Influence of Soil Characteristics on Copper Sorption from a Copper Oxychloride Fungicide

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The objective of this work was to assess the sorption of copper (Cu) applied as a Cu-oxychloride metalaxyl formulation by soils characterized by anthropogenic accumulation of Cu due to agricultural activity. The methods involved batch incubation of soils with a Cu-oxychloride metalaxy-based fungicide suspended in 0.01 M CaCl₂, phase separation, and determination of the concentration of Cu (Cu) in solution. Results showed that specific soil properties influenced solubilization of the Cu from the fungicide. The amount of dissolved Cu depended on the soil pH, its potential acidity, and its cation exchange capacity. The amount of anthropogenic Cu in the soil had a minor influence on soluble Cu after the addition of the fungicide. Thus, Cu-based antifungal treatment can increase the local concentration of soluble Cu in acid soils but is not likely to affect the [Cu] in moderately acidic or neutral soils.

KEYWORDS: Copper-oxychloride; fungicide; soil; sorption

INTRODUCTION

Copper (Cu) oxychloride-metalaxyl mixtures are commonly sprayed on crop foliage to control fungal disease. Fungicide can enter the soil by off-target deposition and wash-off from treated foliage (*1*). Rainfall can promote fungicide loss; therefore, fungicide application may be repeated up to 15 times in rainy weather, with each application ranging from 0.2 to 0.99 kg Cu ha⁻¹, depending on the recommendations of the manufacturer or the farmer. The result is the accumulation of Cu in the soil (*2, 3*). Most long-term accumulation results from application of the traditional Bordeaux mixture (*4, 5*), but the use of formulas based on Cu-oxychloride is also widespread.

Models that describe the fate and the transport of substances via surface runoff and infiltration into soil are used frequently to evaluate future metal and pesticide accumulation in agricultural land (*6*). To evaluate the mobility of Cu in soil−water systems, modelers rely on data about the partitioning of metal in soil (*7*) gained from batch experiments using aqueous solutions of Cu standards in the forms of CuCl₂ or Cu(NO₃)₂. However, current commercial fungicide formulations are mixtures of Cu-oxychloride, metalaxyl, and adjuvants that facilitate spray application. Foliar wash-off can transport Cu-oxychloride-based fungicides from treated surfaces as particles suspended in water (*8*); consequently, most of the Cu enters the soil as Cu-oxychloride. Despite the fact that the formulation of the

pesticide influences Cu partitioning in field conditions, the influence of the commercial Cu-oxychloride-based and organic pesticides on the sorption of Cu in soil has not been studied. However, toxicity to earthworms stemming from the interaction of Cu-oxychloride with the soil has been evaluated (*9*).

The objective of this work was to assess the sorption of Cu applied as a Cu-oxychloride-metalaxyl formulation by a set of soils characterized by anthropogenic accumulation of Cu due to agricultural activity. In light of the environmental implications of off-target deposition of pesticides in soil, the partitioning of Cu between the aqueous and solid phases in the soil−water−fungicide system was evaluated.

EXPERIMENTAL PROCEDURES

Fungicide. The commercial fungicide evaluated was Ridomil Gold plus (RGP) from Syngenta Agro (O Porriño, Spain), which is a wettable powder containing Cu-oxychloride [Cu₂(OH)₃Cl; 40% w/w in Cu], metalaxyl [methyl *N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-DL-alaninate; 2.5% M-mefenoxam, the 100% active metalaxyl isomer], and other proprietary components not specified by the manufacturer. Copper oxychloride is a mixture of cupric hydroxy minerals, most of which decompose in acidic environments and are stable at pH > 6 (*10*), while others (i.e., paratacamite) are stable in oxidizing, acidic environments (*11*). The fungicide used here contained atacamite and paratacamite, with the former being most abundant, as determined by X-ray diffraction (Siemens D-5000; Siemens, Karlsruhe, Germany). The particle size of the fungicide powder equilibrated in 0.01 M CaCl₂, pH 6.7, was measured by dynamic light scattering over the range of 0.6 nm to 6 μm (Zetasizer Nano, Malvern Instruments. Ltd., UK); the mean hydrodynamic diameter was 1046 μm, with a distribution of ± 396 μm.

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Table 1. Soil Characteristics[a]

soil	pH_W	pH_{KCl}	C (%)	ECEC	Al_E	sand (%)	silt (%)	clay (%)	Cu_E	Cu_T
A	7.4	6.6	3.6	33.2	<0.01	46	35	19	5.0	60
B	7.0	5.4	3.1	12.8	<0.01	67	15	18	6.5	107
C	5.3	4.6	3.1	8.6	0.41	53	30	17	6.5	96
D	5.5	5.0	4.1	24.7	<0.01	65	19	16	8.0	274

[a] Mean values and variation coefficients of replicates were less than 5% in all cases. Key: C, total organic carbon; ECEC, effective cation exchange capacity ($cmol_{(c)}$ kg^{-1}); Al_E exchangeable Al ($cmol_{(c)}$ kg^{-1}); Cu_E, exchangeable Cu measured in the 0.2 M NH_4Cl extracts (mg kg^{-1}); Cu_T, total Cu content measured in the aqua-regia plus hydrofluoric acid extracts (mg kg^{-1}).

Soil Samples and Kaolinite. Soils were developed from granite rock and were coarse textured Typic Haplumbrepts (*12*). Two of these soils were subject to lime application. Four composite samples taken from five points from the top 0−20 cm of the soil were obtained from each of four Rías Baixas vineyards in the Galician province of Pontevedra (northwestern Spain). In the laboratory, the samples were thoroughly mixed and dried at room temperature, passed through a 2-mm mesh sieve, and stored at room temperature until analysis.

Partition tests were also performed with kaolin. Kaolin is a mineral colloid typical of acid soils in temperate regions; its properties and reactions have been evaluated in a number of works (*13−16*). The results obtained from partition tests with kaolinite were compared with those obtained from tests with soil. Kaolin was obtained from Sigma-Aldrich, (Steinheim, Germany). X-ray diffraction analysis showed that the mineral phase was kaolinite with traces of microcline and quartz. Kaolin contains less than 0.1% organic carbon. Prior to use, kaolin was clean-washed and equilibrated with 0.01 M $CaCl_2$ by five 15-min cycles of stirring, centrifugation for 30 min at 300*g*, phase separation, and resuspension in fresh 0.01 M $CaCl_2$, pH 6.7, with a liquid/solid ratio of 10:2 (w/w).

Analytical Methods. Active and potential soil acidities were determined by measuring the pH of 1:2.5 (soil/liquid) suspensions in distilled water and in 0.1 M KCl using a combined glass electrode. Organic carbon content was determined by elemental analysis using a ThermoFinnigan 1112 series NC instrument (Austin, EE.UU). The proportions of sand (the 0.05−2.00 mm fraction), silt (0.002−0.05 mm), and clay (<0.002 mm) were determined by wet sieving and pipetting methods (*17*). Exchangeable cations (Na, K, Ca, and Mg) were extracted with 0.2 M NH_4Cl (*18*), and exchangeable Al was extracted with 1 M KCl. Effective cation exchange capacity (ECEC) was calculated as the sum of exchangeable Na, K, Ca, Mg, and Al. Soluble Cu is referred to by its concentration in the aqueous phase after 24 h of incubation with 0.01 M $CaCl_2$, pH 6.7, with a liquid/solid ratio of 10:2 (w/w). Total Cu (Cu_T) was measured following total digestion with aqua-regia plus hydrofluoric acid (*19*). All inorganic cations in the extracts were measured by atomic absorption spectrometry (AAS) using a Thermo Solar M series spectrometer (Austin, EE. UU).

The [Cu] in solution in the soils was estimated by suspending 5 g of dry soil in 50 mL of 0.01 M $CaCl_2$, pH 6.7. The sample was stirred for 24 h and then centrifuged at 300*g* for 30 min. The Cu present in the supernatant was determined by AAS. The detection limit for Cu in aqueous extracts was 0.05 mg L^{-1}. All determinations were performed on triplicate subsamples of each soil.

Liquid−Solid Partitioning Experiments. Preliminary kinetic tests were performed using a stirred suspension of RGP in 0.01 M $CaCl_2$ containing 48 mg L^{-1} of Cu at 25 ± 1 °C. Suspensions were sampled at 1, 4, 8, and 30 min, and at 2, 8, 24, and 48 h, and immediately centrifuged for 15 min at 300*g* to measure [Cu] in the liquid phase. Kinetic experiments demonstrated that 8 h of contact was sufficient to achieve equilibrium; no decay in dissolved [Cu] occurred before 48 h. Therefore, all partitioning experiments were performed with 24 h of incubation time.

To assess the distribution of RGP at a range of concentrations, a set of batch experiments were performed with soil or kaolinite using the RGP formulation containing both metalaxyl and Cu-oxychloride. In each assay, a 2-g sample of soil or kaolinite was suspended in 10 mL of the fungicide/0.01 M $CaCl_2$ solution. These suspensions were shaken at 200 rpm for 24 h at 25 ± 1 °C, after which they were centrifuged for 15 min at 300*g*. pH and [Cu] in the supernatant were measured following centrifugation. All experiments were performed in triplicate.
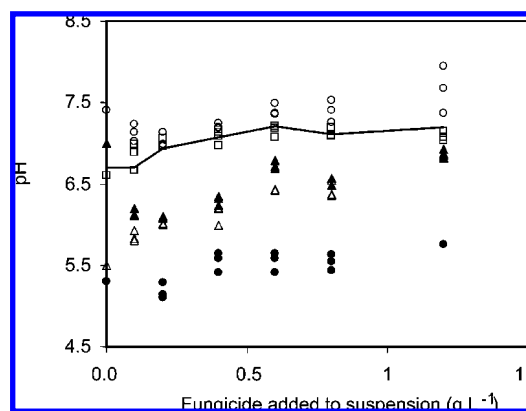

Figure 1. pH of the fungicide/0.01 M $CaCl_2$/soil suspensions following the addition of increasing amounts of RGP. —, control suspension (no soil, no kaolinite); □, kaolinite; ○, soil A; ▲, soil B; ●, soil C; △, soil D.

Aqueous suspensions of RGP ([Cu] range = 0.25−30 mg L^{-1}; eight concentrations) were made from a stock suspension of RGP (8 g L^{-1} in distilled water) diluted in 0.01 M $CaCl_2$ (pH 6.7). The suspensions were allowed to equilibrate at room temperature for at least 24 h and stirred by hand at discrete times. The stock suspension of RGP was kept homogeneous by vigorous vortex stirring. At the recommended dosage, the concentration of metalaxyl in the spray is 100 mg L^{-1} and the concentration of Cu-oxychloride is 1.6 g L^{-1}. The varying nature of rainfall-induced wash-off can cause the concentrations of fungicide that reach soil by off-target spray and canopy drip to span from zero to concentrations exceeding that in the spray because the fungicide concentration on the foliage can increase following evaporation of water and sedimentation of solid ingredients.

RESULTS AND DISCUSSION

The soils studied had sandy loam texture but differed in organic carbon content [ranging from 3.1 to 4.1% (w/w)], pH_W (ranging from 5.3 to 7.4), and pH_{KCl} (ranging from 4.6 to 6.6; **Table 1**). The neutral pH values of soils A and B were attributed to liming. Cation exchange capacities ranged from 8.6 to 33.2, varying according to pH and clay and organic carbon content. Exchangeable Al was detected only in soil C (0.41 $cmol_{(c)}$ kg^{-1}). Total Cu content ranged from 60 to 274 mg kg^{-1} and resulted from the prolonged application of Cu-based fungicides; variations can be attributed to varying applications of antifungal agents (**Table 1**). These values are comparable to those reported for other similar soils (*3, 5, 20*). Metalaxyl was detected in the four soils at levels below the quantification limit (25 μg kg^{-1}).

Effect of Fungicide Addition on the pH of the Suspensions. The addition of fungicide to the control suspensions (no added soil) increased the pH relative to the sample with the least amount of added RPG/0.01 M $CaCl_2$ due to dissolution of Cu-oxychloride (**Figure 1**). The addition of increasing amounts of RGP/0.01 M $CaCl_2$ to the soil suspensions (**Figure 1**) promoted changes in pH relative to the control suspension. Soils A, B,

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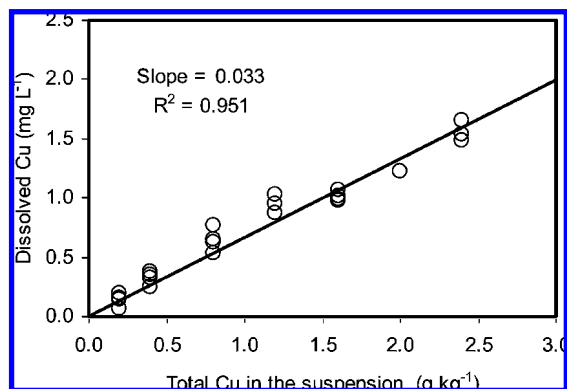*J. Agric. Food Chem.,* Vol. 57, No. 7, 2009 **2845**

Figure 2. Partitioning of dissolved Cu according to total Cu in the suspension, added as RGP in 0.01 M $CaCl_2$, pH 6.7. The approximate linear partition coefficient is 290 L kg^{-1}.

and C showed significant decreases (Student's *t*-test) in pH with the addition of less than 0.1 g L^{-1} of RGP for soil A and less than 0.2 g L^{-1} for soils B and C, corresponding to 1 and 2 g kg^{-1} of RGP in the soil, respectively. However, soil D showed no decrease in pH.

While the pH drops for soils A and B following the addition of small amounts of RGP were significant, they were minor. The most remarkable differences between these two soils were the Cu_T in the soil prior to the addition of RGP and the difference in the current acidity minus potential acidity values; soil A had lower difference (0.8) than soil B (1.6). For the more acidic soil C, the small drop in pH following the addition of a small amount of RPG was probably due to its exchangeable Al content. The RPG-induced changes in pH could be explained by the release of Cu into the solution from Cu-oxychloride. Cation exchange reactions with the added Ca from $CaCl_2$ and the Cu from the RGP can cause the release of exchangeable acid cations from soil exchange complexes, and the behavior of soils A, B, and C for small additions of RGP is consistent with displacement of potential acidity by such a mechanism. The lack of a decrease in pH for soil D was due to its low potential acidity, indicated by the minor difference between its actual and potential pH relative to soil C. However, the pH of all soil solutions increased with the addition of greater amounts of RGP (more than 0.2 g L^{-1}), likely due to the release of hydroxyl groups when the Cu-oxychloride dissolved.

The addition of small amounts of RGP did not decrease the pH of the kaolinite suspension, whereas the pH did increase with the addition of larger amounts of RGP (suggesting that no potential acidity is released by Cu exchange with saturated Ca-kaolinite). Together, these results support the hypothesis that the pH changes in soils were due to the combination of acid cation release from the exchange complexes and a buffering effect by RGP.

Copper Partitioning. The interaction of soil with the Cu from RGP was analyzed on the basis of Cu partitioning between the liquid and solid phases of the soil−RGP−water suspension. When RGP was suspended in 0.01 M $CaCl_2$ without soil (**Figure 2**), the concentration of Cu released into the $CaCl_2$ solution increased linearly with the dose of the fungicide. For a suspended concentration of 0.1 g L^{-1} RGP, pH 7.5 (corresponding to 0.4 g kg^{-1} of Cu in solid phase), 0.6 mg L^{-1} Cu was dissolved. This value is close to the speciation calculations for equilibrium with atacamite oversaturated in 0.01 M $CaCl_2$ ([Cu] = 0.74 mg L^{-1}; speciation calculations were performed using the MINTEQ program) (*21*). An indication about the Cu species formed in the fungicide suspension was obtained by simulating

Table 2. Visual MINTEQ (*21*) Simulation of the Speciation of a Saturated Mineral Phase $Cu_2Cl(OH)_3$ as Atacamite in Equilibrium with $CaCl_2$ 0.01 M and in Equilibrium with the Atmosphere at 25 °C[a]

species	concentration	activity	log activity
H^+	3.87×10^{-7}	3.29×10^{-7}	−6.482
Cu^{2+}	1.38×10^{-5}	7.23×10^{-6}	−5.141
$CuOH^+$	8.22×10^{-7}	6.99×10^{-7}	−6.155
$CuCl^+$	2.85×10^{-7}	2.42×10^{-7}	−6.615
$CuCO_{3\,(aq)}$	1.05×10^{-7}	1.06×10^{-7}	−6.975
$Cu_2(OH)_2^{+2}$	2.96×10^{-8}	1.55×10^{-8}	−7.811
$CuHCO_3^+$	9.37×10^{-9}	7.97×10^{-9}	−8.099
$Cu(OH)_{2\,(aq)}$	3.90×10^{-9}	3.93×10^{-9}	−8.406
$CuCl_{2\,(aq)}$	1.11×10^{-9}	1.12×10^{-9}	−8.950

[a] Concentrations and activities are in mol L^{-1}. Species with activities less than 10^{-9} M are not shown.
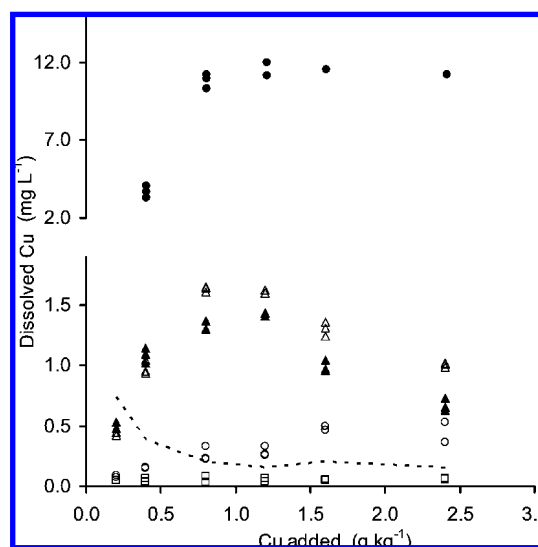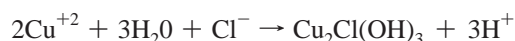

Figure 3. Copper in solution as a function of the dose of RGP (2.5% w/w as metalaxyl + 40% w/w Cu as oxychloride). ---, calculations made with MINTEQ; □, kaolin; ○, soil A; ▲, soil B; ●, soil C; △, soil D.

a saturated Cu-oxychloride suspension in equilibrium with 0.01 M $CaCl_2$ at 25 °C (**Table 2**), assuming the following chemical reaction:

$$2Cu^{+2} + 3H_2O + Cl^- \rightarrow Cu_2Cl(OH)_3 + 3H^+$$

using log $K = 7.381$ and the enthalpy of the reaction = −93.43 kJ mol^{-1}, according to the National Institute of Standards and Technology Database (*22*). The results showed that the pH was 6.48 and that most of the Cu existed as Cu^{2+} (91.7% of total Cu), followed by $CuOH^+$ (5.5%), $CuCl^+$ (1.9%), and $CuCO_3$ (0.7%). Therefore, most of the reactions between the fungicide and the soil would occur via complex formation between Cu^{2+} and the reactive soil surfaces.

Nevertheless, when the concentration of RGP in the suspension was increased, the amount of Cu in solution increased 5 to 10 times more than that predicted by the speciation calculations. The presence of other Cu species more soluble than atacamite in the commercial formulation or substances that promote the solubilization of Cu could explain this increase.

Figure 3 shows that the type of soil affected whether the [Cu] in solution increased or decreased when Cu was added as RPG/0.01 M $CaCl_2$. In the case of soil A, the [Cu] in solution was <0.53 mg L^{-1}, and it increased with the dose of Cu added in the fungicide up to that corresponding to 2.4 g Cu per kg soil. For soils B, C, and D, in-solution [Cu] reached maximum

with doses corresponding to 0.8−1.2 g Cu per kg soil. Soil C increased the [Cu] in solution up to 10 times relative to the control, whereas soil A decreased it by a factor of 2 at the highest doses of added Cu. Soil C had the smallest ECEC, pH_W, pH_{KCl}, and the highest exchangeable Al of all soils analyzed; all of these characteristics favor the solubilization of Cu. These results suggest that the addition of increasing amounts of fungicide enabled the Cu-oxychloride minerals to influence the pH and therefore to induce changes in the sorption of Cu by the soil.

The results for soil C are particularly notable because the dramatic increase in [Cu] in solution following the addition of increasing amounts of RGP to the soil C suspension has important environmental implications. Soil C was the most acidic but also had the largest potential acidity, exchangeable Al, and the smallest ECEC of the four soils studied. Soil D was also acidic, but had minor potential acidity (greater pH_{KCl}), a small difference in pH_W minus pH_{KCl}, and a higher ECEC relative to soil C. It is likely that these differences conferred the inability to attenuate [Cu] in solution after fungicide application to soil C. This behavior might be due to the aging of complexes of anthropogenic Cu-soil minerals (*23*) because the processes involved in aging (e.g., intraparticle porous diffusion, ripening, and crystallization of surface complexed and coprecipitated species) make the most of Cu_T unreactive within the laboratory time frame. For soils B and D, the decrease in the dissolved [Cu] at high doses of fungicide indicates that sorption or precipitation of Cu was favored. The most probable explanation for this is that the increase in pH favored the adsorption of Cu on pH-dependent surface charges of the soil colloids and the coprecipitation with hydroxyl groups.

Copper is strongly sorbed to soils (*23*); moreover, the Zeta potential of washed RGP in 0.01 M $CaCl_2$, pH 6.7, is $−75 ±$ 7 mV. Therefore, the surface charge of the fungicide can influence the overall cation exchange, control the pH of the bulk solution, and control Cu sorption.

The mechanisms controlling the amount of Cu in solution in the suspensions were clarified by simulating the equilibrium speciation of atacamite, which is the most reactive mineral in RGP. Simulating the influence of pH on the [Cu] in 0.01 M $CaCl_2$ solution with increasing amounts of atacamite (**Figure 4a**) showed that at low pH, the [Cu] in solution increased until all of the atacamite dissolved. However, as the pH increased, the [Cu] decreased as a result of sorption of Cu^{2+} and $Cu(OH)^+$ to the negatively charged surface groups arising from the deprotonation of surface hydroxyl groups at the atacamite crystal edges. Removal of copper from solution can result from the formation of both monomeric and dimeric surface complexes, as well as through surface precipitation mechanisms (*24*). However, speciation simulations indicated that formation of CuO or $Cu(OH)_2$ (**Table 2**) could be neglected; therefore, so could the sorption of precipitated forms of these compounds.

Both modeling and experimental results showed that sorption influenced the [Cu] in solution. When RGP was incubated with kaolinite in 0.01 M $CaCl_2$, the [Cu] in solution decreased to 0.1 mg L^{-1}, and the concentration was always lower than that obtained in suspensions without kaolinite (**Figure 3**). Notably, there were no differences in pH between fungicide mixtures with and without kaolinite (**Figure 1**).

The influence of the affinity of the sorbent for Cu in solution was evaluated. The adsorption of Cu in a mixture of 1 g of kaolinite in 10 mL of 0.01 M $CaCl_2$ with 0.08 mmol L^{-1} of atacamite (17 mg L^{-1} of atacamite; 10 mg L^{-1} Cu) is shown in **Figure 4b**. The [Cu] in solution as a function of the sorbed
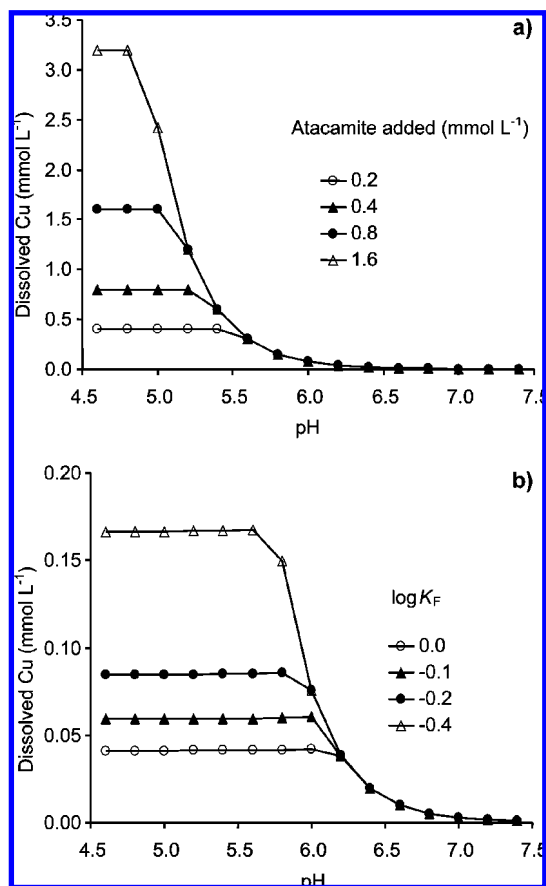

Figure 4. Calculations made with MINTEQ assuming equilibrium. (**a**) Concentration of total dissolved Cu as a function of pH and the concentration of atacamite in suspension with 0.01 M $CaCl_2$. (**b**) Concentration of dissolved Cu in equilibrium with 0.08 mM atacamite (17 mg L^{-1} of atacamite; 10 mg L^{-1} Cu) in suspension with 0.01 M $CaCl_2$ as a function of pH and kaolinite as sorbent. Equilibrium sorption of Cu was simulated assuming a nonlinear isotherm modeled by the Freundlich equation. The different adsorption capacities are indicated by the respective Freundlich's constants (log K_F); the Freundlich exponent was set to 0.6 in all cases.

concentration is given by $[Cu] = (q/K_F)^{1/0.6}$, were q is the sorbed concentration, K_F is the Freundlich adsorption coefficient, and 0.6 is the average value of the Freundlich exponent for the adsorption of Cu on soils (*25*). The same fitted value has been reported for Cu sorption on kaolinite (*14, 16*). Results indicated that [Cu] in solution depended on the sorption capacity of kaolinite when large amounts of Cu were released from the atacamite mineral lattice; MINTEQ simulations indicated that this occurred at pH lower than 6.2. We hypothesized that the maximum [Cu] in solution in the experiments with soils could have been the result of electrochemical conditions (such as pH, concentration of ions in solution, variable charge of sorbing species, etc.) that favor a local maximum of soluble Cu.

Sorption of Cu on Soil. The differences between the [Cu] in the RGP/0.01 M $CaCl_2$ mixtures with and without soil measured in the aqueous phase were used to calculate the [Cu] in the solid phase, according to the following equation:

$$C_S = [C_{L(control)} - C_{L(soil)}]V/m \qquad (1)$$

where C_S is the concentration in the solid phase, $C_{L(control)}$ is the concentration in the liquid phase of control samples, $C_{L(soil)}$ is the concentration in the liquid phase in samples with soil after
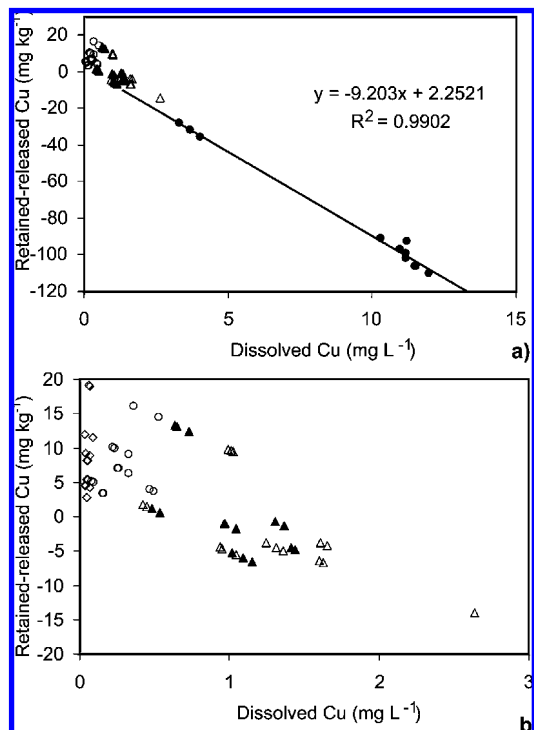
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Figure 5. (**a**) Partitioning of Cu in solution and in solid phase. The concentration in solid phase is calculated from dissolved [Cu] in the control sample minus [Cu] relative to the calculated control as a function of the dose of the fungicide (2.5% w/w metalaxyl + 40% w/w Cu as oxychloride). The line represents the best-fitted line. ○, soil A; ▲, soil B; ●, soil C; △, soil D; ◇, kaolinite. (**b**) Rescaled plotting of data for soils A, B, D, and kaolinite.

24 h, V is the volume of the liquid phase, and m is the mass of solid phase in the test tubes. The relationship between C_S and $C_{L(soil)}$ was used to assess the influence of soil on the partitioning between dissolved Cu and Cu sorbed to the solid phases of the fungicide in the soil/0.01 M CaCl$_2$ suspension. **Figure 5** shows how the partitioning depended on the soil studied and the dose of the fungicide. The concentration in the solid phase increased with the dose of RPG in soil A, while in soils B, C, and D, the addition of the fungicide promoted the release of Cu. In the case of soil C, the amount of Cu released peaked at $106-110$ mg kg^{-1} after the addition of 6 to 8 g of RGP per kg of soil. These amounts exceeded the Cu$_T$ in this soil, indicating that some of the released Cu came from RGP. In the cases of soils B and D, the released Cu exceeded the amount of Cu$_E$. A closer look at the data for soils A, B, and D revealed that net sorption occurred only with soil A (**Figure 5b**), while desorption occurred for soils B and D with the addition of intermediate amounts of RGP ($0.4-0.8$ g L^{-1}). These results indicate that the relationship between C_S and C_L does not follow a well-defined isotherm. Instead, the distribution of points in the figure was determined by several processes, such as the dissolution of the Cu from RPG, and the subsequent change in the pH of the suspension, cation exchange, and specific sorption of Cu and other acid cations onto/from the soil colloids.

Conclusions. These findings indicate that soil properties have a strong influence on the solubilization of Cu from oxychloride-based fungicides. Soluble Cu does not increase linearly with the fungicide dose because soluble Cu depends on the pH$_W$, pH$_{KCl}$, and cation exchange capacity of the soil. The amount of anthropogenic Cu in the soil does not have an immediate

influence on the soluble Cu after the addition of Cu-oxychloride. However, very acidic soils exceed the neutralizing effect produced by the dissolution of the Cu-oxychloride. Thus, copper oxychloride-based fungicides can increase the concentration of soluble Cu in acidic soils but not in moderately acidic and neutral soils.

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