

## Geochemical Modeling of Trace Element Release from Biosolids

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### Abstract

Biosolids-borne trace elements may be released to the environment when biosolids are used as fertilizers in farm land. Trace element leachate concentrations from biosolids are known to be limited by both organic and inorganic sorbent surfaces; this experimental evidence has not been previously verified with geochemical modeling of sorption reactions. In this study, pH-dependent leaching experiments and sorption isotherm experiments were coupled with a multisurface geochemical modeling approach. Biosolids samples were obtained from Toledo and Chicago wastewater treatment plants; their sorbent surfaces were defined and modeled as a combination of organic matter (OM) and Fe-, Al-, and Mn-oxides. The multisurface geochemical modeling approach was partially successful in predicting the pH-dependent leachate concentrations of As, Cd, Cr, Cu, Mo, Ni, and Zn. Both modeled and experimental data indicated that As and Mo in biosolids were bound to Fe-oxides; Cd, Cr, and Cu were bound mainly to OM; and as pH increased the fractions of Cd and Cu bound to Fe-oxides in the biosolids matrix increased. Ni and Zn were distributed between OM and Fe-oxides, and the percentage of each fraction depended on the pH. This study showed that the multisurface geochemical model could be used to generate As (and to a lesser extent Cd) Freundlich isotherm parameters for biosolids. However, the composition and reactivity of solid and dissolved OM was identified as a source of uncertainty in the modeling results. Therefore, more detailed studies focusing on the reactivity of isolated biosolids OM fractions with regard to proton and metal binding are needed to improve the capability of geochemical models to predict the fate of biosolids-borne trace metals in the environment.

**Key words:** biosolids; Visual MINTEQ; modeling; metal leaching; multisurface modeling

### Introduction

**B**IOSOLIDS ARE A byproduct of municipal wastewater treatment process that meet the regulatory requirements for recycling as specified in the U.S. Environmental Agency's 40 CFR Part 503 Rule (McFarland, 2001). Biosolids contain large amounts of nutrients such as N, P, K, and organic carbon (OC) that make them an excellent fertilizer. However, biosolids may also contain detectable levels of trace metals and As, which may pose human health and ecological risks if released to the environment.

There is a large body of literature on the fate and transport of trace metals and As from land-applied biosolids (Haynes *et al.*, 2009). It is now well known that only a fraction of the total trace element concentrations is available in biosolids (Haynes *et al.*, 2009) and other contaminated matrices (Kosson *et al.*, 2002). To evaluate the availability of trace elements,

sequential fractionation methods have been used and concentrations of trace elements in operationally defined biosolids fractions have been reported (Alvarez *et al.*, 2002; Alonso *et al.*, 2006). Yet, the interpretation of these data can be difficult because of lack of specificity, selectivity, and validity of sequential fractionation methods (Kot and Namiesnik, 2000). In equilibrium conditions, trace element availability in contaminated matrices is dictated by relevant sorption (Meima and Comans, 1998) or dissolution/precipitation reactions (Mijno *et al.*, 2004) and these reactions are largely affected by pH. Thus, leaching the contaminated matrix at varying pH conditions can be an effective alternative method for assessing the solubility and availability of trace elements in contaminated matrices (Kosson *et al.*, 2002). Batch pH-dependent leaching experiments have been successfully coupled with geochemical modeling to evaluate the processes that control metal release from natural aquatic sediments (Davis *et al.*, 1998; Wen *et al.*, 1998), contaminated soils (Weng *et al.*, 2001; Dijkstra *et al.*, 2004, 2009; Khai *et al.*, 2008), steel slag (Apul *et al.*, 2005), and municipal solid waste incinerator bottom ash (Meima and Comans, 1998). In geochemical modeling of these complex matrices, a multisurface approach can be used, in which

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aqueous complexation reactions, surface complexation reactions for different metal oxides, and cation–humic substance interactions are simultaneously simulated.

The multisurface geochemical modeling approach also holds promise for addressing some knowledge gaps related to the availability of trace elements in biosolids. The relative importance of organic and inorganic sorbents in biosolids has been a topic of controversy (Basta *et al.*, 2005). It has been hypothesized that following the cessation of application of organic byproducts such as biosolids, bound trace metals and As would be released into soluble forms due to loss of organic fraction, which occurs because of natural decomposition of organic matter (OM) and soil acidification (McBride, 1995). Prior experimental research has shown that the retention of trace metals in biosolids is attributed to not only the presence of OM but also oxides of iron (Fe), manganese (Mn), and Al (Merrington and Smernik, 2004; Basta *et al.*, 2005; Hettiarachchi *et al.*, 2006). Although it is known that both organic and inorganic surfaces play a role in metal availability from biosolids, the reactions between metals and these surfaces have not been previously investigated using the multisurface geochemical modeling approach; a description of the geochemical reactions affecting trace element availability has been missing in the literature.

The goal of this research was to improve the knowledge on how As and trace metals (Cd, Cr, Cu, Mo, Ni, Pb, and Zn) partition between organic and inorganic phases in the complex environmental matrix of biosolids and make use of this information to predict the release of these elements into solution. It was hypothesized that the biosolids matrix could be defined as a combination of minerals such as Fe-, Al-, and Mn-oxides, and OM such as fulvic acids (FAs) and humic acids (HAs), and that a multisurface geochemical modeling approach could be used to predict the solid–solution equilibrium concentrations of trace metals and As. A surface complexation modeling approach (Dzombak and Morel, 1990) was coupled with NICA-Donnan model (Kinniburgh *et al.*, 1999) to develop a multisurface geochemical model for biosolids. To achieve a general validity of the modeling approach, the surface complexation and NICA-Donnan models and associated parameter sets were not modified; in addition, only published thermodynamic and binding parameters were used without parameter fitting. The research hypothesis was evaluated by comparing model predictions to experimental data obtained from (1) equilibration experiments over a wide range of pH, and (2) isotherm experiments for As (anionic species) and Cd (cationic species). The developed model was

also used to evaluate the importance of organic and inorganic surfaces in the retention of trace elements in the biosolids matrix.

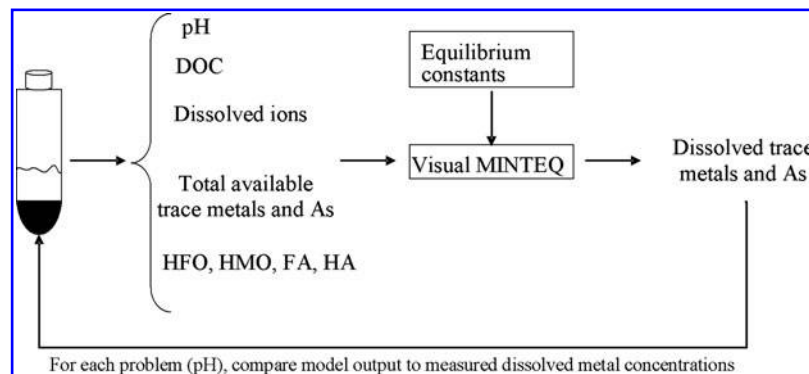
## Materials and Methods

A general scheme of how the multisurface geochemical modeling approach was used is presented in Fig. 1. The container on the left represents the experiments that were carried out to determine the necessary input parameters. The pH-dependent leaching experiments yielded the pH, dissolved OC (DOC), dissolved ions (background analytes concentrations of  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{SiO}_4^{4-}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Al}^{3+}$ , and  $\text{F}^-$ ), and total available trace element concentrations (As, Cd, Cu, Cr, Mo, Pb, Ni, and Zn). In modeling the pH-dependent leaching of trace elements, the total available concentration input in the model can be estimated from “availability” tests (Apul *et al.*, 2005) or from the total dissolved concentration of the element measured at the lowest (for cationic species) and highest pH (for anionic species) for a large pH range such as from pH 2–4 to 12 (Dijkstra *et al.*, 2008). In the present study, the highest dissolved concentration measured from the pH-dependent leaching experiments was used as the total available concentration. This approach is often used in modeling instead of the total element concentration of the sample because only a fraction of the total metal content is available and this availability is pH dependent (Kosson *et al.*, 2002). The selective chemical extractions yielded the concentrations of sorptive sites present in the system, which remained constant for all the simulations. The input parameters were introduced in the software along with the equilibrium constants for all the processes modeled and the model predicted the equilibration of the trace elements between the solid and aqueous phases for selected pH values. The model predictions were compared with the dissolved element concentrations measured in the equilibration experiments.

### Biosolids samples

Biosolids characteristics may vary based on different wastewater treatment plants (Haynes *et al.*, 2009). To evaluate the validity of the model, biosolids samples were obtained from two different wastewater treatment plants: Bay View wastewater treatment plant in Toledo, and Stickney Water Reclamation Plant of the Metropolitan Water Reclamation District of Greater Chicago. Toledo sample was collected in 2006 in an ~2.5-kg plastic container and brought to the

**FIG. 1.** General scheme for the multisurface geochemical modeling approach. DOC, dissolved organic carbon; FA, fulvic acid; HA, humic acid; HFO, hydrous ferric oxide; HMO, hydrous manganese oxide.



laboratory. Chicago sample (1.5 kg) was collected in 2005 and shipped in a glass container from Chicago to Toledo. Both samples were stored at 4°C until further processing, which took place within 1 month of collection. A subset of each sample was measured for its water content using ASTM Standard D 2216 (2005). The measured water content was used in estimating the dry mass basis of biosolids used in experiments.

#### Sodium hydroxide extraction of C from OM

The method of Gustafsson and van Schaik (2003) was followed for the extraction of C. Sequential extraction with HCl and NaOH was carried out to dissolve carbonates and OM (Fig. 2). About 1.00 g of sample (on a dry basis) was mixed with 20 mL of 0.02 M HCl and left to equilibrate for 16 h in a wrist-action shaker. The sample was centrifuged at 4,000 rpm for at least 15 min and the supernatant was separated and analyzed for total OC (TOC) and inorganic carbon (IC). The OC dissolved in this step was assumed to be from FAs and the IC was assumed to be carbonates. The remaining solid fraction was mixed with 20 mL of 0.1 M NaOH and left to equilibrate for 2 h in the wrist-action shaker. The sample was centrifuged at 4,000 rpm for at least 15 min and the supernatant was separated. The solid fraction was treated again with 0.1 M NaOH similarly to the previous step. The supernatants obtained from the two NaOH treatments were combined and two separate aliquots were obtained. The first aliquot was analyzed for TOC and IC; the OC dissolved in this step consisted of both FAs and HAs. The second aliquot was acidified with 0.02 M HCl to pH 2, which would cause the HAs to precipitate. The sample was centrifuged and the supernatant was separated and analyzed for TOC and IC. The OC dissolved in this step was assumed to be from FAs.

#### Selective chemical extractions for metal oxides

The experimental protocol of Dijkstra *et al.* (2004) was followed to obtain concentrations of reactive Fe-, Al-, and Mn-(hydr)oxide surface sites involved in surface complexation of trace elements. All extractions were done in triplicates for each sample. Iron and manganese from amorphous and crystalline Fe- and Mn-oxides were extracted with dithionite-citrate (van Reeuwijk, 1992). Specifically, 1.00 g of dry sample was mixed with 50 mL of citrate-dithionite solution (17% [w/v]  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  and 1.7% [w/v]  $\text{Na}_2\text{S}_2\text{O}_4$ ) and placed in a wrist-action shaker. The suspension was left to equilibrate for 16 h. The sample was centrifuged for at least 15 min at 4,000 rpm. The supernatant was filtered and diluted 10 times with deionized water. The sample was analyzed for Fe and Mn with inductively coupled plasma-optical emission spectroscopy (ICP-OES).

The ascorbate extraction method of Kostka and Luther (1994) was used to quantify iron associated with amorphous (hydr)oxides. A mass of 1.00 g dry sample was mixed with 100 mL of the ascorbate buffer solution (10 g of  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  and 10 g of  $\text{NaHCO}_3$  in 200 mL of deionized water, and 4 g of  $\text{C}_6\text{H}_8\text{O}_6$  for a final pH of 8.0) and placed in a wrist-action shaker. The suspension was left to equilibrate for 24 h. The sample was centrifuged for at least 15 min at 4,000 rpm. The supernatant was filtered and diluted with deionized water. The sample was analyzed for Fe with ICP-OES.

To estimate the aluminum (hydr)oxide concentrations, 1.00 g of sample (on a dry basis) was mixed with 100 mL of oxalate buffer solution and placed in a wrist-action shaker (van Reeuwijk, 1992). The oxalate solution was prepared by mixing 500 mL of 0.2 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and 380 mL of 0.2 M  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  to obtain a solution with pH 3.0. The suspension was left to equilibrate for 4 h in the dark. The

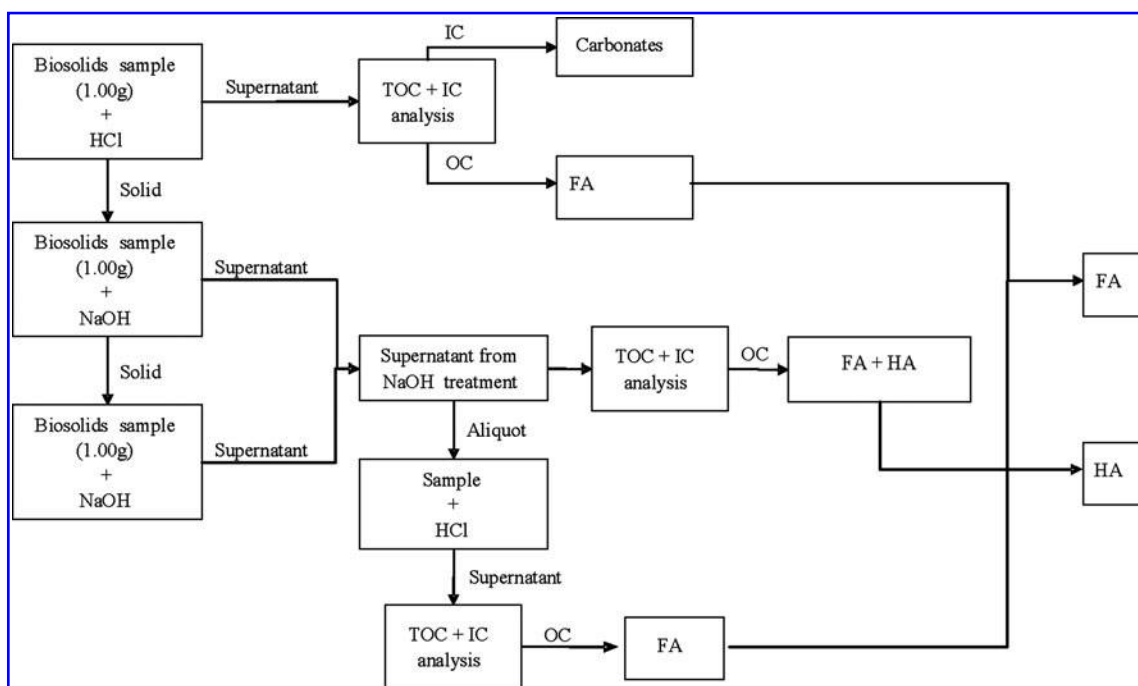


FIG. 2. Schematic of selective chemical extraction for OM. IC, inorganic carbon; OM, organic matter; TOC, total organic carbon.

sample was centrifuged at 4,000 rpm for at least 15 min, filtered, and then diluted five times. The supernatant was analyzed for total aluminum. It should be noted that the assignment of this fraction to aluminum (hydr)oxide is a simplification because in reality poorly ordered aluminosilicates and organically bound aluminum may also be included in this fraction.

### Equilibration experiments

Two types of equilibration experiments were conducted. In pH-dependent leaching experiments, first the buffering capacity of a subsample was measured by adding acid (2 M HNO<sub>3</sub>) or base (2 M NaOH) (Kosson *et al.*, 2002) (see Supplemental Fig. S1). Using the buffering capacity of the subsample, the pH of other subsamples was adjusted to values ranging from 2 to 12. The subsamples were then leached for 76 h in close containers (spherical-bottomed polycarbonate centrifuge bottles) placed in a wrist-action shaker. The liquid:solid ratio was 50 L/kg; 2.00 g biosolids (on a dry basis) was added to 100 mL of deionized water containing a background electrolyte concentration of 0.01 M NaNO<sub>3</sub>. After the agitation period, the subsamples were centrifuged at 2,500 rpm for 30 min and the subsamples' final pH and Eh were recorded. Three different aliquots were obtained from these pH-dependent leaching experiments: the first aliquot was immediately placed in vials and analyzed using a Shimadzu TOC-VCSH TOC analyzer for OC and IC; the second aliquot was analyzed using a Dionex ICS-1000 Ion Chromatography System for F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup>; the third aliquot was filtered through a 0.2- $\mu$ m membrane filter, preserved with ultrapure 2 M HNO<sub>3</sub>, and refrigerated at 4°C until analyzed for Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, and Zn using ICP-OES. Further, to provide an estimate of the aromaticity and the "humic-like" characteristics of the dissolved C in the batch experiments, the specific ultraviolet absorbance (SUVA) was measured at 254 nm for the "pH-dependent" extracts of the Toledo sample using a spectrophotometer.

Sorption equilibrium experiments were done and the leachate from them were processed in a way similar to the pH-dependent leaching experiments. However, no acid or base was added to the sample to adjust the pH; instead, subsamples were spiked with Cd and As. A Cd standard solution [Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O] and As standard solution (Na<sub>2</sub>HAsO<sub>4</sub> · 7H<sub>2</sub>O) were quantitatively added to give a known Cd or As concentration. Spiking with various concentrations of As did not change the pH of the subsamples much (average and standard deviation of pH: 6.8 ± 0.1), but the Cd-spiked samples had a slightly higher pH (average and standard deviation of pH: 7.4 ± 0.1). The amounts of Cd or As sorbed were calculated using equation (1):

$$q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

where  $q_e$  ( $\mu$ mol/g) is the adsorbed As or Cd quantity per gram of biosolids,  $M$  (g) is the mass of biosolids,  $V$  (L) is the solution volume, and  $C_i$  ( $\mu$ M) and  $C_e$  ( $\mu$ M) are initial and equilibrium As or Cd concentrations.

All experiments were performed at standard laboratory conditions; room temperature was ~20°C. All glassware used in various experiments were washed first with a deter-

gent, rinsed with deionized water three times, soaked in a 10% HNO<sub>3</sub> acid bath for 8 h, and then rinsed again with deionized water three times.

### Model platform

The model was implemented in the Visual MINTEQ software (Gustafsson, 2009). Visual MINTEQ allows for the incorporation of aqueous complexation reactions, dissolution of minerals, and sorption processes. The equilibrium constants for most aqueous species are from the NIST compilation (Smith *et al.*, 2003) and most constants for solid phases have been drawn from MINTEQA2 (USEPA, 1999).

### Modeling approach

In an initial set of oxidation/reduction simulations, the Eh (mV) and pH values and all dissolved species concentrations measured in equilibration experiments were input in the model; only aqueous complexation and oxidation/reduction reactions were allowed in these simulations. The oxidation/reduction simulations showed that the primary species of As, Mn, and Cr present in these conditions were AsO<sub>4</sub><sup>3-</sup>, Mn<sup>2+</sup>, and Cr(OH)<sub>2</sub><sup>+</sup>. Therefore, following the approach of Khai *et al.* (2008), in all other simulations, oxidation/reduction reactions were suppressed and As, Mn, and Cr were input in Visual MINTEQ as AsO<sub>4</sub><sup>3-</sup>, Mn<sup>2+</sup>, and Cr(OH)<sub>2</sub><sup>+</sup>. Next, saturation indices (SI) were estimated. In the SI simulations, pH values and all dissolved species concentrations measured in equilibration experiments were input in the model; only aqueous complexation reactions and complexation to dissolved OM (DOM) were allowed. The model calculated the SI of the aqueous sample with respect to different possible mineral phases at each pH value. Finally, the leaching processes and sorption isotherms were simulated by including NICA-Donnan (Kinniburgh *et al.*, 1999), surface complexation, and aqueous complexation reactions in the model configuration. To simulate pH-dependent leaching, total available concentrations were input in the model for trace elements of interest (As, Cd, Cr, Cu, Mo, Pb, Ni, Zn); these total available concentrations then partitioned among organic sorbent, inorganic sorbent, and aqueous phases. To simulate the effects of the background analytes, the dissolved concentrations of SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, SiO<sub>4</sub><sup>4-</sup>, Fe<sup>3+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, Al<sup>3+</sup>, and F<sup>-</sup> were input in the model as fixed values for each pH; thus, for background analytes, the model calculated the sorbed concentrations while the dissolved concentrations remained fixed (Dijkstra *et al.*, 2004). Sorption simulations were conducted in exactly the same way as pH-dependent leaching simulations except that the total available concentrations input as As or Cd varied for each isotherm point based on total As or Cd in the system.

In simulating pH-dependent leaching and sorption isotherms, the inorganic sites present in the system were assumed to be Fe-, Al-, and Mn-(hydr)oxides. Ideal solution was assumed; therefore, the activity of solids present could be quantified as their molar concentration in the overall solid solution. The diffuse layer surface complexation model for specific binding of cations and (oxy)anions to hydrous ferric oxide (HFO) (Dzombak and Morel, 1990) was included to account for sorption onto amorphous and crystalline Fe- and Al-oxides according to Dijkstra *et al.* (2004) and Apul *et al.* (2005), and the diffuse layer surface complexation model with

constants from Tonkin *et al.* (2004) was included to account for sorption onto Mn-oxides.

The specific surface areas used in the model for amorphous and crystalline HFO were 600 and 100 m<sup>2</sup>/g, respectively (Dzombak and Morel, 1990; Dijkstra *et al.*, 2004). The total amount of amorphous HFO was calculated from Fe concentration obtained from the ascorbate extraction (Fe-Asc) (Dijkstra *et al.*, 2004). The difference between Fe concentration from the dithionite extraction (Fe-Dith) and Fe-Asc was used to calculate the total amount of crystalline HFO (Dijkstra *et al.*, 2004). The total amount of Al-oxides was estimated using oxalate extraction data (Al-Ox), and their specific surface area and site density were assumed to be the same as for HFO (Dijkstra *et al.*, 2004). The concentration of hydrous manganese oxides (HMO) was calculated using a specific area of 746 m<sup>2</sup>/g (Tonkin *et al.*, 2004); total amount of HMO was calculated from Mn concentration obtained from the dithionite extraction (Mn-Dith).

The reactive OM was assumed to be composed of only FAs and HAs. The NICA-Donnan model (Kinniburgh *et al.*, 1999) with generic parameters (Milne *et al.*, 2003) was included to describe the interaction between cations and humic substances. The inputs required by this model are total concentration of FAs, HAs, DOC, the percentage of the DOC that is active DOM (ADOM), and the percentage of ADOM that is FA. Total concentrations of FAs and HAs were calculated from OC concentrations measured in the selective chemical extraction. FAs and HAs were assumed to be composed of 50% C and 60% C, respectively (McBride, 1994; Weng *et al.*, 2002). The percentage of ADOM assumed to be FAs was set at 100%; however, if there is not enough total FA to make up the total ADOM the model adjusted this parameter so that HA could contribute to ADOM. The ADOM/DOC ratio was set at the default value provided by Visual MINTEQ (1.4); this is close to the value of 1.3 that has been found to work well for soil systems in earlier modeling work (Weng *et al.*, 2002; Gustafsson and Kleja, 2005). However, because the properties of biosolids DOM is not well known, the present study included model simulations in which a lower ADOM/DOC ratio was used (0.25; see Results section).

#### Freundlich model parameter estimation

Isotherm data from experiments are often modeled using the Langmuir and Freundlich isotherm models, the former

typically providing better fits for systems with single, homogeneous sorbents and the latter providing better fits for systems with multiple, heterogeneous sorbents with variable binding affinities (Benjamin, 2001). These two models have only two parameters but can provide good descriptions of some isotherms (Benjamin, 2001). The experimental or modeled data in the present study could not be represented with the Langmuir isotherm. However, parameters for the Freundlich isotherm model were determined using the linearized form of the Freundlich equation:

$$\log q_e = \log K_f + n \log C_e \quad (2)$$

where  $q_e$  ( $\mu\text{mol/g}$ ) is the adsorbed As or Cd quantity per gram of biosolids,  $C_e$  ( $\mu\text{M}$ ) is the equilibrium As or Cd concentration, and  $K_f$  and  $n$  are the constants of the Freundlich isotherm.

## Results and Discussion

### Selective chemical extractions

Results from selective chemical extractions and relevant data collected from the literature are shown in Table 1. In general, the Toledo sample had higher concentrations of sorbents than the Chicago sample (Table 1). High concentrations of carbon in both samples suggest that OM is the most abundant sorbent. Carbon in FA and HA fractions were evenly distributed in the Toledo sample. The Chicago sample contained more FA but much less HA than the Toledo sample. The FA and HA contents of both samples were lower than those reported for New York City biosolids (Jaynes *et al.*, 2003). The HA content in the Chicago sample was comparable to the HA content of soils but the FA contents of both samples were much higher than those reported for soils (Dijkstra *et al.*, 2004).

Amorphous and crystalline forms of Fe-oxides were the most abundant inorganic sites in both samples. The Fe- and Mn-oxide concentrations in the Chicago sample were higher than the concentrations observed for soils (Dijkstra *et al.*, 2004). Toledo sample had much higher inorganic site concentrations than those of the Chicago sample and those reported for soils (Dijkstra *et al.*, 2004). Both samples also had much higher Fe- and Mn-oxide concentrations than those reported for Brisbane, Australia biosolids (Burton *et al.*, 2003).

TABLE 1. RESULTS FROM SELECTIVE CHEMICAL EXTRACTIONS

	Chicago sample	Toledo sample	Literature data
Natural pH	7.36 ± 0.01	6.67 ± 0.01	
Fe-Asc (mmol Fe/kg ± SD)	134.3 ± 12.5	471.0 ± 23.3	(1–54 <sup>a</sup> )
Fe-Dith (mmol Fe/kg ± SD)	270.4 ± 7.2	1,330.5 ± 41.2	(12–179 <sup>a</sup> ) (27 <sup>b</sup> )
Al-Ox (mmol Al/kg ± SD)	85.2 ± 11.1	163.1 ± 3.6	(2–111 <sup>a</sup> )
Mn-Dith (mmol Mn/kg ± SD)	15.8 ± 0.5	89.2 ± 3.6	(2.55 <sup>b</sup> )
Extractable fulvic acid (mol C/kg ± SD)	5.7	4.0 ± 0.2	(13.7 <sup>c</sup> ) (0.04–0.16 <sup>a</sup> )
Extractable humic acid (mol C/kg ± SD)	0.4	4.6 ± 0.5	(11.1 <sup>c</sup> ) (0.08–0.83 <sup>a</sup> )

<sup>a</sup>Dutch soils (Dijkstra *et al.*, 2004).

<sup>b</sup>Australia biosolids (Burton *et al.*, 2003). Following the method of Tessier *et al.* (1979), 0.04 M NH<sub>2</sub>OH · HCl was used in Fe- and Mn-oxide extractions.

<sup>c</sup>New York City biosolids (Jaynes *et al.*, 2003).

SD, standard deviation for the three replicates.

### Possible dissolved phases

Visual MINTEQ database included 208 possible mineral phases for the chemical species measured in the present study. Of these 208 mineral phases, 8 were found to be in possible equilibrium (i.e.,  $-1 < SI < 1$  for most pH values): quartz ( $\text{SiO}_2$ ), chalcedony ( $\text{SiO}_2$ ), cristobalite ( $\text{SiO}_2$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), calcite ( $\text{CaCO}_3$ ), zincite ( $\text{ZnO}$ ),  $\text{ZnCO}_3$ , and  $\text{Ca}_3(\text{PO}_4)_2$  (am2). Quartz has been reported to be the main mineral component in biosolids (Hsiao and Lo, 1997). Carbonate, silicate, and phosphate phases have also been reported as partially responsible for retention of trace metals in biosolids (Merrington and Smernik, 2004; Basta *et al.*, 2005; Hettiarachchi *et al.*, 2006). But these sorption processes were not modeled in the present study because there is a scarcity of literature data on surface complexation reaction parameters for these sorbents. Attempts to model zincite and  $\text{ZnCO}_3$  dissolution to predict dissolved concentrations of Zn were not successful. The dissolution of the other six relevant minerals was modeled both individually and simultaneously in an attempt to predict dissolved concentrations of the background analytes; however, combining dissolution of minerals with sorption models in a system with multiple components led to computer model errors; therefore, dissolution and precipita-

tion equilibriums of mineral phases were not modeled. Instead, the species included in these minerals were considered as background analytes and their aqueous concentrations were fixed in the pH-dependent leaching and sorption isotherm simulations.

### Oxyanions

The available As concentration for Toledo (0.6 mg/L) and Chicago (0.4 mg/L) samples were similar (Fig. 3). The pH-dependent leachate concentrations of As varied by almost 100 times for the Toledo sample and by only about 5 times for the Chicago sample. Ito *et al.* (2001) observed higher As availability (7.0 mg/L) in Japanese biosolids. However, similar to the Chicago sample, the As leachate concentrations from Japanese biosolids also only slightly increased with pH (from 1.5 to 7.0 mg/L from pH 1 to 11). Dissolved concentrations of As were lowest around pH 5. As the pH increased, the amount of As dissolved also increased. This observation is likely due to As binding to iron oxides in oxidizing environments (Hartley *et al.*, 2004; Sracek *et al.*, 2004); the surface charge of the iron oxides changes with pH from positive charge at lower pH values, which attracts the anions to negative charge at higher pH values, which then repels the anions.

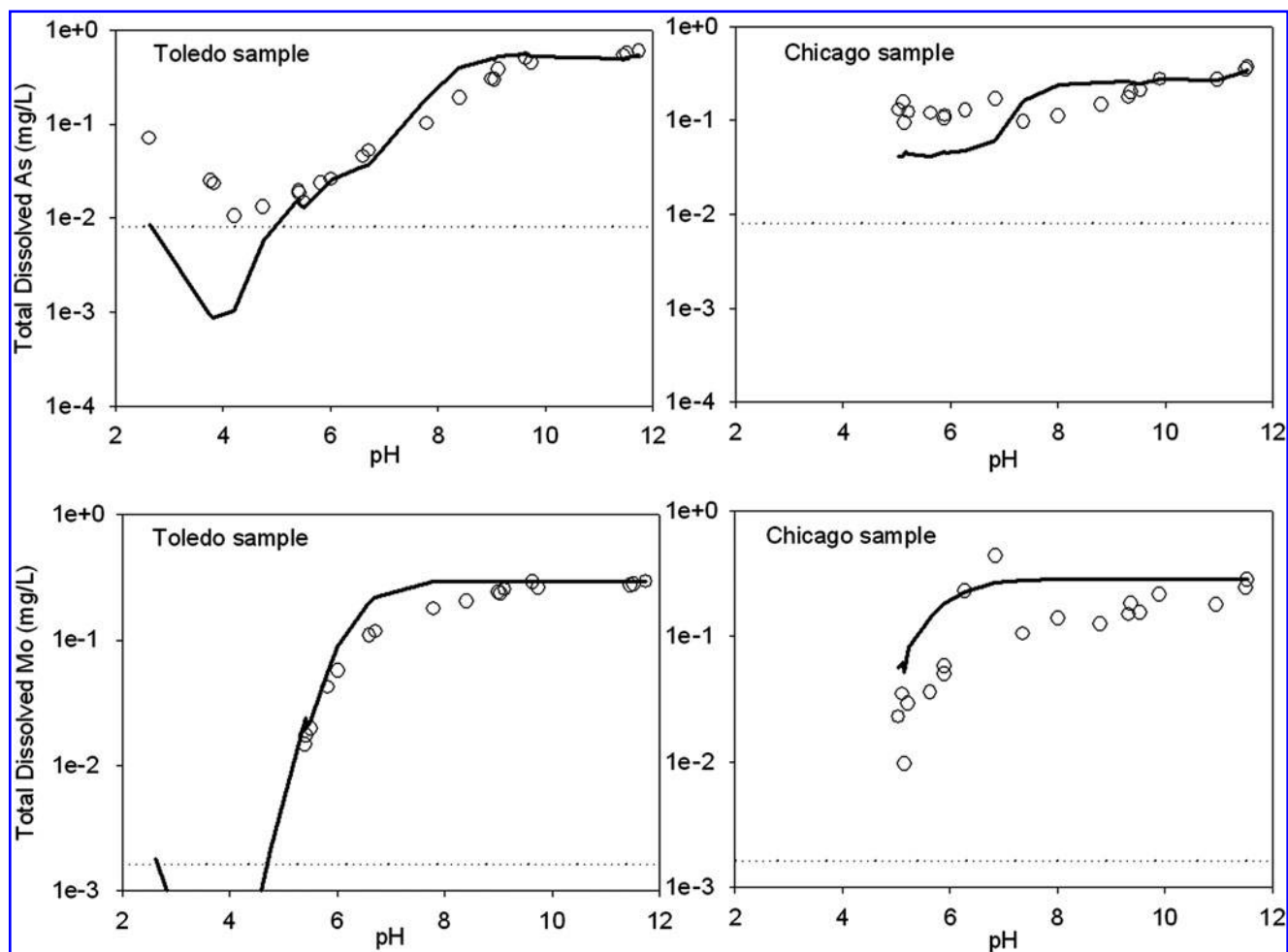


FIG. 3. Experimental (circles) and modeled (solid lines) results for As and Mo. Dotted line represents the method detection limit.



The match between the modeled and experimental data were good for both samples but much better for the Toledo sample except below pH 5 at which the model underestimated the dissolved concentration by more than an order of magnitude. One limitation of this modeling approach is that the concentration of Fe-oxides is kept constant throughout the pH range, when in reality some dissolution of Fe-oxides occurs at low pH values, which could account for the failure of the model at lower pH. Since the model only accounts for As sorption onto HFO, based on the modeling results it can be assumed that this sorption process dictated the binding of As in biosolids.

Total dissolved concentration of Mo displayed a similar pattern to that of As; concentrations increased with increasing pH. The model predicted that for pH values above 7, Mo was completely dissolved; however, in the pH-dependent experiments it was observed that the dissolved concentration of Mo increased with increasing pH. Increasing concentrations of Mo with increasing pH values as obtained in our model and pH-dependent leaching experiments are in good agreement with McBride *et al.* (2004), who found that CaCl<sub>2</sub>-extractable soil Mo increased as the pH increased.

#### ADOM/DOC ratio

To the authors' knowledge, the reactivity of the biosolids DOM in terms of proton and metal binding has not been previously reported for biosolids; therefore, the ADOM/DOC ratio is likely to represent a considerable uncertainty in the case of cationic elements (for oxyanions such as As and Mo, this parameter is of very little importance because As does not interact directly with OM in the model). It has been reported that biosolids humic compounds have a lower content of functional groups (carboxyls and phenolic hydroxyls) when compared with typical soils and other organic amendments (Sposito *et al.*, 1982; Boyd and Sommers, 1990; Pandeya and Singh, 2000; Bergkvist, 2003).

The SUVA determinations carried out for Toledo biosolids indicate a very low aromaticity of the extracted DOM (see Supplemental Fig. S2); on average the SUVA value was 0.62 L/(mg · C · m) across a range of pH values. Natural FAs and HAs commonly have SUVA values between 3 and 6 L/(mg · C · m) (Amery *et al.*, 2008; Yang *et al.*, 2008). This lends some additional support to the idea that the extracted DOM from biosolids may have weaker proton- and metal-binding properties than pure FAs or HAs. In the model, one can try to account for this by using a lower ADOM/DOC ratio than the one used for soil systems (1.3–1.4). The use of a lower ADOM/DOC ratio also provided better fits (in terms of lower root-mean square errors) for some trace metals. Therefore, included in results is a second model simulation in which the ADOM/DOC ratio was set at a very low value (0.25). It is possible that the "real" ratio is somewhere between these extremes (0.25–1.4). A related problem is the uncertainty of the values for solid-phase HA and FA in biosolids. In the model the NaOH is assumed to quantitatively extract OM as HA and FA; this assumption seems to work well for soils (Gustafsson and van Schaik, 2003; Dijkstra *et al.*, 2009). If, for biosolids, only a minor part of the OM is HA and FA, the model results for cationic elements will indicate weaker binding to HA and FA, which in turn will increase the dissolved concentration of these elements.

#### Cations

Both samples contained approximately equal concentration of available Cd and both samples displayed a very similar release pattern as a function of pH with minimum release occurring around neutral pH values (Fig. 4). The model with an ADOM/DOC ratio of 1.4 overestimated the dissolved concentrations of Cd, particularly between pH 5 and 8. After adjusting the ADOM/DOC ratio to 0.25 the model prediction for Cd for pH values below 8 improved considerably, providing good agreements with the experimental data, especially for the Toledo sample. For the Chicago sample, the adjusted model provided an improvement in its predictions; however, it still overestimated the dissolved concentrations for most of the pH range. Even the adjusted model predicted that Cd was mostly bound to OM (Table 2). Cd has very low affinity for HFO (Meima and Comans, 1998); however, some of the Cd was sorbed on HFO in the basic pH range.

Cr and Cu showed a similar dissolution pattern as a function of pH with considerably less release occurring between pH 4 and 6 (Fig. 4). Above pH 5, Cr and Cu concentrations increased, possibly because of the complexation with DOM. DOC concentration also increased in this pH range (see Supplemental Fig. S3). The model speciation results show that most of the dissolved Cr (~100%) and Cu (>90%) formed complexes with DOM in this pH range. Using an ADOM/DOC ratio of 1.4, the model showed a good agreement with the experimental data in the basic pH range but overestimated the dissolved concentrations in the acid pH range. In contrast, the model with a low ADOM/DOC ratio considerably improved the predictions for Cr and Cu in the acid side of the pH range, but provided poorer fits in the more alkaline pH range. OM was found to be the predominant reactive surface for Cr and Cu (Table 2), although at higher pH values the small fraction of Cu remained sorbed was found to be bound to Fe-oxides. Using the method of sequential extractions of Tessier *et al.* (1979), other researchers also found that Cu was mostly bound to OM or was a part of the residual fraction of the biosolids matrix (McLaren and Clucas, 2001; Burton *et al.*, 2003).

Chicago and Toledo samples showed a similar dissolution pattern for Ni as a function of pH; minimum release of Ni occurred around neutral pH (Fig. 5). Overall, the model using a higher ADOM/DOC ratio was able to describe the Ni results very well for both samples and there was very small difference in the outputs of the original and adjusted models in the acidic pH range. In the alkaline pH range, the model with a low ADOM/DOC ratio underestimated the total dissolved Ni for both samples.

In the geochemical model, Ni was bound to OM and oxides of iron (Table 2), which is in good agreement with the findings of McLaren and Clucas (2001), who reported that Ni was bound to the metal oxides and OM at high pH. Most of the sorbed Ni was bound to OM at low pH values and to HFO at higher pH values. Analysis of the adjusted model for the Toledo sample suggested that in the acid pH range, dissolved Ni was primarily as a free metal ion with >50% of dissolved Ni found as a free metal ion at pH 6.7; however, Ni formed complexes with DOM at higher pH values with 96% of dissolved Ni complexed with DOM at pH 7.8.

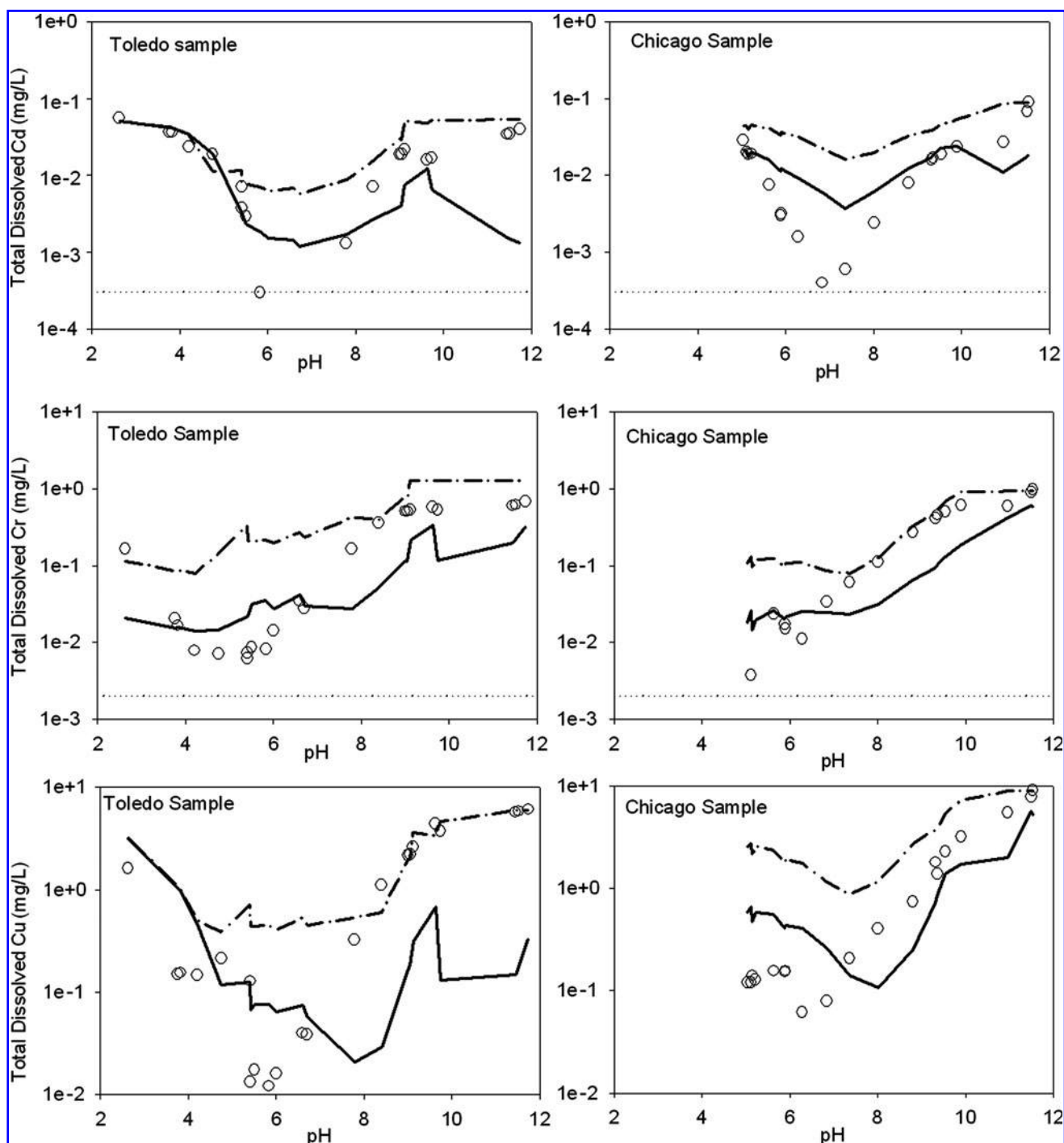


FIG. 4. Experimental (circles), model with ADOM/DOC = 1.4 (dashed line), and model with ADOM/DOC = 0.25 (solid line) results for Cd, Cr, and Cu. Dotted horizontal line represents the method detection limit. ADOM, active dissolved organic matter.

Dissolved concentrations of Pb were below the method detection limit in acidic conditions, but both samples showed an increasing concentration with increasing pH in basic conditions (Fig. 5). The model for Toledo was unsuccessful in predicting the dissolved Pb concentrations. At  $\text{pH} > 8$ , the model for Chicago sample was in good agreement with the experimental data and Pb was primarily bound to HMO in this pH range. The

adjusted model largely underestimated Pb leachate concentrations.

Minimum release of Zn occurred around neutral pH for both samples (Fig. 5). For the Toledo sample there was no difference between the predictions of the two models in the acid pH range; in the alkaline range the adjusted model underestimated the dissolved Zn concentrations more than the unadjusted model. For the Chicago sample, the model





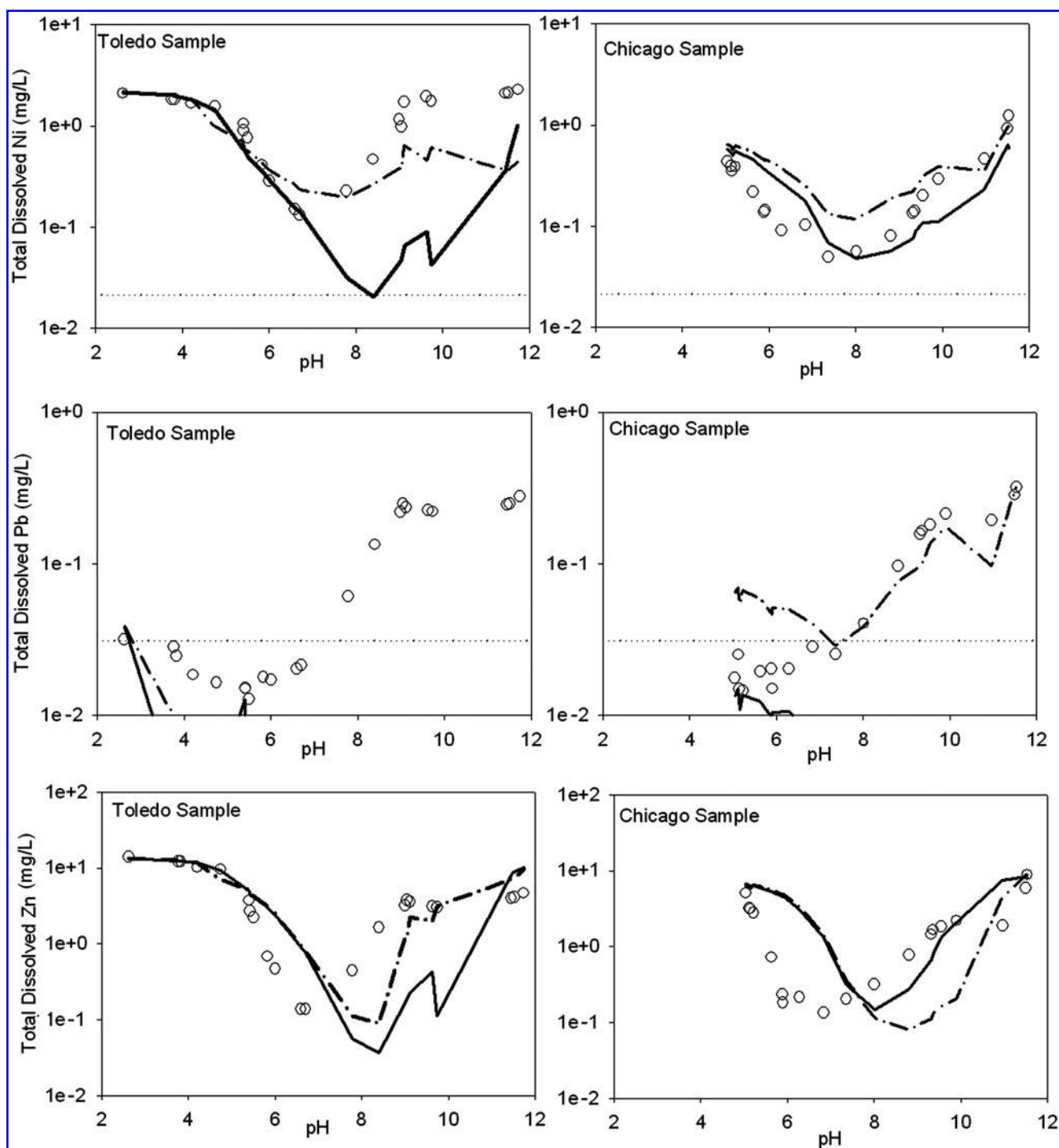


FIG. 5. Experimental (circles), model with ADOM/DOC = 1.4 (dashed line), and model with ADOM/DOC = 0.25 (solid line) results for Ni, Pb, and Zn. Dotted line represents the method detection limit.

employing a high ADOM/DOC ratio predicted the general v-shaped behavior but the predictions were off by  $\sim 1$  order of magnitude, and contrary to the results for other metals (and for results of Zn of the Toledo sample), the model with a low ADOM/DOC ratio provided better predictions in the alkaline pH range. Similar to Ni, Zn was bound primarily to OM at low pH values and to HFO at higher pH values (Table 2). A small fraction of sorbed Zn ( $<4\%$ ) was also found on HMO surfaces. These findings agree with the sequential extraction

results of Burton *et al.* (2003), who also reported Zn to be associated with primarily organic and Fe/Mn-oxide fractions of biosolids.

The results for cations showed that to a large extent the success of the model depended on assumptions regarding the reactivity of DOM. Modeling alone did not give a consistent clue as to which, of any, of the two extreme ADOM/DOC ratios would be the most realistic. In addition, it is possible that mineral-organic complexation constants are not the same

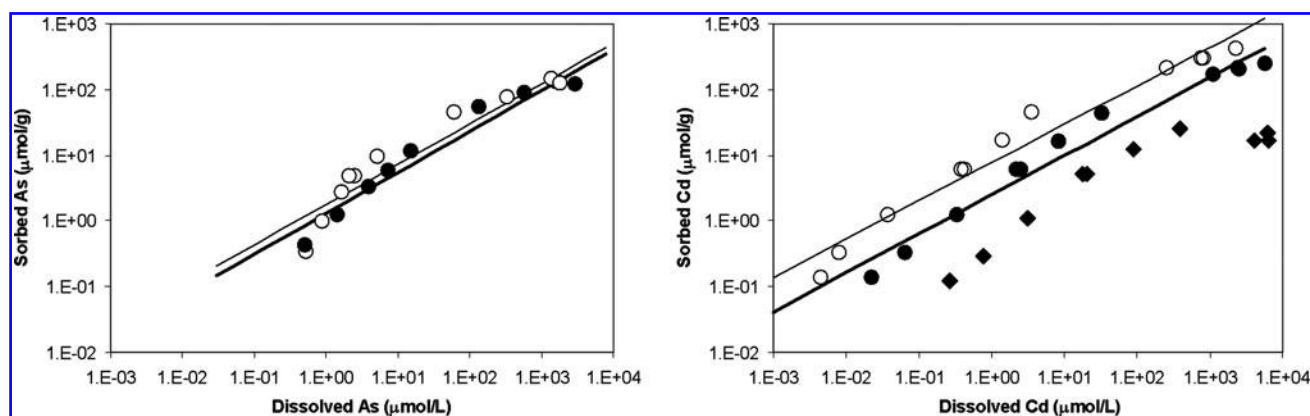


FIG. 6. Experimental (empty circles) and adjusted model (ADOM/DOC = 0.25; filled circles) results for Toledo biosolids isotherms. Filled diamonds represent the model without OM. Thin and thick straight lines are the Freundlich models fit to experimental and modeled data, respectively.

for biosolids DOM as for natural DOM. Therefore, more detailed studies focusing on the reactivity of isolated DOM fractions with respect to proton and metal binding are needed to improve the capability of geochemical models to predict the fate of biosolids-borne trace metals in the environment.

#### Sorption isotherms

As expected, when total concentrations in the system increased, both the dissolved and sorbed concentrations of As and Cd increased (Fig. 6). The maximum sorption capacity was not achieved in these experiments. The slope of the isotherms decreased with increasing total As and Cd concentrations, but the slopes did not completely level off. The isotherms showed that the Toledo biosolids had at least 45 mg Cd/g and 12 mg As/g sorption capacity. This sorption capacity for the Toledo sample for Cd was similar to the Cu maximum sorption capacity (50 mg Cu/g biosolids) reported for biosolids from Alabama (Bahaminyakamwe *et al.*, 2006).

The geochemical model fits the experimental isotherm data better for As than for Cd. The geochemical model for Cd followed a similar trend as experimental data, but it underestimated the experimental sorption isotherm within 1 order of magnitude. At low Cd concentrations, >90% of the Cd was in the sorbed phase, and as Cd concentration increased, the percentage of Cd sorbed decreased ultimately to half of the total available Cd in the system.

OM was the primary sorbent for Cd for the entire isotherm. At low Cd concentrations, >95% of the sorbed Cd was bound to OM. As total Cd concentration in the system increased, the inorganic sites became more important; up to 22% of sorbed Cd was found on the inorganic sorbents within the concen-

tration ranges studied. A model scenario in which the OM was completely removed showed that the biosolids still retained considerable sorption capacity for Cd even in the absence of OM, which is in good agreement with the findings of Hettiarachchi *et al.* (2003). In the scenario, without the OM, the sorbed concentrations did not continuously increase; they leveled off at a maximum sorption capacity of 2 mg Cd/g biosolids. Given a certain level of sorbed concentration, the corresponding dissolved concentration was at least 1 order of magnitude higher without the OM than with OM.

Linear regression fits of experimental and modeled data to equation (2) provided reasonably good  $R^2$  values for both As and Cd (Table 3). For As, Freundlich isotherm parameters  $K_f$  and  $n$  estimated from modeled data were very similar to those estimated from experimental data. For Cd, Freundlich isotherm constant  $n$  estimated for the modeled and experimental data were similar, but the  $K_f$  constant of the modeled isotherm was smaller than the  $K_f$  constant of the experimental isotherm.

#### Summary and Conclusions

In the present study, pH-dependent leaching experiments and sorption isotherm experiments were coupled with the multisurface geochemical modeling approach to study the leaching behavior and equilibrium reactions of trace metals and As in biosolids. Biosolids samples obtained from Toledo and Chicago wastewater treatment plants had either comparable or higher concentrations of organic and inorganic sorbents compared with soils (Dijkstra *et al.*, 2004). The multisurface geochemical modeling approach was partially successful in predicting the dissolution of trace metals and As from biosolids as a function of pH. Further, the modeling

TABLE 3. FREUNDLICH MODEL PARAMETERS FOR THE TOLEDO ISOTHERMS OBTAINED FROM LABORATORY EXPERIMENTS AND GEOCHEMICAL MODELING

	As		Cd	
	Experimental	Geochemical model	Experimental	Geochemical model
$n$	0.613	0.624	0.576	0.595
$K_f$	1.771	1.297	9.226	2.506
$R^2$	0.927	0.948	0.983	0.970

approach also successfully predicted (within 1 order of magnitude) the dissolved concentrations in isotherm experiments of As and Cd. The present study showed that the multisurface geochemical model could be used to generate As and (to a lesser extent) Cd Freundlich isotherm parameters for the Toledo sample. Thus, the geochemical modeling approach holds good promise for determining biosolids Freundlich isotherm parameters; such parameters can be useful as inputs to fate and transport models that include multiple processes (e.g., plant uptake, advection, diffusion, and dispersion) and therefore allow only a limited description (such as a two-parameter Freundlich model) of the solid-liquid equilibrium partitioning of metals.

Both the modeled and experimental data indicated that As and Mo in biosolids were bound to Fe-oxides; Cd, Cr, and Cu were bound mainly to OM; and as pH increased, the fractions of Cd and Cu bound to Fe-oxides in the biosolids matrix increased. Ni and Zn were distributed between OM and Fe-oxides, and the percentage of each fraction depended on the pH. Pb was primarily bound to HMO at pH above 8. Isotherms also showed that both organic and inorganic sites were responsible for retention of trace elements in biosolids. The model predictions for the sorption isotherms for Cd suggested that even in the absence of OM fraction, the biosolids may maintain a 2 mg Cd/g biosolids sorption capacity. However, from modeling results, it was observed that the dissolved concentrations in absence of OM may still be at least 1 order of magnitude higher than with OM in the biosolids.

For geochemical modeling purposes, the ADOM/DOC ratio as well as the metal-organic complexation constants and the reactivity and composition of the solid-phase OM represent considerable uncertainties that need to be addressed by obtaining more information on the properties of biosolids-derived OM. The present study was not able to include in the model the dissolution/precipitation reactions; this could be an important future step that could lead to improved model predictions.

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### Author Disclosure Statement

No competing financial interests exist.

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