5.5±0.6	0.017±0.0027	0.9978	0.005 0	3.7±0.4	0.0187±0.0029	0.9630	0.0211
4	4.2±0.4	0.016±0.0025	0.9912	0.0093	3.2±0.3	0.0129±0.0019	0.8038	0.0368
		Amph2				Gra2		
1	6.2±0.6	0.016±0.0024	0.9895	0.0101	7.3±0.7	0.0154±0.0022	0.9906	0.0091
2	5.6±0.5	0.013±0.0020	0.9920	0.0082	8.8±0.9	0.0175±0.0027	0.9923	0.0095
3	3.9±0.4	0.012±0.0018	0.9887	0.0092	7.6±0.8	0.0186±0.0029	0.9951	0.0079
4	6.7±0.7	0.015±0.0022	0.9828	0.0123	5.4±0. 6	0.0196±0.0033	0.9755	0.0137

† Root mean square error.

‡ r^2 degree of correlation between the observed and calculated q values for SFC experiments.