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Long-Term Aging of Copper Added to Soils

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Aging refers to the processes by which the mobility and bioavailability/toxicity of metals added to soil decline with time. Although long-term aging is a key process that needs to be considered in the risk assessment of metals in field soils, the long-term aging of Cu added to soils has not been studied in detail. In this study, the effects of aging on Cu isotopic exchangeability, total Cu in soil pore water, pore water free Cu^{2+} activity, and "available" Cu measured by the technique of diffusive gradient in thin film (DGT-Cu) were investigated in 19 European soils at two total Cu concentrations shown to inhibit plant (tomato) growth by 10 and 90%. After addition of Cu, the soils were leached, incubated outdoors, and sampled regularly over a 2-year period. The results showed that when water soluble Cu was added to soils, concentrations of Cu determined by each of the techniques tended to decrease rapidly initially, followed by further decreases at slow rates. Soil pH was a vital factor affecting the aging rate of Cu added to soils. The relatively low solubility products and low isotopic exchangeabilities of Cu in calcareous soils immediately after addition of soluble Cu^{2+} suggested Cu^{2+} probably precipitated in these soils as $Cu_2(OH)_2CO_3$ (malachite) and $Cu(OH)_2$. Isotopic dilution was found to be a robust technique for measuring rates of long-term aging reactions. A semi-mechanistic model was developed to describe the rate and extent of Cu aging across soils as affected by soil pH and other physicochemical parameters. Although not measured directly, it is inferred from soil physicochemical controls on Cu aging that processes of precipitation/nucleation of Cu in soils and hydrolysis of Cu^{2+} followed by a diffusion process controlled the decrease in Cu availability with time. The model was validated by testing it against field soils with different contamination histories and was found to successfully predict the isotopic exchangeability of Cu added to soils based on two parameters: soil pH and time.

Introduction

After soluble Cu is added to soil, several reactions may occur which change the concentration of Cu in the soil pore water and the fraction of added Cu available to organisms. After the initial partitioning of soluble Cu between solid and solution phases, it is usually observed that there is a continuing, but slow, reaction of soluble Cu with soil that slowly reduces availability to organisms over time. We term these reactions as "aging" reactions to distinguish them operationally from reversible partitioning reactions.

Working on whole soils, Hogg et al. (*1*) studied the desorption of added Cu at a small addition rate ($+7$ mg kg^{-1}) with time of soil−Cu contact varying from 24 h to 12 weeks and found increasing the period of soil−Cu contact reduced desorption of added Cu. For Cu, the extractability and bioavailability/toxicity have been shown to decrease with time after Cu addition (*2*, *3*). For instance, a series of Cu toxicity studies performed in Danish soils showed that the toxicity of Cu to plants or invertebrates in laboratory-contaminated soils was higher than that observed in field-contaminated soils, with the difference attributed to the effects of aging on the toxicity of added Cu (*4*−*6*).

The decrease in metal availability that occurs with time after metal addition to soil has generally been attributed to micropore diffusion, cavity entrapment, occlusion in solid phases by coprecipitation and co-flocculation, and surface precipitation/crystal growth (*7*−*10*). In a preceding paper (*10*), we indicated that the relatively low apparent solubility products and low isotopic exchangeability of Cu in calcareous soils immediately after addition of soluble Cu suggested Cu^{2+} probably precipitated in these soils as $Cu_2(OH)_2CO_3$ (malachite) and $Cu(OH)_2$. Cavity entrapment of Cu in swelling silicates, such as montmorillonite, has been noted after heating of soil minerals (*11*). With time, added Cu is likely to be retained by swelling silicates, and like Zn (*12*), diffuses into interlayers (*13*) and becomes entrapped in pseudo-hexagonal cavities at ambient temperature. The diffusion of ions has been extensively studied in microporous pure solids, such as zeolite, layer silicates, and oxides (*14*, *15*). Although there is no direct evidence from spectroscopic and microscopic studies for diffusion of added metals into micropores in clays and soils, the slow processes following rapid adsorption by these materials can be described by a diffusion equation, which suggests that diffusion is the rate-limiting process occurring (*13*, *16*−*19*).

Since long-term aging reactions modify Cu availability and toxicity over time, they are important in considering the risk from diffuse or point source additions of Cu to soil. However, current environmental criteria and protocols for risk assessment of metals in soils do not consider the effect of aging on availability and toxicity of metals in soils (*20*−*23*), and few data are available for Cu in this regard. If the aging processes of Cu added to soil are significant and rapid, then exposure and risks associated with slow incremental additions of Cu to soil may be overestimated by investigations based on spiking of soils with soluble Cu and assessing ecotoxic effects immediately after spiking (*24*). In this study, we complement our previous work on short-term (over 30 days) aging of Cu in soil (*10*) with findings from a new experiment where the long-term aging of Cu (up to 2 years) added to 19 European soils incubated outdoors. We also developed a semi-mechanistic model for long-term aging of soluble Cu added to soils based on incubation time and soil pH. The model was validated using field-contaminated soils.

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TABLE 1. Soil Properties and Total Cu Added to Soils at Two Effective Concentrations (EC10 and EC90)

soil no.	soil location	pH	clay (%)	organic C (%)	$CaCO_3$ (%)	total Cu (mg kg^{-1})	EC10 (mg kg^{-1})	EC90 (mg kg^{-1})
1	Gudow (Germany)	2.98	7	5.12	<0.5	1.7	59.8	463
2	Nottingham (UK)	3.36	13	5.20	<0.5	17.3	70.0	442
3	Houthalen (Belgium)	3.38	5	1.86	<0.5	2.4	10.3	93.0
4	Rhydtalog (UK)	4.20	13	12.94	<0.5	13.8	300	1191
5	Zegveld (The Netherlands)	4.75	24	23.32	<0.5	69.7	620	1993
6	Kövlinge I (Sweden)	4.76	7	1.63	<0.5	6.2	140	474
7	Souli (Greece)	4.80	38	0.41	<0.5	31.0	100	365
8	Kövlinge II (Sweden)	5.06	9	2.35	<0.5	8.5	130	528
9	Montpellier (France)	5.18	9	0.76	<0.5	4.6	125	477
10	Aluminusa (Italy)	5.44	51	0.87	<0.5	21.1	230	592
11	Woburn (UK)	6.36	21	4.40	<0.5	21.8	250	1497
12	Ter Munck (Belgium)	6.80	15	0.98	<0.5	16.0	180	700
13	Vault de Lugny (France)	7.29	38	2.19	10.3	21.1	160	1500
14	Rots (France)	7.38	27	3.04	14.9	14.0	650	1800
15	Souli (Greece)	7.38	46	8.05	47.4	33.6	80	350
16	Marknesse (The Netherlands)	7.52	26	2.47	10.0	17.6	500	2000
17	Barcelona (Spain)	7.49	21	2.34	6.3	88.0	160	1500
18	Brécy (France)	7.51	50	3.63	15.8	31.0	100	2400
19	Guadalajara (Spain)	7.52	25	4.00	36.5	7.3	450	1800

Materials and Methods

Soil Samples and Treatments. A set of 19 soils covering a range of soil properties was collected from nine European countries. Selected chemical and physical characteristics of the soils are reported in Table 1. Soil pH was measured in 0.01 M $CaCl_2$ (soil:solution ratio 1:5), soil organic carbon was measured by dry combustion, and soil clay content was determined using a standard pipet method. The amount of carbonate in soil (as $CaCO_3$) was determined by treating each soil with HCl and measuring the liberated CO_2. The "total" concentration of Cu in the soils was determined using an aqua regia (a fresh mixture (1:3) of concentrated HNO_3 and HCl) digestion followed by elemental analyses using inductively coupled plasma optical emission spectroscopy (ICP−OES). The analytical procedures are described in detail by Oorts et al. (*25*).

Samples equivalent to 1.5 kg oven-dried soil were dosed with soluble Cu at two concentrations, which were predetermined as the total Cu concentrations that would decrease plant growth by 10 and 90% in each soil (EC10 and EC90), respectively (*26*). Addition of Cu was conducted by dispensing 75 mL $CuCl_2$ over the soil sample with a pipet, in which the Cu concentrations ranged from 0.2 to 13 g Cu L^{-1} for the EC10 treatments and from 2 to 48 g Cu L^{-1} for the EC90 treatments. After Cu addition, the soils were thoroughly mixed and then leached with simulated rainwater, following the procedure described by Oorts et al. (*27*), in order to avoid salt effects on metal partitioning (*28*). The total Cu concentrations in the soils after leaching are reported in Table 1. After leaching, the soil samples were incubated outdoors in Canberra, Australia, where the climatic conditions are intermediate between those of Southern and Northern European countries. Periodically, soil samples were collected from the pots (as a column from soil surface to bottom). All samples were air-dried and passed through a 2 mm sieve.

Extraction and Analysis of Soil Pore Water. Soil samples (air-dried, two replications) were placed in 1 L glass jars, and the amount of deionised water required to bring the soil water potential to pF 2.0 (log 100 cm water suction) was added and thoroughly mixed. After mixing, the wetted soil was then stored for 3 days in darkness in an incubation room at 20 °C. The soil sample was transferred to a 50 mL plastic syringe filled previously with 0.5 cm quartz wool following the method of Thibault and Sheppard (*29*). Solution pH, electrical conductivity, and free Cu^{2+} activity were measured immediately on an aliquot of the separated solution. The pH in the soil pore water was measured using an Orion pH meter (model 420). The electrical conductivity in the soil pore water was measured using a conductivity meter (CDM 210). The concentration of Cu in the soil pore water was measured by ICP−OES or graphite furnace atomic absorption spectroscopy (GF−AAS, Perkin-Elmer, AAnalyst 600). This analysis was performed at day 4, 90, and 180 after spiking of the soils (at EC10 level).

Determination of Free Cu^{2+} Activity. Cupric ion activity in soil pore water was measured using a cupric ion selective electrode (Cu−ISE, Orion 94-29) coupled with a reference electrode (Orion 900200) and a mV meter (Orion 720). The method was fully described by Oliver et al. (*30*). Free Cu^{2+} concentrations were calculated from free Cu^{2+} activities, with the activity coefficients calculated from the Davies equation. Pore water ionic strength (IS) was calculated from EC using an empirical relationship developed previously for Australian soils (*31*): $IS = 0.014 \times EC - 4 \times 10^{-4}$, where units for IS and EC are mol L^{-1} and mS cm^{-1}, respectively. This analysis was performed at day 4, 90, and 360, and 540 after spiking of the soils (at EC10 level).

Determination of DGT-Cu. Diffusive gradient in thin film (DGT) devices, from DGT Research Ltd (UK), were deployed on soils spiked at EC10 level and equilibrated for 4, 90, and 180 days. The concentration of DGT-extractable Cu in soils was measured using the technique of Hooda et al. (*32*). Briefly, appropriate amounts of MilliQ water were added to soil samples (20 g, air-dried, sieved <2 mm, 2 replications) to obtain the water potential at pF 0, then maintained at 20 °C for 24 h. One standard cylindrical DGT unit was deployed in each Petri dish with the incubated soil for 24 h at 20 °C. After deployment, the DGT units were retrieved from the soil and rinsed with MilliQ water. The resin gel was retrieved and placed into a clean plastic vial. The Cu in the resin layer was determined by eluting with 1 M HNO_3 (1 mL) for 24 h and then analyzed by ICP−AES or GF−AAS. The concentration of metal measured by DGT (C_{DGT}) was calculated using the following equation (*33*):

$$C_{DGT} = M\Delta g/(DtA)$$

where M is the mass accumulated in the resin gel, Δg is the thickness of the diffusive gel (0.8 mm) plus the thickness of the filter membrane (0.13 mm), D is the diffusion coefficient of Cu in the gel (5.42×10^{-6} cm^2 sec^{-1} at 20 °C), which was measured using a diffusion cell (*34*), t is deployment time, and A is the exposure area ($A = 3.14$ cm^2). The value of C_{DGT} reflects supply from both solid phases and solution.

Determination and Modeling of Cu Lability. The lability (E value or isotopically exchangeable pool) of Cu in the soil samples was determined using a radioactive ^{64}Cu isotope dilution technique. The procedures and calculation details were previously given in Nolan et al. (*35*). E values were measured for soils spiked at both EC10 and EC90 and equilibrated for 21, 90, 180, and 360 days. We also attempted a semi-mechanistic modeling of the changes in Cu lability. The rationale for choosing this availability parameter is due to two main considerations. First, this technique allows a direct assessment of Cu in equilibrium with the soil solution (and therefore potentially available) and Cu non-isotopically exchangeable, and therefore, is well suited to be described with a semi-mechanistic model that is based (see below) on processes that remove Cu from the exchangeable pool (namely micropore diffusion and precipitation). Second, the E value dataset was the most extended (including soils spiked at both EC10 and EC90). The theoretical considerations that were made to develop a semi-mechanistic model of Cu lability follow. When water soluble Cu is added to soils, it partitions quickly between solution and solid phases, followed by further, slow processes that gradually decrease the isotopic exchangeability of the added Cu. The fast processes operative at high pH, which led to decreased isotopic exchangeability of the added Cu (E_{add} value) (*10*, *36*), can most likely be attributed to the precipitation/nucleation of Cu-bearing minerals in soils. Short-term adsorption reactions would not decrease the E_{add} value since the adsorbed Cu would still be isotopically exchangeable. This precipitation/nucleation process is considered to be related to the formation of $Cu(OH)^+$ in clay minerals and Fe oxides in soils (*13*, *37*, *38*). The reaction (eq 1), expressed as follows:

$$[Cu(H_2O)_n]^{2+} = [Cu(OH)(H_2O)_{n-x-1}]^+ + xH_2O + H^+ \quad (pK^\circ = 7.7) \quad (1)$$

where the forward reaction is promoted upon pH increase. Furthermore, proton dissociation from water molecules often takes place more readily on the surfaces of soil solids than in bulk solutions (*39*). The proportion of $Cu(OH)^+$ to total Cu ions ($Cu(OH)^+$ plus Cu^{2+}) can be expressed by the following equation (eq 2):

$$\frac{[Cu(OH)^+]}{[Cu(OH)^+] + [Cu^{2+}]} = \frac{1}{10^{(pK^\circ - pH)} + 1} \quad (2)$$

It is further postulated that the fast processes (precipitation/nucleation) are linearly related to the proportion of $Cu(OH)^+$ to total Cu ions ($Cu(OH)^+$ plus Cu^{2+}) in solution and can be described as follows (eq 3):

$$Y_1 = \frac{B}{10^{(pK^\circ - pH)} + 1} \times t^{C/t} \quad (3)$$

where Y_1 represents the change (%) in E_{add} value of added Cu due to the fast processes (precipitation/nucleation); B is a coefficient which is considered to be related to the effect of precipitation/nucleation; t is aging time (day); pK° is the first hydrolysis constant of Cu; the reciprocal power exponential equation $t^{C/t}$ (C is a constant) is used to describe the kinetics of these relatively fast processes; and pH is the soil pH measured in 0.01 M $CaCl_2$.

In a previous work describing the short-term aging of Cu in soil (*10*) we used a function in which the decrease in E values (%) due to diffusion processes was proportional to the $\sqrt{t}$ (*40*, *41*). However, after the initial stage of the diffusion processes that are linearly related to the square root of time, the diffusion processes can be described by the simplified Elovich equation (*42*). In this case the diffusion process is linearly related to the natural logarithm of time. In order to predict the long-term change in the isotopic exchangeability of Cu added to soils, especially for the long-term field soils, the model was further developed as follows (eq 4):

$$\text{Ln-model: } E_{add} \text{ value } (\%) = 100 - \frac{B}{10^{(pK^\circ - pH)} + 1} \times t^{C/t} - F \times \ln(t) \quad (4)$$

where F is a coefficient which is considered to be related to the effect of micropore diffusion.

The parameters in the model were optimized by minimizing the sum of the squares of the residual variation of the data points from the model.

TABLE 2. Model Parameters and Regression Coefficients (R^2) Derived from 19 Soils with Four Different Incubation Times and Two Effective Cu Concentrations (EC10 and EC90) When pK° was Fixed at 7.7

$$E_{add} \text{ value} = 100 - \frac{B}{10^{(pK^\circ - pH)} + 1} \times t^{C/t} - F \times \ln(t)$$

Cu added	B	C	F	R^{2a}
EC10	86.7	0.1	5.19	0.75
EC90	98.8	1	4.59	0.79
EC10 and EC90	89.8	1	4.92	0.76

[a] indicates significance at $P \le 0.001$.

Validation of the Model. A number of field soils contaminated with Cu salts were selected from seven long-term sites to validate the model described above (Table 2). For each site, soils spanning a gradient in total Cu concentration were sampled, together with an uncontaminated control soil (used for determined the Cu background concentration and lability). Hygum soils, which were contaminated 78 years ago by a wood impregnation facility in Denmark (*43*), were sampled at intervals of approximately 8 meters in a linear transect starting from the edge of the field and moving toward the centre. Wageningen soils were sampled from plots of a long-term field experiment with four levels of copper addition (0, 250, 500, and 750 kg Cu ha^{-1} as $CuSO_4$) in 1982 (*44*). Woburn soils (sandy loam) (*45*) were sampled from plots of a long-term field experiment for Cu (added as $CuSO_4$ from 1995 to 1997) contamination in UK (*46*). The soils from Hungary (calcareous silty clay loam) were collected from plots of a long-term field experiment in Nagyhörcsök with 810 kg Cu ha^{-1} added as $CuSO_4$ in 1991 (*47*). The Italian soils were sampled in Trentino from a vineyard, which was over 80 years old and had been contaminated with Cu due to the application of Cu-containing fungicides (as $CuSO_4$).

Statistical Analyses. Statistical analyses, including analysis of variance and regression analysis were conducted using the Genstat 6.1 for Window (*48*).

Results and Discussion

Soil Pore Water. The electrical conductivity (EC) in pore water in EC10-treated soils varied from 0.08 to 6.87 mS cm^{-1} and decreased with leaching and incubation time for all soils. The mean pore water EC values in the EC10-treated soils were initially 3.30 mS cm^{-1}, but decreased with time to 1.47 (90 days), 1.15 (360 days) and 0.66 mS cm^{-1} (540 days). The initial pH of soil pore water in the EC10-treated soils was on average 0.7 units lower than that in the soils leached and incubated for 90 days.

Total Cu in soil pore waters in the unleached EC10-treated soils ranged from 0.03 mg L^{-1} to 3.72 mg L^{-1}. After incubation and leaching the total Cu in pore waters ranged from 0.03

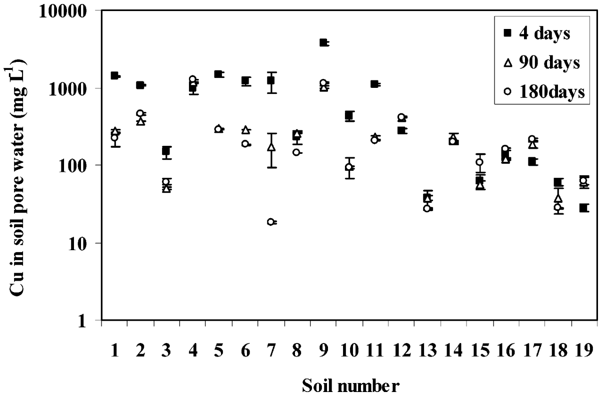

FIGURE 1. The total Cu concentration in soil pore water extracted after 4, 90, and 180 days of incubation from EC10-treated soils.

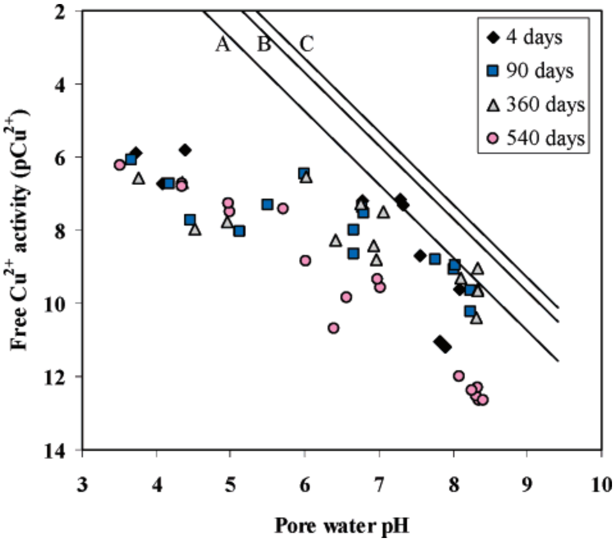

FIGURE 2. Free Cu^{2+} activity (pCu^{2+}) in pore water in the EC10-treated soils as a function of pore water pH and time. The solid lines are solubility limits for $Cu_2(OH)_2CO_3$ (malachite) assuming 0.03 (line A) and 0.0003 (line B) CO_2 partial atmospheric pressures and for $Cu(OH)_2$ (line C).

mg L^{-1} to 1.03 mg L^{-1} at 90 days, and from 0.02 mg L^{-1} to 1.15 mg L^{-1} at 180 days. Therefore, as can be noted from Figure 1, the decreases in total Cu in soil pore water from unleached soil to the soil leached and incubated for 90 days occurred mostly in the soils with pH ≤ 6.4 (soil 1−11, except for soils 4 and 8), in other cases there was not a significant decrease in soil pore water Cu after leaching and incubation.

Free Cu^{2+} Activity. Upon addition of water soluble Cu to the soils, the free Cu^{2+} activity in soil pore waters was high (low pCu^{2+}) (Figure 2). The free Cu^{2+} activity in the soils with low pH (<5.5) and with high organic matter (nos. 4 and 5) was not significantly affected by incubation time. For the other soils, the free Cu^{2+} activity in soil pore water decreased with incubation time, as evidenced by the linear correlation coefficient between pCu^{2+} (= −log Cu^{2+} activity) and incubation time ($r = 0.325$, ≤ 0.01). Similar results for changes in free Zn^{2+} activity in soils with incubation time were reported by Tye et al. (*49*). Also, McBride et al. (*50*), using a Cu−ISE to study the time-dependent solubility of free Cu^{2+} ions in suspensions of natural organic matter and iron oxide (FeOOH), discerned a clear aging effect on free Cu^{2+} activity. In the EC10-treated soils the initial high free Cu^{2+} activities were attributed to higher water soluble Cu concentrations and lower pH caused by Cu salt addition. After Cu addition, a downward trend of free Cu^{2+} activity in soil pore water could be attributed to shifting pH and aging effects, although there were also minor effects on the free Cu^{2+} activity in soil pore water from changes in electrical conductivity and total soluble Cu.

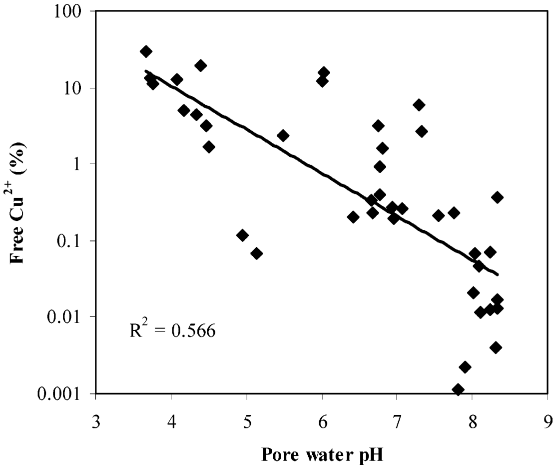

FIGURE 3. Free Cu^{2+} as a percentage of total Cu in soil pore water as a function of soil pH.

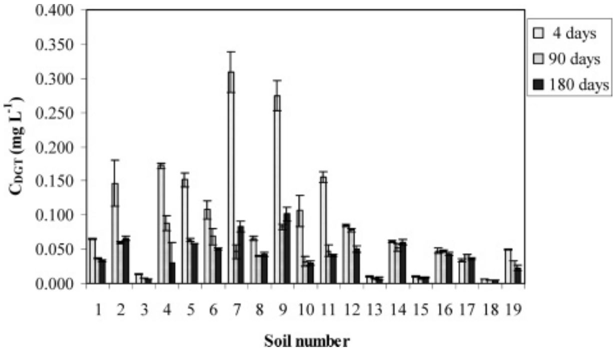

FIGURE 4. The concentration of Cu measured by DGT (C_{DGT}) in EC10-treated soils as a function of time. Vertical lines on top of bars represent standard errors.

The free Cu^{2+} activity in soil pore water measured using Cu−ISE was found to be in good agreement with that predicted by the equilibrium speciation program WHAM model VI (*51*). The pCu^{2+} in pore waters in EC10-treated soils ranged from 5.8 to 12.7, and was influenced mainly by soil pH (Figure 2). The slope of the pCu^{2+}/pH relationship varied with incubation time from 0.62 to 1.41 for the soils with incubation times from 4 to 540 days. The slopes of pCu^{2+}/pH reported in the literature vary and include 2.0 (*52*), 1.79 (*51*), 1.40 (*53*), 1.07 (*54*), and 1.2−2.0 (*55*). The observed differences in pCu^{2+} - pH relationships may be related to both the nature of the processes controlling free Cu^{2+} activity (such as adsorption−desorption and precipitation−dissolution) and other factors (such as pH, exchangeable cation compositions in soils and organic matter contents).

A solubility diagram was plotted according to equilibrium constants of Cu minerals (*52*) in order to determine if the solutions were supersaturated with respect to any known pure mineral phases of Cu. In such diagrams, two partial atmospheric pressures of CO_2 in soil pore water were assumed as 0.03 and 0.0003 atm (*52*, *56*). When viewed in comparison to Cu minerals displayed in these diagrams, the calcareous soils in this study (13−19, pH ≥ 7.3) were, in general, undersaturated with respect to $CuCO_3$, but the solubility products in the calcareous soils often approached the solubility product of $Cu_2(OH)_2CO_3$ and $Cu(OH)_2$ (Figure 2). This suggests that added Cu^{2+} may have precipitated in these soils as $Cu_2(OH)_2CO_3$ (malachite) and/or $Cu(OH)_2$. Clay or carbonate mineral surfaces in these soils probably acted as

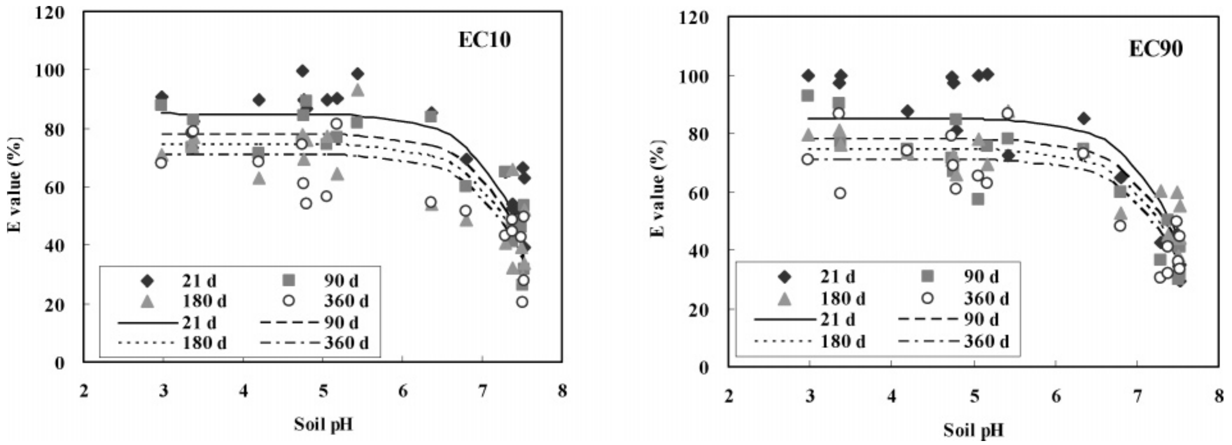

FIGURE 5. The E_{add} values (% of total added Cu) for added Cu measured in the EC10- and EC90-treated soils incubated for different times (symbols) and the curves predicted by the semi-mechanistic model.

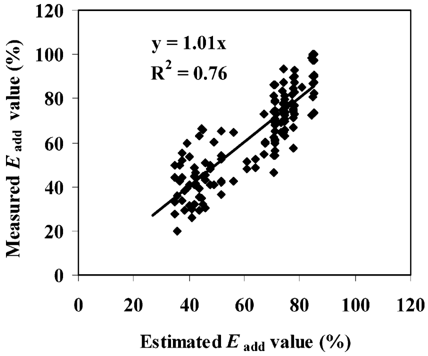

FIGURE 6. The measured E_{add} values (%) of added Cu in the EC10- and EC90-treated soils incubated for different times up to 1 year versus the E_{add} values (%) estimated by the semi-mechanistic model.

nucleation sites for precipitating Cu^{2+} (*9*), thereby reducing the apparent solubility product in much the same way that pure clays appear to reduce the solubility products by surface adsorption (*57*). It is possible that when water-soluble Cu was added to these calcareous soils, the Cu ions were quickly adsorbed on solid surfaces and precipitated, with further decreases in free Cu^{2+} activity in the soils occurring due to ongoing slow reactions (such as micropore diffusion). After incubation for 540 days, the solubility products of soil Cu in the calcareous soils were far from the solubility product of $Cu_2(OH)_2CO_3$ and $Cu(OH)_2$ (Figure 2), which suggested that the free Cu^{2+} activity in soil pore water was not controlled by $Cu_2(OH)_2CO_3$ and $Cu(OH)_2$ in the long-term incubation, even though their precipitation may have occurred initially.

The percentages of free Cu^{2+} concentration to total Cu in pore water were estimated from free Cu^{2+} activity, the activity coefficient, and total Cu concentration in soil pore water. The activity coefficients were calculated from the Davies equation and pore water ionic strength. The results (Figure 3) showed free Cu^{2+} concentrations as percentages of total Cu in pore water ranged from 29.2% to 0.001%, which were affected significantly by soil pH. The results are similar to that reported by Vulkan et al. (*51*) and Nolan et al. (*56*). However, in the calcareous soils (pH ≥ 7.3), the free Cu^{2+} concentration as a percentage of total Cu in pore water varied across 4 orders of magnitude.

DGT-Cu. The concentrations of Cu in EC10-treated soils measured by DGT (C_{DGT}) varied from 4.4 to 309 μg L^{-1} (Figure 4). When the soil pH was ≤ 6.4, the initial concentrations of Cu in soils measured by DGT (C_{DGT}) were significantly higher than those in the soils leached and incubated for 90 and 180 days. From 90 to 180 days, C_{DGT} concentrations were generally constant, with only three soils showing any significant reduction after 90 days. C_{DGT} has been used previously to predict Cu phytoavailability (*33*), where it was found that the Cu concentrations in plants (*Lepidium herophyllum*) were linearly related and highly correlated with C_{DGT}, but were more scattered and nonlinear with respect to free Cu^{2+} activity, EDTA extraction, or soil solution concentrations.

Isotopically Exchangeable Cu. In untreated control soils, the concentrations of isotopically exchangeable Cu (*E* value) ranged from 0.6 to 14 mg kg^{-1}, with a mean of 3.7 mg kg^{-1} across all soils. For the Cu-treated soils, the *E* values varied from 6.2 to 422 mg kg^{-1}, with a mean of 132 mg kg^{-1} for EC10 treatments, and from 60 to 1950 mg kg^{-1}, with a mean of 580 mg kg^{-1}, for EC90 treatments. The isotopic exchangeability (lability) of added Cu (E_{add}) expressed as a percentage of total Cu added was calculated by subtracting the *E* value of the untreated control soil from the total *E* value measured in the respective soils with added Cu, and dividing by the measured Cu dose (total Cu in spiked soil minus total Cu in control soil). The coefficient of variation of the *E* values were less than 10.2% with an average of 3.7% which was considered to be low since these values are the result of several independent measurements. The E_{add} values (%) varied from 20.1 to 99.6% for EC10-treated soils and from 29.3 to 100.3% for EC90-treated soils (Figure 5).

Modeling of Isotopically Exchangeable Cu. The semi-mechanistic model based on the processes of Cu precipitation/nucleation and micropore diffusion was used to describe the aging processes which led to the decrease in the isotopic exchangeability of Cu added to soils. When the data were fitted by the model using the Solver function in Microsoft Excel, the parameters B and C were subjected to the constraints: 0 ≤ B ≤ 110 and 0.1 ≤ C ≤ 1, with 0.000001 precision, 5% tolerance and 0.0001 convergence. The reciprocal power exponential equation $t^{C/t}$ (*C* is a constant) was used to describe the fast processes of precipitation/nucleation. When $C \leq 1$, $t^{C/t}$ is nearly stable when time is greater than 30 days. The parameters in the models are shown in Table 2. The regression coefficients (R^2) for the models were 0.75−0.79. The coefficient (B) for EC10-treated soils was lower than that for EC90-treated soils and the difference was significant at $P \leq 0.01$. These results suggest a greater possibility of precipitation/nucleation of Cu when added at higher concentrations (EC90). However, the difference between the two Cu doses could be ignored in order to simplify the model, as below:

$$E_{add}\text{ value (\%)} = 100 - \frac{89.8}{10^{(pK^{\circ} - pH)} + 1} \times t^{1/t} - 4.92 \times \ln(t) \quad (5)$$

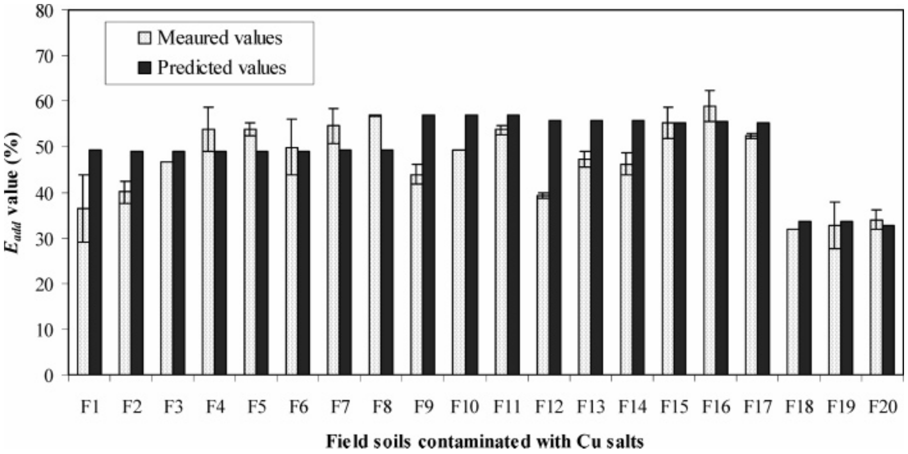

FIGURE 7. The measured and the predicted E_{add} values of exogenous Cu in the field soils contaminated with Cu salts for more than 8 years. Vertical lines represent standard errors where they exceed the height of columns.

The value of the first hydrolysis constant of Cu in bulk solution (pK°) was fixed at 7.7 in the models in accordance with the value reported in the literature (*52*, *58*). When the pK° parameter in the models was optimized, the model was improved and R^2 increased marginally. The values of pK° ranged from 6.89 to 7.14, all of which are lower than the first hydrolysis constant of Cu in bulk solution (7.7). The results were in agreement with the results of the hydrolysis of Cu ions in soils promoted by soil solid surfaces (*39*, *57*, *59*). However, to keep fewer variables in the model, the first hydrolysis constant of Cu (pK°) in the models was kept constant at 7.7.

The measured E_{add} values as a function of incubation time and soil pH and the E_{add} values estimated by the model (using the parameter for combined EC10 and EC90 values) were linearly related ($P < 0.00001$) with the correlation coefficient $R^2 = 0.76$ (Figures 5 and 6). It can be seen that the isotopic exchangeability of Cu added to soils decreased rapidly after addition, especially at high pH. The aging rate was fast initially and then decreased with increasing incubation time. Although the slow aging processes could take years to attain equilibrium, the decrease in isotopic exchangeability of added Cu was less than 1% per year after 5 years.

In the model, when soil pH < 5 only slow aging processes (likely diffusion) occurred, with the fast processes (likely precipitation/nucleation) in soils insignificant (<0.3%). The isotopically exchangeable Cu species retained by soils at pH < 5 is likely to be Cu^{2+} (both in solution and sorbed). The decrease in E_{add} values due to precipitation/nucleation was only 2.0% at pH 6, however, these fast processes of precipitation/nucleation were significantly increased at pH > 6, and at pH 7.5 they were the predominant processes leading to decreases in E_{add} values. Above pH 7.7, $Cu(OH)^+$ would be the dominant species of Cu in soil solution. The threshold value of pH 6 observed here above which isotopic exchangeability decreased with increased pH is higher than that noted in the studies of Cu retention by ferric hydroxide coated sands (pH 4.5) (*37*). Any effect of pH on diffusion of Cu into micropores was ignored in the semi-mechanistic model. However, soil pH and precipitation/nucleation processes affect the diffusion process by controlling the amount of diffusible Cu in soil solution and the Cu species present on solid surfaces. The model also allows for redissolution of Cu precipitation/nucleation products when solution Cu decreases due to the continual diffusion of Cu into micropores.

TABLE 3. Soil pH, Total Cu (mg kg^{-1}), *E* Values (mg kg^{-1}) and Time (yr) Since Soil Field-Contamination with Cu Salts (C1−C7: Uncontaminated Control Soils).

soil no.	location	soil pH	total Cu	*E* value	time
C1	Hygum 0	5.43	21.1	7.1	-
F1	Hygum 1	5.43	114.4	41.1	78
F2	Hygum 2	5.53	191.2	75.3	78
F3	Hygum 3	5.63	436.9	201.0	78
F4	Hygum 4	5.49	561.4	298.2	78
F5	Hygum 5	5.62	573.6	304.5	78
F6	Hygum 6	5.48	681.7	337.1	78
F7	Hygum 7	5.42	752.2	406.4	78
F8	Hygum 8	5.19	824.8	463.6	78
C2	Woburn 0	6.36	14.0	13.8	-
F9	Woburn 1	6.36	86.3	45.6	8
F10	Woburn 2	6.36	167.9	89.8	8
F11	Woburn 3	6.36	203.4	115.6	8
C3	Wageningen A0	4.34	19.0	5.8	-
F12	Wageningen A1	3.86	74.1	27.5	22
F13	Wageningen A2	3.87	102.7	45.4	22
F14	Wageningen A3	3.98	103.6	44.9	22
C4	Wageningen D0	5.01	19.0	6.6	-
F15	Wageningen D1	5.43	90.2	46.0	22
F16	Wageningen D2	5.14	102.0	55.5	22
F17	Wageningen D3	5.48	142.1	71.2	22
C6	Italy 0	7.14	27.2	3.0	-
F18	Italy 1	7.14	206.6	60.2	40
F19	Italy 2	7.14	389.4	121.8	40
C7	Hungary 0	7.30	21.0	<0.5	-
F20	Hungary 1	7.30	140.4	40.5	13

Model Validation. The measured E_{add} values from field-contaminated/incubated soils were in good agreement with those predicted by the model (Figure 7), with the difference between measured and predicted values being less than 10% (range 0.07−9.6%, 4.2% on average), except for the field soils F1, F9, and F12. In these three soils, the difference between the measured and predicted E_{add} values of exogenous Cu were found to be 13.2% for soil F1, 12.9% for soil F9, and 16.5% for soil F12. The total Cu concentrations in these soils (F1, F9, and F12) were generally lower than in other soils (Table 3), and this may have led to the discrepancy between the modeled and measured Cu aging. In such soils, Cu ions may migrate from non-labile forms to the labile pool, driven by the depletion of Cu from continued long-term uptake by plants or leaching, at a slower rate than the initial diffusion into micropores. This process has been suggested to occur for *P* in soils (*60*). Thus a hysteresis in the rate of the forward and reverse processes of micropore diffusion may be the cause of measured E_{add} values being lower than values predicted by the model in soils with “low” total Cu. However, the predictive power of this simple model (based only on pH and time) is satisfactory, particularly when considering that long-term aging of Cu in the soils investigated occurred at widely varying soil moisture contents, temperatures, and under different long-term leaching and plant uptake rates.

The model was able to predict the isotopic exchangeability of soluble Cu added to soils (E_{add} value) for time periods up to 80 years (which is well outside the time frame used to calibrate the model, i.e., 1 year), and for soils of widely differing physicochemical characteristics. A limitation of the model is that it is not dynamic, i.e., one aging period was used for the calculation even though, such as in the case of the vineyard soil, Cu additions in the field often occur repeatedly over time. However, even in these situations the model seemed to accurately describe the overall aging of added Cu. The model is less likely to accurately predict the aging of Cu applied to soils in other forms (such as Cu in sewage sludge, organic manure, and mining wastes) because different sources of Cu, due to matrix effects, will most likely exhibit different behavior and have different fates in soils.

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Literature Cited

(1) Hogg, D. S.; McLaren, R. G.; Swift, R. S. Desorption of copper from some New Zealand soils. *Soil Sci. Soc. Am. J.* **1993**, *57*, 361−366.

(2) McLaren, R. G.; Ritchie, G. S. P. The long-term fate of copper fertilizer applied to a lateritic sandy soil in Western Australia. *Aust. J. Soil Res.* **1993**, *31*, 39−50.

(3) Brennan, R. F.; Gartrell, J. W.; Robson, A. D. The decline in the availability to plants of applied copper fertilizer. *Aust. J. Soil Res.* **1986**, *37*, 107−113.

(4) Bruus Pedersen, M.; Kjær, C.; Elmegaard, N. Toxicity and bioaccumulation of copper to black bindweed (*Fallopia convolvulus*) in relation to bioavailability and the age of soil contamination. *Arch. Environ. Contam. Toxicol.* **2000**, *39*, 431−439.

(5) Bruus Pedersen, M.; van Gestel, C. A. M. Toxicity of copper to the collembolan *Folsomia fimetaria* in relation to the age of soil contamination. *Ecotoxicol. Environ. Safety* **2001**, *49*, 54−59.

(6) Scott-Fordsmand, J. J.; Weeks, J. M.; Hopkins, S. P. Importance of contamination history for understanding toxicity of copper to earthworm *Eisenia fetica* (oligochaeta: annelida), using neutral-red retention assay. *Environ. Toxicol. Chem.* **2000**, *19*, 1774−1780.

(7) Schosseler, P. M.; Wehrli, B.; Schweiger, A. Uptake of Cu^{2+} by calcium carbonates vaterite and calcite as studied by continuous wave (CW) and pulse electron paramagnetic resonance. *Geochim. Cosmochim. Acta.* **1999**, *63*, 1955−1967.

(8) Elzinga, E. J.; Reeder, R. J. X-ray adsorption spectroscopy study of Cu^{2+} and Zn^{2+} adsorption complexes at the calcite surface: Implications for site-specific metal incorporation preferences during calcite crystal growth. *Geochim. Cosmochim. Acta.* **2002**, *66*, 3943−3954.

(9) Cavallaro, N.; McBride, M. B. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. *Soil Sci. Soc. Am. J.* **1978**, *42*, 550−556.

(10) Ma, Y. B.; Lombi, E.; Nolan, A. L.; McLaughlin, M. J. Short-term natural attention of copper in soils: effects of time, temperature, and soil characteristics. *Environ. Toxicol. Chem.* **2006**, *25*, 652−658.

(11) He, H. P.; Guo, J. G.; Xie, X. D.; Peng, J. L. Location and migration of cations in Cu^{2+}-adsorbed montmorillonite. *Environ. Int.* **2001**, *26*, 347−352.

(12) Ma, Y. B.; Uren, N. C. Dehydration, diffusion and entrapment of zinc in bentonite. *Clay Clay Miner.* **1998**, *46*, 132−138.

(13) Al-Qunaibit, M. H.; Mekhemer, W. K.; Zaghloul, A. A. The adsorption of Cu(II) ions on bentonite−a kinetic study. *J. Colloid Interface Sci.* **2005**, *283*, 316−321.

(14) Kärger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; John Wiley & Sons: New York, 1992.

(15) Axe, L.; Trivedi, P. Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe, and Mn oxides. *J. Colloid Interface Sci.* **2002**, *247*, 259−265.

(16) Barrow, N. J. Testing a mechanistic model. II. The effects of time and temperature on the reaction of zinc with a soil. *J. Soil Sci.* **1986**, *37*, 277−286.

(17) Bruemmer, G. W.; Gerth, J.; Tiller, K. G. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals. *J. Soil Sci.* **1988**, *39*, 37−52.

(18) Trivedi, P.; Axe, L. Modeling Cd and Zn sorption to hydrous metal oxides. *Environ. Sci. Technol.* **2000**, *34*, 2215−2223.

(19) Scheinost, A. C.; Abend, S.; Pandya, K. I.; Sparks, D. L. Kinetic controls on Cu and Pb sorption by ferrihydrite. *Environ. Sci. Technol.* **2001**, *35*, 1090−1096.

(20) USEPA In *OPPTS Harmonized Test Guidelines: Series 850 Ecological Effects Test Guidelines,* Guideline 850−4150; U.S. Government Printing Office: Washington, DC, 1996.

(21) Stephenson, G. L.; Solomon, K. R.; Hale, B.; Greenberg, B. M.; Scroggins, R. P. In *Environmental Toxicology and Risk Assessment: modeling and risk assessment;* Dwyer, F. J., Doane, T. R., Hinman, M. L., Eds.; American Society for Testing and Materials: Philadelphia, PA, 1997; pp 474−489T.

(22) ASTM (American Society for Testing and Materials) *Standard Guide for Conducting Terrestrial Plant Toxicity Tests* E1963−98, Annual Book of Standards; ASTM: Conshohocken, PA, 1999.

(23) OECD (Organisation for Economic Co-operation and Development) *Guideline for the Testing of Chemicals: Terrestrial Plant Test,* no. 208 and no. 227 (draft documents); OECD: Paris, 2003.

(24) Lock, K.; Janssen, C. R. Influence of aging on metal availability in soils. *Rev. Environ. Contam. Toxicol.* **2003**, *178*, 1−21.

(25) Oorts, K.; Ghesquière, U.; Swinnen, K.; Smolders, E. Soil properties affecting the toxicity of $CuCl_2$ and $NiCl_2$ for soil microbial processes in freshly spiked soils. *Environ. Toxicol. Chem.* **2006**, *25*, 836−844.

(26) Rooney, C. P.; Zhao, F.-J.; McGrath, S. P. Soil factors controlling the expression of copper toxicity to plants in a wide range of European soils. *Environ. Toxicol. Chem.* **2006**, *25*, 726−732.

(27) Oorts, K.; Bronckaers, H.; Smolders, E. Discrepancy of the microbial response to elevated copper between freshly spiked and long-term contaminated soils. *Environ. Toxicol. Chem.* **2006**, *25*, 845−853.

(28) Stevens, D. P.; McLaughlin, M. J.; Heinrich, T. Determining toxicity of lead and zinc runoff in soils: salinity effects on metal partitioning and on phytotoxicity. *Environ. Toxicol. Chem.* **2003**, *22*, 3017−3024.

(29) Thibault, D. H.; Sheppard, M. I. A disposable system for soil pore-water extraction by centrifugation. *Commun. Soil Sci. Plant Anal.* **1992**, *23*, 1629−1641.

(30) Oliver, I. W.; Merrington, G.; McLaughlin, M. J. Australian biosolids: characterization and determination of available copper. *Environ. Chem.* **2004**, *1*, 116−124.

(31) McLaughlin, M. J.; Tiller, K. G.; Smart, M. K. Speciation of cadmium in soil solutions of saline/sodic soils and relationship with cadmium concentrations in potato tubers (*Solanum tuberosum L.*). *Aust. J. Soil Res.* **1997**, *35*, 183−198.

(32) Hooda, P. S.; Zhang, H.; Davison, H.; Edwards, A. C. DGT. - A new in situ procedure for measuring bioavailable trace metals in soils. *Eur. J. Soil Sci.* **1999**, *50*, 285−294.

(33) Zhang, H.; Zhao, F.-J.; Sun, B.; Davidson, W.; McGrath, S. P. A new method to measure effective soil solution concentration predicts Cu availability to plants. *Environ. Sci. Technol.* **2001**, *35*, 2602−2607.

(34) Zhang, H.; Davison, W. Diffusional characteristics of hydrogels used in DGT and DET techniques. *Anal. Chim. Acta.* **1999**, *398*, 329−340.

(35) Nolan, A. L; Ma, Y. B.; Lombi, E.; McLaughlin, M. J. Measuring labile Cu using stable isotope dilution and isotope ratio analysis by ICP-MS. *Anal. Bioanal. Chem.* **2004**, *380*, 789−797.

(36) Scheckel, K. G.; Scheinost, A. C.; Ford, R. G.; Sparks, D. L. Stability of layered Ni hydroxide surface precipitates - A dissolution kinetics study. *Geochim. Cosmochim. Acta.* **2000**, *64*, 2727−2735.

(37) Al-Sewailem, M. S.; Khaled, E. M.; Mashhady, A. S. Retention of copper by desert sands coated with ferric hydroxides. *Gerderma* **1999**, *89*, 249−258.

(38) Gier, S.; Johns, W. D. Heavy metal-adsorption on micas and clay minerals studied by X-ray photoelectron spectroscopy. *Appl. Clay Sci.* **2000**, *16*, 289−299.

(39) Farmer, V. C. In *The Chemistry of Soil Constituents*; Greenland, D. J., Hayes, M. H. B., Eds.; John Wiley & Sons: New York, 1978; pp 405−448.
(40) Crank, J. *The Mathematics of Diffusion*; Oxford University Press: London, 1975.
(41) Ma, Y. B.; Uren, N. C. The effects of temperature, time, and cycles of drying and rewetting on the extractability of zinc added to soil. *Geoderma* **1997**, *75*, 89−97.
(42) Aharoni, C.; Sparks, D. L. In *Rate of Soil Chemical Processes*, Sparks, D. L., Suarez, D. L., Eds.; Academic Press: New York, 1991; pp 1−18.
(43) Bruus Pedersen, M.; Axelsen, J. A.; Strandberg, B.; Jensen, J.; Attrill, M. J. The impact of a copper gradient on a microarthropod field community. *Ecotoxicology* **1999**, *8*, 467−483.
(44) Korthals, G. W.; Alexiev, A. D.; Lexmond, T. M.; Kammenga, J. E.; Bongers, T. Long-term effects of copper and pH on the nematode community in an agroecosystem. *Environ. Toxicol. Chem.* **2005**, *15*, 979−985.
(45) Knight, B. P.; Chaudri, A. M.; McGrath, S. P.; Giller, K. E. Determination of chemical availability of cadmium and zinc using inert soil moisture samplers. *Environ. Pollut.* **1998**, *99*, 293−298.
(46) Gibbs, P. A.; Chambers, B. J.; Chaudri, A. M.; McGrath, S. P.; Harlton-Smith, C. H.; Godley, A. R.; Bacon, J. R.; Campbell, C. D.; Aitken, M. N. In *Proceedings of the 8th International Conference on the Biogeochemistry of Trace Elements,* Adelaide, Australia, April 3−7 2005; CSIRO: Collingwood, Australia, 2005; pp 404−405.
(47) Bakonyi, G.; Nagy, P.; Kádár, I. Long term effects of heavy metals and microelements on nematode assemblage. *Toxicol. Lett.* **2003**, *140−141*, 391−401.
(48) Genstat Committee, Rothamsted Research *Genstat 6.1 for Windows*; VSN International Ltd: Oxford, 2002.
(49) Tye, A. M.; Young, S. D.; Crout, N. M. J.; Zhang, H.; Preston, S.; Barbosa-Jefferson, V. L.; Davison, W.; McGrath, S. P.; Paton, G. I.; Kilham, K.; Resende, L. Predicting the activity of Cd^{2+} and Zn^{2+} in soil pore water from the radio-labile metal fraction. *Geochim. Cosmochim. Acta.* **2003**, *67*, 375−385.
(50) McBride, M.; Martínez, C. E.; Sauvé, S. Copper (II) activity in aged suspensions of goethite and organic matter. *Soil Sci. Soc. Am. J.* **1998**, *62*, 1542−1548.
(51) Vulkan, R.; Zhao, F.-J.; Barbosa-Jefferson, V.; Preston, S.; Paton, G. I.; McGrath, S. P. Copper speciation and impacts on bacterial biosensors in the pore water of copper contaminated soils. *Environ. Sci. Technol.* **2000**, *34*, 5115−5121.
(52) Lindsay, W. L. *Chemical Equilibria in Soils*; John Wiley & Sons: New York, 1979.
(53) Sauvé, S.; McBride, M. B.; Norvell, W. A.; Hendershot, W. H. Copper solubility and speciation of in situ contaminated soils: effects of copper level, pH and organic matter. *Water Air Soil Pollut.* **1997**, *100*, 133−149.
(54) Lexmond, T. M. The effect of soil pH on copper toxicity to forage maize grown under field conditions. *Neth. J. Agric. Sci.* **1980**, *28*, 164−184.
(55) Cavallaro, N.; McBride, M. B. Activities of Cu^{2+} and Cd^{2+} in soil solutions as affected by pH. *Soil Sci. Soc. Am. J.* **1980**, *44*, 729−732.
(56) Nolan, A. L.; McLaughlin, M. J.; Mason, S. D. Chemical speciation of Zn, Cd, Cu and Pb in pore waters of agricultural and contaminated soils using Donnan dialysis. *Environ. Sci. Technol.* **2003**, *37*, 90−98.
(57) Farrah, H.; Pickering, W. F. The sorption of copper species by clay minerals. II. Illite and montmorillonite. *Aust. J. Chem.* **1976**, *29*, 1177−1184.
(58) Wolt, J. D. *Soil Solution Chemistry: Applications to Environmental Science and Agriculture;* John Wiley & Sons: New York, 1994.
(59) McBride, M. B. Hydrolysis and dehydration reactions of exchangeable Cu^{2+} on hectorite. *Clays Clay Miner.* **1982**, *30*, 200−206.
(60) Barrow, N. J.; Shaw, T. C. The slow reaction between soils and anions: effect of time and temperature on the decrease in phosphate concentration in the soil solution. *Soil Sci.* **1975**, *119*, 311−320.

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