



## Copper distribution in water-dispersible colloids of swine manure and its transport through quartz sand

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### ABSTRACT

To demonstrate the potential risks associated with the application of solid agricultural wastes, we investigated Cu distribution in water-dispersible colloids derived from swine manure and its transport through quartz sand. Samples were sequentially centrifuged to obtain five colloid suspensions ( $<10$ ,  $<1$ ,  $<0.45$ ,  $<0.2$ , and  $<0.02$   $\mu\text{m}$ ) and four colloid subsamples (1–10, 0.45–1, 0.2–0.45, and 0.02–0.2  $\mu\text{m}$ ). We observed that 2% of Cu in the swine manure was found in the 0.02–10  $\mu\text{m}$  colloid fractions, while 18% was observed in the  $<0.02$   $\mu\text{m}$  colloid suspension. The highest accumulation of Cu was found in the 0.02–0.2  $\mu\text{m}$  fraction of colloids, in which organic carbon was the major component. The Cu in the 1–10  $\mu\text{m}$  colloid fraction existed in both inorganic compounds and organic associations, whereas it mainly existed as organic complexes in colloids  $<1$   $\mu\text{m}$  ( $<0.53$   $\mu\text{m}$ , specifically). Furthermore, large colloids (1–10  $\mu\text{m}$ ) of swine manure were partially filtered out as they passed through the sand particles, and fine colloids facilitated the transport of Cu. The formation of organic complexes was hypothesized to enhance the mobility of Cu. Further research is needed to incorporate our experimental findings into a realistic model of particle mobilization and transport through soil or groundwater aquifers.

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### 1. Introduction

The land application of swine manure as an optional nutrient source or soil amendment has increased in recent years because it is not only more economically beneficial than using chemical fertilizer but also an environmentally friendly way to reduce manure pollution in areas with high swine densities. However, elevated concentrations of heavy metals in some of these swine or other animal production solid wastes may pose a significant threat to soil and groundwater qualities [1–3]. For example, swine feed and animal manure collected from England and Wales were found to contain Cu and Zn in the range of 150–2920 mg/kg and 18–227 mg/kg, respectively [4,5]. Similarly, the Cu concentration in swine manure under intensive farming conditions in China was found to be as high as 1726 mg/kg [6].

The transport of ionic or complex metals associated with dispersed colloid particles through soil macropores has been reported in several studies [7–11]. This colloid-mediated metal transport could explain the negative mass balance of metals found by some researchers attempting to account for losses of solid waste-applied heavy metals in soils [11]. Mobile colloids can have a great affinity

for heavy metals and may provide a vehicle for continuous metal transport due to their high organic carbon content and large surface area [11].

The role of heavy metals in the environment is directly related to their physicochemical forms [12,13]. In aquatic environments, heavy metals generally exist as free metal ions, inorganic complexes, organic complexes, and in association with colloids, where colloids are particles with diameters of less than 10  $\mu\text{m}$  [14]. The distribution of these metals among different species will depend on the nature of each metal, different chemical parameters (such as pH), the concentration of primary cations and anions, and the type and amount of organic and colloidal materials [15–17]. Generally, more than 80% of the colloids in the smaller size fractions ( $<1$   $\mu\text{m}$ ) are organic, while the larger colloids (1–100  $\mu\text{m}$ ) are primarily inorganic particles, particularly carbonates, silicates, and iron oxides [15,18]. Due to the high levels of organic matter, salts, and alkalinity in swine manure, heavy metals passed through a filter are likely to be present in different forms (e.g., fine colloidal matter and dissolved organic or inorganic complexes) [19]. The form, rather than the total concentration of a heavy metal, is more important in determining its availability for plant uptake or leachability into groundwater [20].

Due to the differences in the transport of the dissolved and particulate fractions of heavy metals, accurate estimation of the characteristics of dissolved and particle-associated metals is crucial. To date, efforts toward understanding the distribution of heavy metals in different particle size fractions have been focused on sys-

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**Table 1**  
Swine manure properties.<sup>a</sup>

Properties	Swine manure
pH <sup>b</sup>	8.4 ± 0.2
Moisture content <sup>c</sup> (%)	49.5 ± 1.3
Organic matter <sup>d</sup> (g/kg DW)	674.54 ± 27.76
Cation exchange capacity <sup>e</sup> (CEC) (cmol/kg DW)	42.01 ± 6.40
Total N <sup>f</sup> (g/kg DW)	18.74 ± 2.36
Total P <sup>g</sup> (g/kg DW)	5.33 ± 1.02
Metal content <sup>h</sup>	
Cu (mg/kg DW)	784.61 ± 22.24
Fe (g/kg DW)	6.07 ± 0.19
Al (g/kg DW)	12.64 ± 0.56
Ca (g/kg DW)	3.35 ± 0.13

<sup>a</sup> Mean ± S.E. (n = 3).<sup>b</sup> Sampler:water = 1:5.<sup>c</sup> Determined after drying to a constant weight at 105 °C.<sup>d</sup> Loss on ignition at 550 °C for 4 h.<sup>e</sup> Measured by the ammonium acetate method.<sup>f</sup> Measured by the Kjeldahl method.<sup>g</sup> Digested by HNO<sub>3</sub>-HClO<sub>4</sub> and determined using the colorimetric method of Murphy and Riley.<sup>h</sup> Digested by HF-HNO<sub>3</sub> and measured by inductively coupled plasma atomic emission spectrometer (ICP-AES).

tems such as landfill leachates [15,16], river sediments [21,22], runoff from residential and highway storm sewers [23–25], and drainage solutions from abandoned mines [17,26]. However, very little is known about the characteristics of colloidal-bound heavy metals in swine manure and its environmental fate in agricultural ecological systems.

The objectives of this study were as follows: (1) to assess the distribution of Cu in water-dispersible colloids and determine the characteristics of colloidal-bound Cu in swine manure and (2) to evaluate the mobility of colloid-bound Cu in various colloidal fractions (<10, <1, and <0.02 μm) and different forms (colloidal, dissolved and ionic) through saturated quartz sand.

## 2. Materials and methods

Swine manure was collected from Red Mountain Farm in Hangzhou, China (N30°3'E120°2'). Samples were placed in sealable plastic bags and stored under refrigeration at 4 °C with 80–90% RH. The basic characteristics of the manure are shown in Table 1.

### 2.1. Colloid generation

Water-dispersible colloids were fractionated from bulk samples of swine manure by placing 20 g of the sample in a 600 ml centrifuge tube, which was then brought to 600 ml volume with deionized (DI) water. The slurry was mixed using a reciprocating shaker for 1 h and centrifuged at 750 rpm for 3.5 min (Biofuge Stratos, Heraeus Instr., UK). The process was repeated twice for each 20 g of manure. After that, the colloid particles <10 μm remaining in suspension were decanted and saved as a stock solution [9].

### 2.2. Colloid fractionation

The particle size distribution of water-dispersible colloids was analyzed by fractional centrifugation [27] and gravimetric determination. The stock solutions (containing <10 μm colloids) were centrifuged at 5000 rpm for 8 min to obtain the <1 μm fraction. The supernatant was decanted and the colloids was re-suspended in DI water and centrifuged to ensure the recovery of any remaining 1–10 μm particles. This process was performed in triplicate, and the decanted supernatants from the three centrifuge runs were then pooled. The same process was performed to obtain the <0.45 and <0.2 μm fractions by centrifuging at 10,000 rpm for 10 min

and 50 min, respectively. To obtain the <0.02 μm fraction, the supernatants were ultracentrifuged (Preparative Ultracentrifuges, Beckman Instr., USA) at 70,000 rpm for 4 h [27].

This procedure resulted in the production of five colloid suspensions (<10, <1, <0.45, <0.2 and <0.02 μm) and four colloid subsamples (1–10, 0.45–1, 0.2–0.45 and 0.02–0.2 μm) (Fig. 1). The suspensions were stored at 4 °C in the dark and used within one week. The colloid subsamples were freeze-dried for analysis.

### 2.3. Physical and chemical analyses

The size distribution of colloid subsamples was studied by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instr., UK). Particle morphology was determined by transmission electron microscopy (TEM) (CM120, Philips Instr., Netherlands).

The Cu, Fe, Al, and Ca concentrations of the different samples were determined following acid digestion. Four-milliliter of high-purity nitric acid (G. R., 65–68%) was added to 25 ml of the sample, after which this mixture was digested at 220 °C on a hot plate and stored in the dark until analysis. Copper content was quantified using an atomic absorption spectrophotometer (AAS) (AA100, Perkin Elmer Instr., USA). The Fe, Al, and Ca concentrations were measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Instr., Japan). Samples for total organic carbon (TOC) analysis were acidified to a pH of 1–2 with H<sub>2</sub>SO<sub>4</sub> [24]. TOC was performed with a TOC analyzer (multi N/C 3100, Jena Instr., Germany) based on the principle of catalytic high-temperature oxidation. All analyses were performed in triplicate.

### 2.4. Cu adsorption isotherm experiments

Adsorption isotherms were generated to evaluate the affinity of the various colloids for Cu. Five-milliliter aliquots of 200 mg/L colloid suspensions were added to 10 ml test tubes containing 0–40 mg/L Cu and 0.001 M NaNO<sub>3</sub> as a background electrolyte solution. Samples were shaken on a reciprocating shaker for 24 h and centrifuged at 10,000 rpm for 50 min. The 0.02–0.2 μm fraction samples were ultracentrifuged at 70,000 rpm for 4 h. The Cu concentration in the supernatants was determined using AAS [9].

Due to the accumulated native Cu in the colloids, a modified Freundlich equation [Eq. (1)] was used to parameterize the adsorption isotherm data [28]:

$$Q_e + Q_0 = K_F(C_e)^n \quad (1)$$

where  $Q_0$  is the native adsorbed Cu;  $C_e$  is an equilibrium Cu concentration;  $K_F$  is the Freundlich coefficient; and  $n$  is the exponential factor.  $Q_e$  is the amount of Cu adsorbed to the colloids at  $C_e$ . The value of  $C_e$  at  $Q_e = 0$  is the zero equilibrium Cu concentration ( $C_{e0}$ ). A colloid at  $C_{e0}$  displays its maximum intensity for buffering Cu. The slope of the isotherm curve at  $Q_e = 0$  is the linear adsorption coefficient  $K_d$  (the distribution coefficient or the buffer intensity at the  $C_{e0}$ ). This is calculated by taking the derivative of the modified Freundlich equation [Eq. (2)] with respect to  $C_e$  at the  $C_{e0}$ :

$$K_d = \frac{d[K_F(C_e)^n]}{d(C_e)_{C_{e0}}} = nK_F(C_e)^{n-1} \quad (2)$$

All analyses were performed in triplicate, and the average values were used.

### 2.5. Colloid column experiments

Two separate series of experiments were carried out.

– First, step-input experiments were run to evaluate the role of colloids in the transport of Cu. Three different samples of colloid

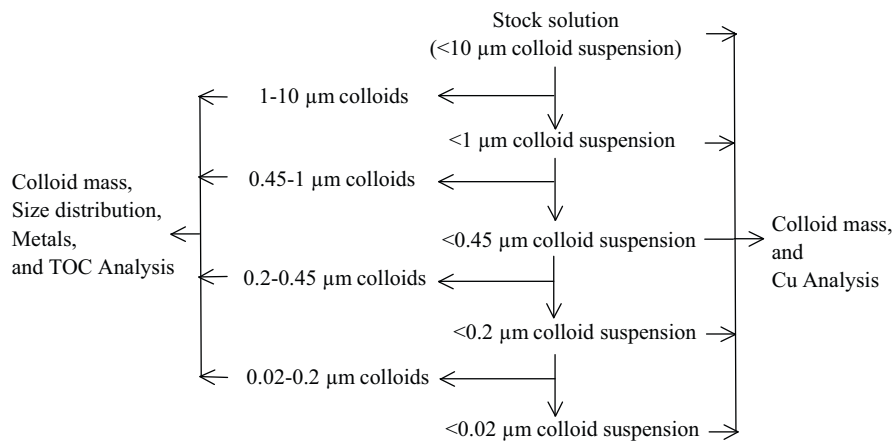


Fig. 1. Fractionation and analysis scheme for samples.

suspensions with particle sizes of  $<10\ \mu\text{m}$  (136.23 mg colloid/L),  $<1\ \mu\text{m}$  (120.67 mg colloid/L) and  $<0.02\ \mu\text{m}$  were prepared and adjusted to the same pH (pH 5).

- Second, short-pulse experiments were conducted to demonstrate the transport of Cu in different forms (colloidal, dissolved, and ionic). The injected solutions included the colloid suspensions of  $<10\ \mu\text{m}$  (2.61 mg Cu/L),  $<1\ \mu\text{m}$  (1.55 mg Cu/L),  $<0.45\ \mu\text{m}$  (1.48 mg Cu/L),  $<0.2\ \mu\text{m}$  (1.43 mg Cu/L), and  $<0.02\ \mu\text{m}$  (1.12 mg Cu/L), and a  $\text{Cu}^{2+}$  solution [1.46 mg Cu/L, prepared from  $>99\%$  purity  $\text{Cu}(\text{NO}_3)_2$  reagent, with 0.001 M  $\text{CaCl}_2$  as an electrolyte solution]. The total Cu concentrations and electrical conductivity of these injections were similar. The pH values were adjusted to 5 to avoid the hydrolysis and precipitation of Cu.

The column setup used for column experiments consisted of the following components: (1) a reservoir to contain injected solutions (colloid suspensions or  $\text{Cu}^{2+}$  solution); (2) a glass chromatography column (2.6 cm inner diameter, 10 cm length) packed with pure quartz sand (340–640  $\mu\text{m}$ ); (3) a fraction collector; and (4) a peristaltic pump to control the steady state upward flow.

After filling the column with pure quartz sand, the porous medium was washed by continuous injection of DI water, then saturated with electrolyte solution (0.001 M  $\text{CaCl}_2$ , pH 5) until a stable outlet pH value was obtained. Conservative tracer (2.0 mM  $\text{NO}_3^-$ ) breakthrough experiments were conducted to determine the pore volume (Pv) and the column Peclet number (Pe). For all the experiments, Pv was between 24.57 and 26.75 ml. The porosity varied from 0.51 to 0.56, and Pe remained higher than 100. The injection flow rate was 1 ml/min (pore water velocity  $\approx 24\ \text{cm/h}$ ). Then, 50 ml (approximately 2 Pv) and 2 ml (equivalent to 0.072–0.082 Pv) solutions were injected at the column entrance in the step-input experiments and short-pulse experiments, respectively.

A new column containing fresh sand was used for each experiment to avoid any possible contamination from the preceding experiment. The experiments were repeated twice in their entirety for reproducibility.

## 2.6. Leachate analysis

Effluents were analyzed periodically with respect to volume, Cu and colloid concentrations. Colloid concentrations were determined turbidimetrically by measuring the optical density of the suspension at 540 nm with an UV-vis detector [10]. The Cu concentration in the effluents was analyzed by AAS after adding 2 M  $\text{HNO}_3\text{--HCl}$  to extract the colloid-bound Cu. Breakthrough curves (BTCs) were constructed

based on metal and colloid concentrations (ratio of effluent concentration to influent concentration =  $C/C_0$ ) and pore volume.

Based on the assumption of first-order deposition kinetics, colloid BTCs resulting from step-input were evaluated by calculating the colloid deposition rate coefficient  $k$  according to Eq. (3) [29–31]:

$$k = -\frac{1}{t_p} \ln \left( \frac{C}{C_0} \right) \quad (3)$$

where  $t_p$  is the average travel time of the colloidal particles through the column;  $C_0$  is the influent colloid concentration; and  $C$  is the final effluent colloid concentration after the breakthrough curve has reached a plateau.

## 2.7. Statistical analyses

Prior to analysis, all data were examined by performing a homogeneity of variance test. For metals and TOC concentrations, an LSD multiple range test was used to compare differences between colloids of different sizes. All statistical analyses were performed with a SPSS version 17.0 software program at  $P < 0.05$  (\*).

## 3. Results and discussion

### 3.1. Colloid particle distribution

The morphologies and size distribution of the 1–10, 0.45–1, 0.2–0.45, and 0.02–0.2  $\mu\text{m}$  colloid fractions are shown in Fig. 2. Based on TEM micrographs, the particles were spheroidal to elliptical or erose-shaped and exhibited considerable surface glaze. The particle distribution ranges of the different size fractions were relatively narrow. Based on the DLS results, the fractions of 1–10  $\mu\text{m}$ , 0.45–1  $\mu\text{m}$ , 0.2–0.45  $\mu\text{m}$  and 0.02–0.2  $\mu\text{m}$  consisted of particles of 0.62–0.96  $\mu\text{m}$ , 0.26–0.53  $\mu\text{m}$ , 0.12–0.40  $\mu\text{m}$  and 0.07–0.40  $\mu\text{m}$ , respectively. Because the separation procedures used were centrifugation and ultracentrifugation, the separation efficiency was dependent on the particle size and density. Thus, obtaining precise size separation was not possible; instead, isolation of particles with similar characteristics, such as size and density, was achievable [15]. Notably, in Fig. 2, we used the volume percentage instead of the intensity percentage, as fine particles, especially those only a few nanometers in diameter, scatter very little light, and the presence of a few larger particles influenced photon intensity because they optically masked the small particles. On the basis of volume percentage, 70.8% of the particles in the 0.02–0.2  $\mu\text{m}$  fraction were in the range of 58.8–78.8 nm, and only 17.7% of par-

**Table 2**  
Mass distribution in colloids with different sizes and concentrations of metals and TOC.<sup>a</sup>

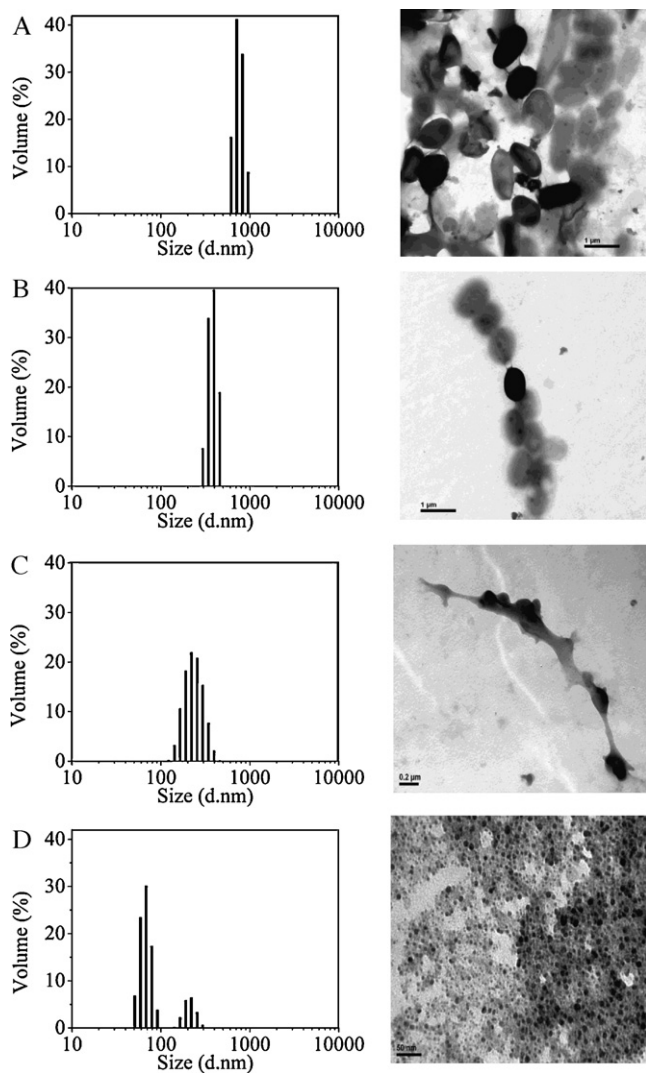
Colloid size ( $\mu\text{m}$ )	Mass distribution <sup>b</sup> (%)	Cu (mg/kg DW)	Fe (g/kg DW)	Al (g/kg DW)	Ca (g/kg DW)	TOC (g/kg DW)
1–10	66.2 $\pm$ 2.2	1560 $\pm$ 34b	11.41 $\pm$ 0.39c	72.12 $\pm$ 5.55	100.42 $\pm$ 3.91c	129.89 $\pm$ 60.15a
0.45–1	8.0 $\pm$ 1.5	1126 $\pm$ 148a	5.86 $\pm$ 0.56b	7.49 $\pm$ 0.64	9.69 $\pm$ 0.72a	402.74 $\pm$ 180.49b
0.2–0.45	3.2 $\pm$ 0.6	1038 $\pm$ 135a	1.47 $\pm$ 0.58a	nd <sup>c</sup>	23.96 $\pm$ 3.04b	225.57 $\pm$ 74.75ab
0.02–0.2	22.7 $\pm$ 3.0	3061 $\pm$ 171c	1.05 $\pm$ 0.14a	nd	25.03 $\pm$ 2.59b	523.56 $\pm$ 255.81b

<sup>a</sup> Mean  $\pm$  S.E. ( $n=3$ ) within column followed by the same letter are not significantly different as determined by LSD multiple comparison procedure using one way ANOVA ( $p < 0.05$ ).

<sup>b</sup> Mass distribution in the colloids of 0.02–10  $\mu\text{m}$ .

<sup>c</sup> nd: not detected (below laboratory reporting limit).

ticles were in the 164–255 nm range. No particles in the 20–50 nm range were observed, probably due to the limitations of DLS. The minimum detectable concentration by DLS is much higher for these fine particles. For the fractions of 1–10  $\mu\text{m}$ , 0.45–1  $\mu\text{m}$  and 0.2–0.45  $\mu\text{m}$ , approximately 75%, 81%, and 76.2% of the particles were in the range of 0.712–0.825  $\mu\text{m}$ , 0.342–0.459  $\mu\text{m}$  and 0.190–0.295  $\mu\text{m}$ , respectively. In all of the samples investigated, good agreement between the DLS results and the TEM particle sizes was observed.



**Fig. 2.** Transmission electron microscopy (TEM) and dynamic light scattering (DLS) analysis of colloids with different sizes. (A) 1–10  $\mu\text{m}$  colloids, (B) 0.45–1  $\mu\text{m}$  colloids, (C) 0.2–0.45  $\mu\text{m}$  colloids, and (D) 0.02–0.2  $\mu\text{m}$  colloids. Colloid concentration for DLS measurement was approximately 300 mg/L.

### 3.2. Distribution of metals and TOC in swine manure

Our results showed that approximately 80% of the total Cu in swine manure was associated with particles  $> 10 \mu\text{m}$  in size, which could be one of the reasons that organic manure has been used as a fixing agent in heavy metal-contaminated soils in the past 10 years. Approximately 18% of total Cu was present in the  $< 0.02 \mu\text{m}$  colloid suspension, but 2% was found in the 0.02–10  $\mu\text{m}$  colloid fractions. Research regarding the Cu distribution in runoff from residential and highway storm sewers showed that Cu was primarily associated with particles  $> 5 \mu\text{m}$  (up to 80%) or was dissolved ( $< 10 \text{kDa}$ ; approximately 22–100%) [24]. In contrast, Grout et al. [25] reported that, in urban stormwater runoff, Cu and Mg in colloids  $< 0.45 \mu\text{m}$  were undetectable. However, these colloids were found to be rich in Cr, Mn and Zn. Therefore, the difference in the Cu distribution is likely to be related to the characteristics of the materials.

In the 0.02–10  $\mu\text{m}$  colloids, the mass distribution in the 1–10, 0.45–1, 0.2–0.45, and 0.02–0.2  $\mu\text{m}$  ranges were 66.2%, 8.0%, 3.2%, and 22.7%, respectively. This meant that the dominant portion of the swine colloids was the 1–10  $\mu\text{m}$  (0.62–0.96  $\mu\text{m}$ , specifically) colloids. The concentrations of metals and TOC in colloids of different sizes are also listed in Table 2. Partitioning estimates showed that approximately 18.3% of Fe, Al, and Ca and 13% of TOC was in the 1–10  $\mu\text{m}$  colloids. These results indicated that Cu in these colloids existed in both inorganic compounds and organic associations. In the  $< 1 \mu\text{m}$  colloids, the proportion of Fe, Al, and Ca was 2.3–2.6%, and 22.6–52.4% of TOC was observed in these colloids. Aluminum was undetectable in the  $< 0.45 \mu\text{m}$  colloids. Colloids  $< 1 \mu\text{m}$  had high content of organic carbon, which was most likely humic substances [32], indicating that Cu mainly existed in organic complexes. The highest accumulation of Cu was found in the 0.02–0.2  $\mu\text{m}$  colloids (3061 mg/kg), and this was nearly two or three times greater than the accumulation in colloids measuring 0.2–0.45, 0.45–1 and 1–10  $\mu\text{m}$  (1038, 1126, and 1560 mg/kg, respectively). The highest concentration of TOC was observed in the 0.02–0.2  $\mu\text{m}$  colloids (523.6 g/kg), and the lowest content was found in the 1–10  $\mu\text{m}$  colloids (129.9 g/kg). There was no significant difference between the TOC levels in the 0.45–1  $\mu\text{m}$  and 0.02–0.2  $\mu\text{m}$  colloids. These results indicated that the concentrations of Cu and TOC did not follow the same order. Therefore, the mechanisms responsible for the Cu distribution may be not only associated with the amount of organic carbon but also related to the type of organic and inorganic constituents, colloid surface area, and charge properties.

### 3.3. Colloid affinity for Cu

The colloid affinity for Cu was assessed through a batch equilibrium experiment. The results indicated various degrees of affinity for Cu of swine manure colloids with different sizes. The data conformed better to the modified Freundlich equation (Table 3) than to the Langmuir equation (data not shown), as indicated by the high correlation coefficient values,  $R^2$ .

The affinity for Cu of these colloids followed the sequence 0.02–0.2  $\mu\text{m} > 0.45–1 \mu\text{m} > 1–10 \mu\text{m} > 0.2–0.45 \mu\text{m}$  according to

**Table 3**  
Modified Freundlich isotherm parameters and statistical fitness for Cu sorption by colloids with different sizes.<sup>a</sup>

Colloid size ( $\mu\text{m}$ )	$n$	$K_F$ ( $\text{L}^n \text{kg}^{-1} \text{mg}^{1-n}$ )	$R^2$	$K_d$ (L/kg)	$C_{e0}$ (mg/L)
1–10	0.4636	25,404	0.9797	297,240	0.0024
0.45–1	0.5839	34,698	0.9670	233,113	0.0028
0.2–0.45	0.6134	23,259	0.9425	101,260	0.0063
0.02–0.2	0.8084	71,203	0.7292	121,348	0.0204

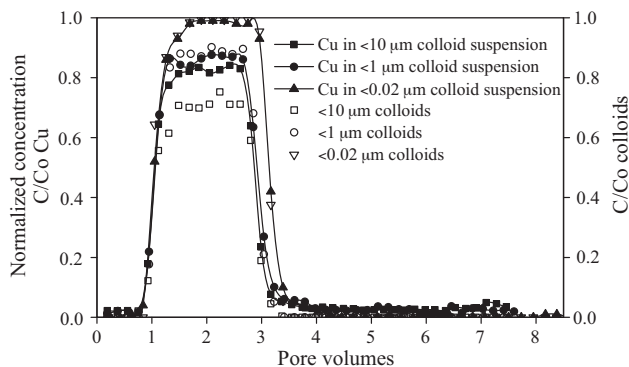
<sup>a</sup> Nine observation points for each colloid size range.

the values of  $K_F$ . The highest affinity for Cu being found for the 0.02–0.2  $\mu\text{m}$  colloids (approximately 2–3 times that of other colloid fractions) likely resulted from the higher TOC concentrations of these fractions, as well as the larger surface area of these fine particles than that of the other particle size fractions. The sorption capacity of colloids of 0.2–0.45  $\mu\text{m}$  was lower than that of colloids of 1–10  $\mu\text{m}$ . However, the concentration of TOC in the 0.2–0.45  $\mu\text{m}$  colloids was two-fold that of the 1–10  $\mu\text{m}$  colloids. This result indicated that higher concentrations of the inorganic components of colloids of 1–10  $\mu\text{m}$  might also play a role in sorbing Cu. In all cases, the  $n$  values of the Freundlich equation were less than 1, suggesting decreasing sorption energy with the increase in surface area [8].

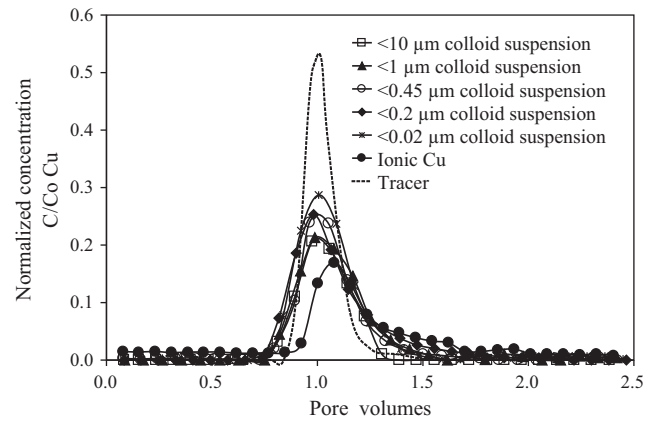
Colloid behavior with respect to Cu exchange in natural systems was best characterized by  $C_{e0}$  and  $K_d$  [28]. The highest  $K_d$  was found for the 1–10  $\mu\text{m}$  colloids (approximately two-fold that of the other size ranges), which indicated that these colloids had a strong potential to maintain a low Cu concentration in solution and a high buffering capacity with respect to external loading of Cu. Meanwhile, the high  $C_{e0}$  of the 0.02–0.2  $\mu\text{m}$  colloids demonstrated that this size range of colloids might serve as a sustained source of Cu input to uncontaminated zones of soil or groundwater aquifers.

### 3.4. Retention and transport of different colloids in saturated porous media

Step-input transport analysis of the different colloid suspensions was conducted. For all of the experiments, no significant difference was observed between the arrival time of Cu and colloids in any of the colloid suspensions (Fig. 3). Colloid transport occurred after approximately 1 Pv, and the transport curves reached a plateau, though they differed in  $C/C_0$  after approximately 1.5 Pv. Colloid effluents of the <10  $\mu\text{m}$ , <1  $\mu\text{m}$  and <0.02  $\mu\text{m}$  suspensions produced fairly symmetrical transport curves that reached maxima of 0.71, 0.88 and 0.99  $C/C_0$ , respectively. The final  $C/C_0$  value at the plateau decreased with increasing size of the colloids, possibly due to physical filtration effects [30]. Based on Eq. (3), the paral-



**Fig. 3.** Transport curves resulting from step-input experiments. The sand column was preconditioned with a  $10^{-3}$  M  $\text{CaCl}_2$  electrolyte solution at pH=5. The suspensions containing organic colloids were injected at a constant flow velocity of 1 ml/min for approximately two pore volumes. Then, the influent was switched to a  $10^{-3}$  M  $\text{CaCl}_2$  electrolyte solution at pH=5.



**Fig. 4.** Breakthrough curves for a conservative solute tracer ( $\text{NO}_3^-$ ), <0.2  $\mu\text{m}$  colloid solution, dissolved solution and  $\text{Cu}^{2+}$  solution through quartz sand. The sand column was preconditioned with a  $10^{-3}$  M  $\text{CaCl}_2$  electrolyte solution at pH=5. Short pulses (2 ml) of samples were injected at a constant flow velocity of 1 ml/min and then were switched to a  $10^{-3}$  M  $\text{CaCl}_2$  electrolyte solution at pH=5.

lel colloid deposition rate coefficient  $k$  was  $2.105 \times 10^{-4} \text{ s}^{-1}$  and  $8.081 \times 10^{-5} \text{ s}^{-1}$  for the <10  $\mu\text{m}$  and <1  $\mu\text{m}$  colloids, respectively. Bridge et al. [33] reported on colloid deposition in quartz sand using fluorescence imaging. The colloids used in their study were red fluorescent labeled 1.9  $\mu\text{m}$  latex microspheres with carboxylate surface groups having a negative surface charge at neutral pH. Based on the observed mobile concentration, first-order accumulation with a rate constant of  $(8 \pm 1.4) \times 10^{-4} \text{ s}^{-1}$  was suggested. The deposition rate coefficient of colloids in the <1  $\mu\text{m}$  colloid suspensions was lower than that in the <10  $\mu\text{m}$  colloid suspensions. This observation suggested a good transport ability of fine colloids through the sand column. The transport curves of Cu in the different initial suspensions were similar to colloids in these suspensions. The ratios of the effluent concentration to the influent concentration of Cu were 0.83, 0.86, and 0.97 for the <10  $\mu\text{m}$ , <1  $\mu\text{m}$  and <0.02  $\mu\text{m}$  suspensions, respectively. The final  $C/C_0$  value of Cu was higher than the value of the colloids in the <10  $\mu\text{m}$  suspension, which showed that fine colloids <1  $\mu\text{m}$  (<0.53  $\mu\text{m}$ , specifically) probably had a higher affinity for Cu than large colloids with sizes between 1 and 10  $\mu\text{m}$  (0.62 and 0.96  $\mu\text{m}$ , specifically). Compared with the <0.02  $\mu\text{m}$  colloid suspension, the lower  $C/C_0$  value of Cu and colloid in <10  $\mu\text{m}$  and <1  $\mu\text{m}$  colloid suspensions indicated that a portion of the colloids that associated with Cu were also deposited.

The transport of Cu in different forms (colloidal, dissolved and ionic) was described based on short-pulse experiments. The obtained breakthrough curves showed that Cu in the <0.2  $\mu\text{m}$  and <0.02  $\mu\text{m}$  colloid suspensions traveled slightly faster through the porous column than the conservative tracer (Fig. 4). Breakthrough occurred after approximately 0.77 pore volumes, which was probably due to chromatographic exclusion, in which colloidal particles were excluded from small pores and transported through part of the total pore space. This phenomenon has also been observed in other studies of colloidal particle transport and macromolecule transport in porous media [34–36]. In addition, the chemical form of Cu may play a role in the facilitated transport of pollutants. In our short-pulse experiments,  $\text{Cu}^{2+}$  traveled relatively more slowly than the conservative tracer. This was the result of the adsorption–desorption of  $\text{Cu}^{2+}$  by sand. The recovery of Cu in the short-pulse experiments was calculated by the ratio of the total mass of Cu in the effluent to that in the influent. The results showed that the recovery of Cu in the various injected solutions followed this sequence: less than 0.02  $\mu\text{m}$  colloid suspension (99%) > less than 0.2  $\mu\text{m}$  colloid suspension (94.4%) > less than 0.45  $\mu\text{m}$  colloid suspension (81.9%) >  $\text{Cu}^{2+}$  suspension (81.4%) > less than 1  $\mu\text{m}$  col-

loid suspension (72%) > less than 10  $\mu\text{m}$  colloid suspension (65.6%).

The different transport rates of Cu observed in the colloid suspensions and ion solutions emphasized the complexity of colloid-associated transport and could be attributed to a number of phenomena, as follows. (i) Increased mobility of organic components or colloids. Organic matter has a strong affinity for Cu. Such Cu-organic complexes would enhance the bioavailability and mobility of Cu [37]. In swine manure, the <0.2  $\mu\text{m}$  colloids and the dissolved fraction exhibited a considerable ability to facilitate metal transport through porous media. (ii) Increased deposition by large colloids. It was reported by Bradford and Bettahar [38] that for a given input concentration, decreasing the sand size and increasing the colloid size would result in increased mass retention in the sand near the column inlet, as well as lower relative concentrations in the effluent. With many particles (>300 nm in size) present, decreased mass recovery was observed in both the <1  $\mu\text{m}$  colloid suspension and the <10  $\mu\text{m}$  colloid suspension. (iii) Facilitated transport of fine colloids. Karathanasis and Johnson [9] reported that up to 50 times more Cu and Zn could be transported through soils in the presence of agricultural waste colloid suspensions compared with control treatments where no colloids were present. Zhang et al. [39] also reported that the Cu concentration in leachates with readily dispersible colloids of Aquic Vertisols was greatly increased after a 1.5 soil pore volume, whereas the Cu concentration in leachates with water was increased after a 4.5 soil pore volume. In our experiments, Cu breakthrough in the colloid suspensions occurred before that in the  $\text{Cu}^{2+}$  solution.

The accepted and regulatory cutoff between colloids and dissolved substances was set at 0.45  $\mu\text{m}$ , but this could result in colloidal materials being inadvertently measured as being dissolved. Although recent studies have begun to examine the colloidal fraction of metals in 0.45  $\mu\text{m}$  filtrates [15–17,21–25], the transport of metals found in <0.45  $\mu\text{m}$  colloids has been found to be scarce. Our findings demonstrated the important role of Cu-associated colloids from swine manure, especially in colloids <0.2  $\mu\text{m}$ , not only as a contaminant source but also as contaminant carriers.

Compared to studies on the transport of artificial colloids (latex microsphere or silica particle), our study was conducted using a natural contaminant-containing colloid source. The results demonstrated the roles of water dispersible colloids of different sizes in the transport of Cu accumulated in swine manure through an artificial porous medium. The effects and mechanisms of transport observed in our laboratory studies using well-sorted silica sand could be enhanced or diminished in the real world. Natural saturated systems have complex solution chemistry and include mixed colloidal phases (e.g., layer silicates, Fe-, Al-, and Si-oxides and natural organic matter), irregularly shaped interconnected pores, and wide pore- and particle-size distributions. Such chemical and physical heterogeneities would affect the colloid behavior at a range of spatial and temporal scales. Understanding colloid transport in partially saturated porous media represents a major challenge. In addition to all of the difficulties posed by physical and chemical heterogeneities in water-saturated systems, predictions of colloid transport in the vadose zone are further complicated by the presence of an air phase in addition to the solid and water phases present in saturated media. Therefore, further research is needed to incorporate our experimental findings into a realistic model of particle mobilization and transport through soil or groundwater aquifers.

#### 4. Conclusions

Isolation of water dispersible colloids with similar sizes was achievable by centrifugation. The Cu found in the 0.02–10  $\mu\text{m}$  colloids accounted for 2% of the total Cu in swine manure, and 18%

was observed in the <0.02  $\mu\text{m}$  colloid suspension. The dominant portion of swine colloids were in the 1–10  $\mu\text{m}$  (0.62–0.96  $\mu\text{m}$ , specifically) colloid fractions. Determination of the chemical composition of colloids showed that Cu in the 1–10  $\mu\text{m}$  colloids existed in both inorganic compounds and organic associations, whereas it mainly existed as organic complexes in the <1  $\mu\text{m}$  (0.53  $\mu\text{m}$ , specifically) colloids. The highest accumulation of Cu was found in the 0.02–0.2  $\mu\text{m}$  colloids, in which organic carbon represented the major component. The mechanisms of Cu distribution should be further studied by considering factors such as the type of organic and inorganic constituents, colloid surface area, total charge, and surface charge densities. Column experiments suggested that two mechanisms are likely to be involved in the observed colloid-associated transport: physical deposition effects for large colloids and chromatographic exclusion, in which colloidal and dissolved Cu-containing colloids and complexes are excluded from small pores and transported through part of the total pore space. Additionally, organic complexes are presumed to enhance the mobility of Cu. Our findings demonstrated the important role of Cu-associated colloids from swine manure, especially in the <0.2  $\mu\text{m}$  colloidal fraction, not only as a contaminant source but also as contaminant carriers.

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