

# Effect of Particle Size on Copper Oxychloride Transport through Saturated Sand Columns

Marcos Paradelo,\* Paula Pérez-Rodríguez, Manuel Arias-Estévez, and J. Eugenio López-Periago

Soil Science and Agricultural Chemistry Group, Department of Plant Biology and Soil Science, Faculty of Sciences, University of Vigo, E-32004 Ourense, Spain

Understanding the mechanisms behind the transport of particulate contaminants in porous media is crucial with a view to evaluating their potential impact on the environment. Much of the copper used in agriculture is sprayed as colloidal copper oxychloride, and despite its potential environmentally adverse consequences, colloidal transport of particulate formulations of copper remains poorly understood. In this work, transport of copper colloids from a commercial copper oxychloride based fungicide formulation was studied by measuring its breakthrough in saturated guartz sand columns. The influence of ionic strength and flow rate on the test results suggests that retention of copper oxychloride based colloids is governed by weak forces. The particle deposition dynamics of the studied copper formulation was consistent with a two-site kinetic attachment model. The proposed colloid retention mechanisms are highly sensitive to the fungicide particle size. A comparison of our test results with reported data for other copper oxychloride wettable powder fungicide formulations revealed that transport of copper oxychloride is strongly influenced by its particle size. This is consistent with the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO), but only if binding occurs at the secondary minimum in the potential, where attachment is less favorable with small particles. The influence of particle size is also consistent with the results of previous studies where deposition was ascribed to retention at a secondary minimum. The mobility of colloidal formulations of these copper-based fungicides in saturated porous media increases with increasing particle size.

KEYWORDS: Copper oxychloride; agrochemicals; colloid transport; porous media

## INTRODUCTION

A wide range of copper-based fungicides have for some time been used against fungal diseases in various crops. This had led to copper accumulating in soil surfaces and subsurfaces (I-7) and to its concentration in some agricultural soils exceeding the European Union recommended limit of 140 mg kg<sup>-1</sup> (8) as a result. The potential environmental problems resulting from the accumulation of copper can restrict its use as a fungicide in agriculture. Because commercial formulations of fungicides are designed to facilitate control of their physicochemical characteristics, the properties of copper formulations may influence the behavior of this metal in the environment. Understanding the way commercial formulations control metal transport in porous systems is important with a view to predicting the fate of copper in agricultural ecosystems.

Off-target deposition and rainfall-induced foliar washoff can facilitate the transfer of copper fungicides to soil. Washoff losses may occur in the form of suspended particles (9, 10). Most commercial copper-based formulations currently used in agriculture are sprayed as colloid-sized water suspensions of copper oxychloride minerals. Because such minerals are scarcely soluble

over the typical pH range for natural waters (viz. 6–7), their transport in soil may occur as colloid-size particles. In fact, high concentrations of total copper ( $250 \pm 146 \text{ mg}$  of Cu kg<sup>-1</sup>) have been detected in deep layers of coarse-textured soils under vineyard crops intensively treated with copper formulations (*11*). Such high concentrations suggest that transport of this metal is more marked than one would have expected from the mobility of its dissolved forms (*12*).

The transport of particles in soil is largely influenced by the way they attach to soil surfaces. The electrochemical conditions of a suspension of particles in a porous medium such as soil determine whether their attachment will be favorable (attractive forces) or unfavorable (repulsive forces). The conditions for particle attachment (repulsion or attraction) are usually modeled on the basis of the theory of Derjaguin, Landau, Verwey, and Overbeek (DL-VO). However, recent studies have exposed the deposition of colloid-size copper oxychloride particles in saturated quartz sand even under unfavorable electrochemical conditions for attachment (13). In this situation, colloid surface forces are weak, and whether particle attachment occurs depends on the particular characteristics of the diffuse layer. Particle retention under these conditions is also influenced by hydrodynamic flow, geometry, and physico-chemical heterogeneity in the surface of porous media (13, 14).

<sup>\*</sup>Corresponding author: telephone, +34 988 387 070; fax, +34 988 387 001; e-mail, mparadelo@uvigo.es.

Cu content (g g <sup>-1</sup> )	0.464
mean particle size $(\mu m)$	0.315
particle size distribution width ( $\mu$ m)	0.122
particle density (g cm $^{-3}$ )	3.205

Copper oxychloride for agricultural uses is commercially available in various formulations. Some characteristics of such formulations (particularly particle size distribution) can dictate their behavior as colloids during transport in porous media. In a recent paper, transport of copper oxychloride in saturated quartz sand (*I3*) was described in terms of particle attachment at the secondary minimum.

The purpose of this work was to study transport in a commercial fungicide based on an aqueous suspension of colloidal copper oxychloride by modeling retention of the colloids during transport in water-saturated quartz sand columns and examining the influence of ionic strength (I) and hydrodynamic variables on it. The results thus obtained were compared with previously reported data (I3) for transport in a particulate copper oxychloride fungicide.

#### MATERIALS AND METHODS

**Fungicide.** The commercial copper-based fungicide ZZ-Cuprocol (CO-PG, manufactured by Syngenta Agro, S.A., Pontevedra, Spain) is a concentrated aqueous suspension containing 64 g of copper and 2 mL of propylene glycol per 100 mL of product. This fungicide is used worldwide to prevent mildew infection in crops. The properties of the studied formulation are summarized in **Table 1**. Based on its mineral composition as determined by X-ray diffraction of crystalline powder, the most abundant mineral phase in CO-PG is atacamite, which is accompanied by traces of paratacamite.

The average particle size and Zeta potential of the particulate fungicide in its aqueous suspension were measured over the range 0.6 nm to 6  $\mu$ m, using dynamic light scattering on Zetasizer Nano equipment from Malvern Instruments, Ltd. (Malvern, U.K.). Particle density was measured picnometrically (15).

The copper content of the studied fungicide was determined in quintuplicate, using acid digestion with aqua regia and hydrofluoric acid until complete dissolution (16). The total suspended copper concentration in the aqueous suspensions was determined by adding 13.5 M HNO<sub>3</sub> in a 1/10 (v/v) proportion to the samples and measuring by acetylene–air flame atomic absorption using a Solaar M5 spectrophotometer from Thermofisher Scientific, Inc. (Waltham, MA). Soluble copper in the samples was measured after filtering through a membrane of 0.45  $\mu$ m pore size. The amount of particulate Cu was calculated as the difference between soluble and total Cu. Particle density measurements were used in conjunction with nominal particle diameters to calculate the number of suspended particles.

**Quartz Sand.** Quartz sand  $(SiO_2)$  was used as the column packing material. Quartz grains (Aldrich Chemical, Milwaukee, WI) were well sorted and had a grain diameter of 0.32 mm. The sand was thoroughly cleaned prior to use (17). Visual inspection by scanning electron microscopy confirmed that the sand grains were prolate spheroidal in shape. The Zeta potential of the sand was measured in a near-micrometer size fraction previously obtained by sedimentation of a suspension of the ground sand sample.

**Transport Tests.** The properties of the quartz sand columns used in the fungicide deposition tests are summarized in **Table 2**. Longitudinal dispersivity was estimated in transport tracer tests involving the application of pulses of 0.29 mM KBr and measurement of the bromide ion concentration in the outflow.

The suspensions used to study colloid transport were prepared by mixing the fungicide with distilled water or 0.01-100 mM NaNO<sub>3</sub> containing 73–83 mg of Cu L<sup>-1</sup> as CO-PG (**Table 3**). All suspensions were vigorously stirred while applied at the top end of the column by means of a peristaltic pump.

 
 Table 2.
 Properties and Parameters of Packed Quartz Sand Columns Used in Fungicide Particle Deposition Tests

•	•	
	collector diameter ( $d_c$ , cm)	0.032
	fluid density ( $\rho_{\rm f}$ , kg m <sup>-3</sup> )	10 <sup>3</sup>
	fluid viscosity ( $\mu$ , kg m <sup>-1</sup> s <sup>-1</sup> )	$8.9 imes10^{-4}$
	temperature (T, K)	298
	Hamaker constant (A, J)	$1.0  imes 10^{-20}$
	porosity (f, -)	0.41
	column length (L, cm)	5
	Happel model parameter $(A_s, -)$	35.72

Table	3.	Properties	of	Colloid	Suspensions	in	Deionized	Water	(DW)
Contai	ning	y Variable E	Elect	rolyte C	oncentrations	Use	d in Transp	ort Test	S

NaNO <sub>3</sub> concn (mM)	pН	/(mM)	Zpotential (mV)	Cu in suspension $(mg L^{-1})$	fungicide concn (mg L <sup>-1</sup> )	particle concn (particle L <sup>-1</sup> )
DW	6.09	<10 <sup>-4</sup>	-40	72.87	157.74	$3.01 imes10^{12}$
0.01	6.12	0.01	-57	83.02	179.7	$3.43\times10^{12}$
10	6.29	10	-71	73.44	158.96	$3.03\times10^{12}$
100	6.11	100	-50	79.81	172.75	$3.29\times10^{12}$

 Table 4. Fitting Parameters for the Two-Site Random Sequential Adsorption

 Model As Estimated from Breakthrough Data for Saturated Packed Quartz

 Sand at Variable Ionic Strength<sup>a</sup>

ľ	S <sub>max2</sub> <sup>c</sup>	k <sub>a2</sub> <sup>d</sup>	s <sub>max1</sub> <sup>c</sup>	k <sub>a1</sub> <sup>d</sup>	SSQ <sup>e</sup>	r <sup>2 f</sup>
DW	35 (0.65)	6.67 (0.259)	33 (2.2)	0.07 (0.007)	0.001	1.000
0.01 mM	35 (0.62)	4.69 (0.238)	100 (7.7)	0.07 (0.005)	0.004	0.999
10 mM	51 (1.71)	3.45 (0.206)	92 (8.9)	0.10 (0.013)	0.028	0.996
100 mM	140 (7.32)	2.44 (0.128)	338 (33.9)	0.16 (0.023)	0.016	0.994

<sup>a</sup> Standard errors are shown in parentheses. <sup>b</sup> Ionic strength (mmol L<sup>-1</sup>). <sup>c</sup> Maximum attachment capacity (mg of Cu (kg of sand)<sup>-1</sup>). <sup>d</sup> Attachment constant (min<sup>-1</sup>). <sup>e</sup> Sum of squares of residuals. <sup>f</sup> Pearson's squared correlation coefficient.

Particle concentrations were determined by measuring light absorption in an  $80 \,\mu\text{L}$  flow-through cell from Hellma GmbH (Müllheim, Germany); measurements were made at 800 nm at 80 s intervals on a Jenway 6310 spectrophotometer. Effluent samples were collected with a fraction collector. Photometric readings were calibrated by correlating the total copper content in the collected samples with the light absorption measurements.

**Partition Tests.** Electrochemical retention of fungicide particles by the sand surface was studied in batch tests intended to elucidate the way the particles distributed between the suspension and collector surface. This involved mixing known amounts of fungicide with the electrolyte and quartz sand and thoroughly blending the mixture for 60 min, after which the sand was allowed to settle for 5 s and the concentration of fungicide particles in suspension measured as described above.

**Experimental Design.** The influence of ionic strength on the fungicide particle deposition rate was examined in column transport tests involving fungicide suspensions containing 0.01-100 mM NaNO<sub>3</sub> and deionized water. The low electrolyte concentrations used were intended to mimic heavy rainfall episodes when the soil solution is highly dilute. The parameters measured in each run included ionic strength, pH, and Zeta potential (**Table 4**).

The effect of changing the ionic strength in a single run was examined in three steps, namely, (i) deposition, which was done similarly as in the above-described transport tests; (ii) elution, which involved washing the quartz sand column containing the deposited fungicide with a fungicidefree solution at the same pH and ionic strength; and (iii) further elution with deionized water, which substantially reduced the ionic strength.

A third type of transport test involving two runs at a Darcy velocity of 0.57 or 2.86 cm min<sup>-1</sup> was performed in order to assess the influence of hydrodynamics on transport of the fungicide.

**Data Analysis.** Colloid transport in porous media can be described by using a modified form of the classical convection—dispersion equation (CDE) and the colloid attachment model. The attachment model assumes first-order kinetic attachment of colloids and uses an attachment coefficient that is reduced by effect of favorable attachment sites being filled or



**Figure 1.** Dependence of Zeta potential for the copper oxychloride colloids from CO-PG (black squares) and quartz sand (white triangles) on the solution ionic strength. Note the Zeta potential minimum at an ionic strength near 10 mM for the colloidal copper oxychloride from CO-PG.

increased by effect of filter ripening. Straining represents the trapping of colloid particles when colloids are retained in pores smaller than some critical size. For an aqueous suspension of monodisperse particles flowing vertically through a packed column of granular collectors, the one-dimensional form of the CDE with two-site kinetic attachment can be written as (18)

$$\theta \frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \theta \left( D \frac{\partial c}{\partial z} - Uc \right) - \rho_{\rm b} \frac{\partial (s_{\rm Att1})}{\partial t} - \rho_{\rm b} \frac{\partial (s_{\rm Att2})}{\partial t}$$
(1)

where *c* is the colloid concentration in the aqueous phase (N L<sup>-3</sup>), *t* (T) time, *z* the vertical spatial coordinate (L),  $\theta$  the volumetric water content (-), *D* the hydrodynamic dispersion coefficient (L<sup>2</sup> T<sup>-1</sup>), *U* the average pore-water velocity (L T<sup>-1</sup>), and  $\rho_b$  the bulk density of the porous matrix (M L<sup>-3</sup>), and  $s_{\text{Att}}$ (N M<sup>-1</sup>) are the concentrations of colloids attached to the two types of sites, which are denoted by subscripts 1 and 2, respectively. The rate of attachment to either type of site is given by

$$\rho_{\rm b} \frac{\partial(s_{\rm Att})}{\partial t} = \theta k_{\rm Att} \psi_{\rm Att} c - \rho_{\rm b} k_{\rm Det} s_{\rm Att}$$
(2)

where  $k_{\text{Att}}$  and  $k_{\text{Det}}$  are the first-order colloid attachment and detachment coefficients, respectively (T<sup>-1</sup>), and  $\psi_{\text{Att}}$  is a dimensionless colloid attachment function (–). Colloid deposition can be explored with the aid of various functions of the Langmuir (19), random sequential adsorption (RSA) (20), ripening, or depth-dependent attachment type (21, 22). The attachment coefficient  $k_{\text{Att}}$  can be determined in the light of the filtration theory (23), which provides a quasi-empirical formulation defining the attachment coefficient in terms of the median grain diameter of the porous medium (often termed the "collector"), pore-water velocity, and collector and collision (sticking) efficiencies, which account for colloid removal by diffusion, interception, and gravitational sedimentation (22, 23). We used the software HYDRUS-1D (18) to interpret the experimental particle breakthrough curves in light of the colloid filtration models and colloid attachment theory.

# **RESULTS AND DISCUSSION**

Electrokinetic Measurements. Figure 1 shows the Zeta potential for CO-PG and colloidal sand at concentrations over the range 0.01-100 mM. As can be seen, the potential decreased, to a greater negative value, with increase in electrolyte concentration up to 10 mM NaNO<sub>3</sub> and then increased, to a smaller negative value, at higher concentrations. A phenomenon known as "over-charging" (24), which is ascribed mainly to the presence of divalent counterions (25), was observed that affected electrophoretic mobility. The effect must have resulted from competition between Cu<sup>2+</sup> dissolved from the copper oxychloride and Na<sup>+</sup> added in the electrolyte for particle surfaces, since monovalent Na<sup>+</sup> cannot change the surface charge.

Propylene glycol present in CO-PG had no effect on electrophoretic mobility; in fact, the Zeta potentials measured in washed



Figure 2. Measured and fitted breakthrough curves for CO-PG colloids at a variable ionic strength: (a) DW, (b) 0.01 mM, (c) 10 mM, and (d) 100 mM. Fitted curves were obtained by using the RSA model with one (red line) or two deposition sites (blue line).

CO-PG water suspensions (without propylene glycol) and waterdiluted CO-PG (with propylene glycol) were identical.

The Zeta potential for the quartz sand was close to -55 mV at ionic strengths up to 10 mM and less negative (-27 mV) over the range 10–100 mM. Under these electrochemical conditions, transport of CO-PG may have been subject to electrostatic repulsion between surfaces. At higher electrolyte concentrations, weak attractive forces may form at the secondary minimum through accumulation of counterions in the diffuse layer, as described by the DLVO theory.

Effect of the Electrolyte on the Fungicide Transport Behavior. Tests conduced at variable electrolyte concentrations (Figure 2) revealed that the deposition rate of CO-PG particles increased with increasing ionic strength. This was a result of a decreased magnitude and range width for repulsive double layer interactions and, hence, of the energy barrier increasing as the ionic strength was raised (26). The ionic strength also influenced the shape of the breakthrough curves (BTCs), especially in their initial steps where the collector was still clean.

The experimental BTCs for the colloids were used to analyze particle deposition in terms of the dispersivity length of the columns (0.01 cm) as determined in the unreactive tracer tests with bromide ion. Various combinations of deposition models were used for this purpose (18). Convergence and uniqueness in the studied parameters were tested in multiple runs involving variable initial parameter values, all of which led to identical results. The experimental concentration profiles were not exponential; therefore, fungicide deposition could not be explained in the light of the first-order deposition model unless it was further modified by introducing some blocking functions. Including the experimental particle concentration profiles in the parameter estimation process had no effect on the final values of the fitted parameters, however. The best fit was obtained with the random sequential adsorption (RSA) model.

The RSA model was used to estimate the maximum attachment capacity,  $s_{max}$ , and attachment rate,  $k_{Att}$ . The model defines the attachment function as follows:

$$\psi_{\text{Att}} = 1 - 4a + 3.308a^2 + 1.4069a^3 \text{ for } s_{\text{Att}} < 0.8s_{\text{max}}$$
 (3)

$$\psi_{\text{Att}} = \frac{(1 - bs_{\text{Att}})^3}{2d_{50}^2 b^3} \text{ for } s_{\text{Att}} \ge 0.8 s_{\text{max}}$$
(4)

where  $b = s_{\text{max}}^{-1}$  and  $a = 0.546 \ s_{\text{Att}}/s_{\text{max}}$ ,  $s_{\text{max}}$  being the maximum solid-phase concentration (M M<sup>-1</sup>). Although the transport model based on one-site attachment reproduced the results quite accurately, the two-site RSA model provided much better predictions for the experimental BTCs (**Figure 2**). **Table 4** shows the best fitting parameters, which are discussed below.

Two distinct deposition sites were detected in all tests. Site 2 exhibited a low retention capacity (a result of the low concentration of sites available for attachment on the clean collector surface) that increased from 35 to 140 mg of Cu (kg of sand)<sup>-1</sup> with increasing ionic strength and high  $k_{\text{Att}}$  values that decreased from 6.67 to 2.44 min<sup>-1</sup> with increase in this variable. On the other hand, site 1 exhibited a high retention capacity (from 33 to 338 mg of Cu (kg of sand)<sup>-1</sup>) in addition to a slow kinetics (0.07–0.17 min<sup>-1</sup>).

The inverse relationship between  $k_{Att2}$  and the ionic strength is consistent with electrostatic repulsion between the fungicide particles and collector (Figure 1).

The results of these tests were compared with those of earlier experiments carried out with another copper oxychloride based fungicide, Oxicol-50 (COF), which is commercially available in a larger particle size (0.979  $\mu$ m) (13). We found substantial differences in transport behavior between the two fungicides, especially in their kinetics of attachment to slow sites. Thus,  $s_{max1}$  and the kinetic constant for COF were about 20 and 10 times greater, respectively, at concentrations ranging from 1454 to 5760 mg of Cu (kg of sand)<sup>-1</sup>.

The differences in deposition parameters between CO-PG and COF were examined in terms of particle interaction energies calculated in the light of the DLVO theory (27, 28), which uses a combination of London-van der Waals attractive forces and electrostatic double-layer repulsion forces. Constant-potential electrostatic double-layer interactions were calculated by using the expression of Hogg et al. (29). The Zeta potential for the fungicide particles and the sand as estimated from electrokinetic measurements was used instead of the respective surface potential for this purpose. Water dielectric constant was used for both fungicides since the low propylene glycol concentration employed (less than 40 mg  $L^{-1}$ ) had virtually no effect on this property for the CO-PG suspension. Therefore, only particle size (315 nm for CO-PG and 979 nm for COF) and Zeta potential were changed. DLVO interactions at four different ionic strengths (Figure 3a) revealed the presence of an energy barrier ranging from 143 to 2795  $k_{\rm B}T$  for COF and 146 to 1546  $k_{\rm B}T$  for CO-PG. Figure 3b, which shows the previous data on a different scale, allows easier viewing of the secondary energy minimum arising at electrolyte concentrations above 10 mM. The depth of the secondary minimum for CO-PG was -20.9 at I = 100 mM and -4.5 $K_{\rm B}T$  at I = 10 mM, whereas that for COF was about 3.5 times greater (viz. -72.8 at I = 100 mM and  $-14.6 K_BT$  at I = 10 mM). Therefore, both the height of the repulsive barrier and the depth of the secondary minimum increased with increasing particle size. Based on the DLVO theory, particle size is related to the sensitivity of particle-collector interactions to changes in ionic strength, which is consistent with the results of the transport tests. In fact, the small particle size of CO-PG accounts for its weaker retention relative to COF. However, the DLVO theory by itself cannot explain our particle deposition results in full (particularly those for COF at low ionic strengths). Although this remains a controversial subject (14, 17, 30), particle attachment under unfavorable conditions is generally ascribed to physicochemical heterogeneity in both particles and collector surfaces. The chemical heterogeneity of COF (13) may facilitate a variety of interactions favoring its retention. Thus, its pore structure was found to affect the results of the batch partitioning tests, where



**Figure 3.** (a) Plot of calculated DLVO interaction energy as a function of the separation distance for copper oxychloride particles [COF data from Paradelo et al. (*13*)] and colloids from the aqueous suspension of copper oxychloride (CO-PG) at a variable ionic strength. (b) Replotted data facilitating the identification of secondary minima.

the fungicide failed to attach to lose collector grains. Interestingly, there was greater sensitivity to the electrochemical conditions during transport (i.e., with the collector packed in a column) than in the batch tests (where the ionic strength had no effect).

**Three-Phase Test.** Based on the previous results, colloid attachment was assumed to depend on the electrolyte concentration. In order to confirm this assumption, a second test using variable electrolyte concentrations and a single breakthrough was conducted (*31*). **Figure 4** shows the BTC obtained in the three-phase test. A suspension of CO-PG containing 100 mg of Cu L<sup>-1</sup> in 100 mM NaNO<sub>3</sub> was applied during phase i to a column packed with quartz sand. A proportion of 8% of CO-PG particles was retained. Rinsing the column with 100 mM NaNO<sub>3</sub> during phase ii failed to elute a measurable amount of fungicide. Also, rinsing with deionized water during phase iii released a part of CO-PG previously retained on the column. These results confirm that the electrochemical conditions influence retention of the fungicide.

However, retention of particles in phase iii, where attachment of the fungicide was subject to a barrier, suggests the influence of additional factors such as physical heterogeneity and pore structure. Pore structure and surface roughness have been shown to influence retention in the three-phase test (14). Disruption of packed sand from the column and stirring with deionized water in a beaker caused all fungicide to be released to the suspension.

**Hydrodynamic Effects.** As can be seen from breakthrough curves (BTCs) obtained at different flow rates (**Figure 5**), reducing the rate five times decreased the maximum outflow concentration by 20%. As can be inferred from the fitted parameters for the two-site kinetic attachment model (**Table 5**), using a low flow rate increased  $s_{max2}$ . Also,  $k_{Att}$  at both sites decreased when the inflow rate became the limiting factor for particle attachment.

Hydrodynamic effects caused the retaining forces for the colloids at attachment sites to be very weak. The assumption of a hydrodynamic influence on particle attachment is consistent



**Figure 4.** Three-phase breakthrough curve for a suspension of fungicide particles in 0.1 M NaNO<sub>3</sub> deposited in phase i (from 0 to 80 min), eluted with 0.1 M NaNO<sub>3</sub> in phase ii (from 80 to 120 min), and further eluted with deionized water in phase iii (from 120 to 160 min). Experimental conditions: water velocity U = 2.83 cm min<sup>-1</sup>; collector diameter 0.032 cm; column diameter 1.5 cm; column length 5 cm; temperature 25 °C.



**Figure 5.** Breakthrough curves for CO-PG particles illustrating the influence of water velocity on particle attachment. Experimental conditions: collector diameter 0.032 cm; bed diameter 1.5 cm; bed depth 5 cm; temperature 25 °C. Symbols denote the results obtained at two different water velocities: U = 2.83 cm min<sup>-1</sup> (circles) and U = 0.566 cm min<sup>-1</sup> (triangles). Lines represent the values fitted to the two-site kinetic model.

 Table 5. Fitting Parameters for the Two-Site Random Sequential Adsorption

 Model As Estimated from Breakthrough Data for Saturated Packed Quartz

 Sand at Two Different Flow Velocities<sup>a</sup>

V <sup>b</sup>	s <sub>max2</sub> c	k <sub>a2</sub> <sup>d</sup>	s <sub>max1</sub> <sup>c</sup>	k <sub>a1</sub> <sup>d</sup>	SSQ <sup>e</sup>	1 <sup>2 f</sup>
2.83	35 (0.6)	6.67 (0.259)	33 (2.2)	0.07 (0.007)	0.001	1.000
0.56	42 (1.7)	4.69 (0.238)	185 (22.3)	0.07 (0.005)	0.004	0.999

<sup>a</sup>Standard errors are shown in parentheses. <sup>b</sup>Darcy velocity (cm min<sup>-1</sup>). <sup>c</sup>Maximum attachment capacity (mg of Cu (kg of sand)<sup>-1</sup>). <sup>d</sup>Attachment constant (min<sup>-1</sup>). <sup>e</sup>Sum of squares of residuals. <sup>f</sup>Pearson's squared correlation coefficient.

with the weak forces observed at the secondary minimum since increased shear stress forces would have pulled the attached colloids away (32). Colloid attachment was only possible in those collector regions where the torque from hydrodynamic shear acting on colloid particles adjacent to collector surfaces was less than the adhesive torque resisting detachment from the secondary minimum (32).

Based on the foregoing, the transport of copper as colloid particles in saturated porous media is influenced by the particle size of its formulation. The observed influence of particle size on the retention dynamics of colloidal copper oxychloride is consistent with the DLVO theory, but only if binding occurs at the secondary minimum favorable to attachment. Also, these results are consistent with those of previous studies where the deposition was ascribed to retention at the secondary minimum, which was more favorable (i.e., it occurred at a more negative potential) with small particles. Colloid transport should be incorporated into environmental impact assessment tests for copper from agricultural uses. Particle size is a major influential factor for the mobility of copper oxychloride. An accurate knowledge of the transport mechanisms of copper oxychloride based fungicide particles can help one design effective formulations with a view to reducing the impact on agricultural soils and groundwater.

## LITERATURE CITED

- (1) Komárek, M.; Vaněk, A.; Chrastný, V.; Száková, J.; Kubová, K.; Drahota, P.; Balík, J. Retention of copper originating from different fungicides in contrasting soil types. J. Hazard. Mater. 2009, 166, 1395–1402.
- (2) Pose, E.; Rial-Otero, R.; Paradelo, M.; López-Periago, J. E. Influence of soil characteristics on copper sorption from a copper oxychloride fungicide. J. Agric. Food Chem. 2009, 57, 2843–2848.
- (3) Fernández-Calviño, D.; Nóvoa-Muñoz, J. C.; López-Periago, E.; Arias-Estévez, M. Changes in copper content and distribution in young, old and abandoned vineyard acid soils due to land use changes. *Land Degrad. Dev.* **2008**, *19*, 165–177.
- (4) Moolenaar, S. W.; Beltrami, P. Heavy metal balances of an Italian soil as affected by sewage sludge and Bordeaux mixture applications. *J. Environ. Qual.* **1998**, *27*, 828–835.
- (5) Pietrzak, U.; McPhail, D. C. Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. *Geoderma* 2004, *122*, 151–166.
- (6) Ribolzi, O.; Valles, V.; Gomez, L.; Voltz, M. Speciation and origin of particulate copper in runoff water from a Mediterranean vineyard catchment. *Environ. Pollut.* **2002**, *117*, 261–271.
- (7) Rusjan, D.; Strlič, M.; Pucko, D.; Korošec-Koruza, Z. Copper accumulation regarding the soil characteristics in Sub-Mediterranean vineyards of Slovenia. *Geoderma* 2007, 141, 111–118.
- (8) European Council Directive 86/278/EEC of 12 June 1986 on the Protection of the Environment, and in Particular of the Soil, when Sewage Sludge Is Used in Agriculture, 1986, pp 6–12.
- (9) Paradelo, M.; Arias-Estévez, M.; Nóvoa-Muñoz, J. C.; Pérez-Rodríguez, P.; Torrado-Agrasar, A.; López-Periago, J. E. Simulating washoff of Cu-based fungicide sprays by using a rotating shear device. J. Agric. Food Chem. 2008, 56, 5795–5800.
- (10) Pose-Juan, E.; Paradelo-Pérez, M.; Rial-Otero, R.; Simal-Gándara, J.; López-Periago, J. E. Detachment of sprayed colloidal copper oxychloride-metalaxyl fungicides by a shallow water flow. *Pest Manag. Sci.* 2009, 65, 615–623.
- (11) Nóvoa-Muñoz, J. C.; Queijeiro, J. M. G.; Blanco-Ward, D.; Álvarez-Olleros, C.; Martínez-Cortizas, A.; García-Rodeja, E. Total copper content and its distribution in acid vineyards soils developed from granitic rocks. *Sci. Total Environ.* 2007, *378*, 23–27.
- (12) Nóvoa-Muñoz, J. C.; Arias-Estévez, M.; Pérez-Novo, C.; López-Periago, J. E. Diffusion-induced changes on exchangeable and organic bound copper fractions in acid soil samples enriched with copper. *Geoderma* **2008**, *148*, 85–90.
- (13) Paradelo, M.; Šimůnek, J.; Nóvoa-Muñoz, J. C.; Arias-Estévez, M.; López-Periago, J. E. Transport of copper oxychloride-based fungicide particles in saturated quartz sand. *Environ. Sci. Technol.* 2009, 43, 8860–8866.
- (14) Torkzaban, S.; Tazehkand, S. S.; Walker, S. L.; Bradford, S. A. Transport and fate of bacteria in porous media: Coupled effects of chemical conditions and pore space geometry. *Water Resour. Res.* 2008, 44, W04403.
- (15) Blake, G. R.; Hartge, K. H. Methods of soil analysis. Part 1: Physical and mineralogical methods, 2nd ed.; SAS, CSSA, SSSA: Madison, 1986; Vol. 5, pp 377–382.
- (16) Hossner, L. R. Dissolution for total elemental analysis. *Methods of soil analysis. Part 3. Chemical methods* 1996, 49–64.

- (17) Johnson, P. R.; Sun, N.; Elimelech, M. Colloid transport in geochemically heterogeneous porous media: Modeling and measurements. *Environ. Sci. Technol.* **1996**, *30*, 3284–3293.
- (18) Simunek, J.; Sejna, M.; Saito, H.; Sakai, M.; Van Genuchten, M. T. The Hydrus-1D Software Package for Simulating the Movement of Water, Heat, and Multiple Solutes in Variably Saturated Media, Version 4.0. Department of Environmental Sciences, University of California Riverside: Riverside, CA, 2008; Vol. 1, p 315.
- (19) Adamczyk, Z.; Siwek, B.; Zembala, M.; Belouschek, P. Kinetics of localized adsorption of colloid particles. *Adv. Colloid Interface Sci.* **1994**, 48, 151–280.
- (20) Johnson, P. R.; Elimelech, M. Dynamics of colloid deposition in porous media: Blocking based on random sequential adsorption. *Langmuir* 1995, 11, 801–812.
- (21) Bradford, S. A.; Simunek, J.; Bettahar, M.; Van Genuchten, M. T.; Yates, S. R. Modeling colloid attachment, straining, and exclusion in saturated porous media. *Environ. Sci. Technol.* **2003**, *37*, 2242–2250.
- (22) Rajagopalan, R.; Tien, C. Trajectory analysis of deep-bed filtration with the sphere-in-cell porous media model. *AIChE J.* 1976, 22, 523– 533.
- (23) Logan, B. E.; Jewett, D. G.; Arnold, R. G.; Bouwer, E. J.; O'Melia, C. R. Clarification of clean-bed filtration models. *J. Environ. Eng.* 1995, *121*, 869–873.
- (24) Quesada-Pérez, M.; González-Tovar, E.; Martín-Molina, A.; Lozada-Cassou, M.; Hidalgo-Álvarez, R. Overcharging in colloids: Beyond the Poisson–Boltzmann approach. *ChemPhysChem* 2003, *4*, 234–248.
- (25) Quesada-Pérez, M.; Martín-Molina, A.; Hidalgo-Álvarez, R. Simulation of electric double layers undergoing charge inversion: Mixtures of mono- and multivalent ions. *Langmuir* 2005, *21*, 9231–9237.

- (26) Elimelech, M.; Gregory, J.; Jia, X.; Williams, R. A. Particle deposition and aggregation: measurement, modelling, and simulation. Butterworth-Heinemann: Oxford, U.K., **1995**; p 433.
- (27) Derjaguin, B. V.; Landau, L. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochim. URSS* **1941**, *14*, 633–662.
- (28) Verwey, E. J. W.; Overbeek, J. T. G. Theory of the stability of lyophobic colloids. *Theory of the Stability of Lyophobic Colloids* 1948.
- (29) Hogg, R.; Healy, T. W.; Fuerstenau, D. W. Mutual coagulation of colloidal dispersions. *Trans. Faraday Soc.* **1966**, *62*, 1638–1651.
- (30) Tufenkji, N.; Elimelech, M. Breakdown of colloid filtration theory: Role of the secondary energy minimum and surface charge heterogeneities. *Langmuir* 2005, *21*, 841–852.
- (31) Hahn, M. W.; O'Melia, C. R. Deposition and reentrainment of Brownian particles in porous media under unfavorable chemical conditions: Some concepts and applications. *Environ. Sci. Technol.* 2004, 38, 210–220.
- (32) Torkzaban, S.; Bradford, S. A.; Walker, S. L. Resolving the coupled effects of hydrodynamics and DLVO forces on colloid attachment in porous media. *Langmuir* 2007, 23, 9652–9660.

Received for review January 29, 2010. Revised manuscript received May 4, 2010. Accepted May 5, 2010. This work was funded by Spain's Ministry of Science and Technology (Project AGL2006-04231/AGR) and Xunta de Galicia (Project INCITE 08PXIB 383190PR). M.P. was additionally funded by the predoctoral fellowship program of the University of Vigo.