Sorption of Oxytetracycline to Iron Oxides and Iron Oxide-Rich Soils

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The sorption interactions of oxytetracycline with goethite, hematite, and two iron oxide-rich soils were investigated using batch sorption experiments. Oxytetracycline sorption coefficients for goethite and hematite increased with pH to maximum values at pH ~8. The sorption edge shape and desorption treatments were consistent with a surface complexation mechanism and could be described by the interaction of divalent anion species with the oxide surface. Oxytetracycline sorption to Georgeville and Orangeburg Ultisol soils decreased with pH. Chemical digestion treatments were used to deduce that soil sorption occurred by complexation to oxide coatings on clay and quartz grains. These results indicate that sorption models must consider the interaction of oxytetracycline, and other similar ionogenic compounds, with soil oxide components in addition to clays and organic matter when predicting sorption in whole soils.

Introduction

The concentrated use of veterinary pharmaceuticals in areas of intense animal husbandry requires improved understanding of the fate of these bioactive compounds in environmental systems. Estimates of antibiotic releases from animal husbandry range from 6600 to 9900 t annually in the U.S., given that about 11,000 t of antibiotics are used each year (1) and that metabolism rates are only 10–40% (2). Resulting concentrations of up to 20 mg/L tetracycline and 40 mg/L sulfadimidine have been detected in liquid manure (see ref 3), while up to 1 mg/L chlorotetracycline has been measured in swine lagoon samples (4). Land application of untreated antibiotic-containing animal wastes has the potential to promote the development of antibiotic resistance among bacterial populations (5–7) or to induce biological responses in nontarget organisms (8). The extensiveness of these biological impacts depends, in part, on the degree to which antibiotic compounds are transported or undergo reactions after release to soil systems. Typical approaches for estimating the fate of contaminants in soils have used solid–water sorption coefficients, Kd, to estimate the factor by which contaminant movement is retarded relative to water percolating through soils (9). At present, Kd values for antibiotics and other veterinary pharmaceuticals must be obtained experimentally. Efforts to predict antibiotic sorption using models developed for nonpolar organic compounds that interact by van der Waals forces underestimate actual antibiotic sorption to soils/sediments by orders of magnitude (10). Moreover, the available experimental values of Kd give little insight into mechanisms of antibiotic interaction with soil/sediment solids and thus are unique to the particular sorbate–sorbent pairs studied (11–16). Thus, there is a need to understand sorption interactions of veterinary pharmaceuticals with soils, sediments, and aquatic particles so that more appropriate mechanism-based predictors can be developed to estimate Kd for evaluations of the mobility, reactivity, and bioavailability of these compounds.

The chemical structures of veterinary antibiotics give clues as to their expected interactions with soil components. For example, oxytetracycline, like most other high-use antibiotics, is a weak polyprotic acid (Figure 1). Thus, dissolved species may have net charges that are positive (pH < 3.6 for oxytetracycline), neutral (3.6 < pH < 7.5), or negative (pH > 7.5). Positively charged species can be expected to undergo cation exchange reactions on clay minerals as has been demonstrated in model sorbent studies (11, 17–21). Unlike the well-characterized interaction of oxytetracycline with clays, sorption to oxide surfaces has not been investigated in detail (22). It is reasonable to postulate that oxytetracycline will interact with soil oxide components because (i) tetracycline compounds are known to complex iron and aluminum in solution (23, 24) and (ii) other polar organic compounds with similar hydroxy, keto, and amine functional groups as oxytetracycline sorb to iron and aluminum oxides (25–28). Detailed study of oxytetracycline sorption to model oxide surfaces is necessary to understand potential antibiotic interactions in soil/sediment aggregates.

The importance of soil oxide components for oxytetracycline sorption to clays has been indicated with statistical approaches. As part of our larger study of antibiotic interactions with soil and sediment phases, Jones et al. (30) measured oxytetracycline sorption to soils with a wide range of soil properties. They deduced that soil texture, exchangeable cation capacity, and free/crystalline oxide content were the most important determinants of oxytetracycline sorption. The positive correlation between oxytetracycline sorption coefficients and soil descriptors of cation exchange capacity and oxide content are clearly consistent with the hypothesized interaction mechanisms for oxytetracycline. The statistical evaluation of oxytetracycline sorption was limited to pH 5.5; thus, the importance of exchange capacity versus oxide

FIGURE 1. Fully protonated form of oxytetracycline showing the acid dissociation constant (29) of relevant functional groups. The bar indicates the charge of the dominant solution phase species as a function of pH. Note that the vertical bars correspond to the pH at which equimolar concentrations of adjacent species are present.

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content at other pH values is unknown. Furthermore, since mass based analyses were used to characterize many soil properties, the statistical measures did not account for aggregate effects. For example, surface coatings may decrease the effective amount of sorbent available for sorbate uptake, as was the case for organic matter coatings on clays (e.g., refs 27 and 31). Alternatively, the aggregation of sorbent components may act to alter sorption coefficients from the range expected for pure sorbents. Celis et al. (32) observed an increase in atrazine sorption to clay in binary montmorillonite/ferrihydrite mixtures that they attributed to sorbate protonation by partially dissociated waters of hydration surrounding iron hydroxy polymers in the clay interlayers. Thus, accurate assessments of oxytetracycline fate in soil systems require knowledge of competition among potential sorbents for the sorbate species.

The purpose of this work was to investigate oxytetracycline sorption to iron oxides. Model sorbent studies with goethite and hematite were first conducted to evaluate the mechanism of oxytetracycline sorption with oxides, independent of other competing sorbents. \( K_d \) as a function of pH was fit with a surface complexation model to calculate an intrinsic iron oxide sorption coefficient for oxytetracycline. The importance of oxytetracycline oxide interactions in real soil aggregates was evaluated for two iron oxide-rich Ultisols. Several treatments were applied to isolate oxide interactions from oxytetracycline sorption to other components of these soils.

**Experimental Procedures**

**Materials.** Oxytetracycline hydrochloride was used as received from the USB Corporation (Cleveland, OH). Sodium and magnesium salts and sodium phosphate monobasic were all certified ACS reagents from Fisher Scientific (Pittsburgh, PA). Sodium azide (99%), PIPES (1,4-piperazinebis(ethane-sulfonic acid), \( \sim \)98.5%), the disodium salt of ethylenediaminetetraacetic acid (EDTA), and sodium hydroxide pellets were obtained from Fisher Scientific. HPLC grade methanol (HPLC grade) and hydrochloric acid (trace metal grade) were from Fisher Scientific. HPLC grade methanol and certified ACS grade phosphoric acid were from J. T. Baker (Phillipsburg, NJ).

**Analytical.** Aqueous oxytetracycline concentration was quantified by HPLC (HP 1050 with DAD) using a Lichrospher RP-18 endcapped column (15 cm \( \times \) 0.46 cm with matching guard column, 5 \( \mu \)m particle size) from Alltech Associates (Deerfield, IL). Samples were eluted isocratically with a mobile phase of 0.02 M phosphate buffer at pH 2.5 (80%) and acetonitrile (trace metal grade) were from Fisher Scientific. HPLC grade methanol and certified ACS grade phosphoric acid were from J. T. Baker (Phillipsburg, NJ).

<table>
<thead>
<tr>
<th>TABLE 1. Sorbent Surface Area by N₂ BET Adsorption</th>
<th>sorbent</th>
<th>surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>17.8*</td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>11.1*</td>
<td></td>
</tr>
<tr>
<td>Georgeville digested Georgeville</td>
<td>34.3</td>
<td></td>
</tr>
<tr>
<td>Orangeburg digested Orangeburg</td>
<td>15.4</td>
<td></td>
</tr>
</tbody>
</table>

* Using EGME method (33).

2000. The specific surface area of goethite measured using the ethylene glycol monoethyl ether (EGME) method (33) was 17.8 m²/g (Table 1). A surface site density of 5.5 OH/nm² and intrinsic acidity constants of 6.7 (\( pK_a \)) and 9.0 (\( pK_a \)) were obtained using potentiometric titrations (34). Hematite mineralogy was also confirmed by X-ray diffraction using Phillips XRG 3000 (35). The specific surface area of hematite using the EGME method was 11.1 m²/g, which was comparable to a previously published N₂ BET value (35). A surface site density of 1.2 OH/nm² and intrinsic acidity constants of 4.9 (\( pK_a \)) and 9.0 (\( pK_a \)) were obtained using standard potentiometric titrations (36).

Two highly weathered Ultisol soils, rich in oxides and clays, were used in this study. Georgeville B horizon (69–94 cm) soil was obtained from Duke Forest in the North Carolina Piedmont (25), while Orangeburg B horizon (45–60 cm) soil was from the Coastal Plains of North Carolina (30). The soil samples were air-dried, passed through a 2 mm sieve, and stored in plastic containers at room temperature. Georgeville (25, 37, 38) and Orangeburg (30) soil properties were previously characterized using standard methods (39, 40) (Tables 1 and 2).

Soil treatments were performed to determine which soil components were responsible for the difference in oxytetracycline sorption to Georgeville and Orangeburg soils. The first treatment consisted of sodium saturation to determine the effect of soil exchangeable cations. The soils were washed twice with 1 M NaCl solution (48 h and 30 min) followed by two 30 min deinonized water washes. The second treatment was citrate–dithionite digestion (similar to citrate–dithionite–bicarbonate digestion) to extract the total free iron and aluminum oxides (39), presumably leaving only the silicate components of the soils. \( N_2 \) BET adsorption (Micromeritics ASAP 2010) was used to measure the surface area.

**Sorption Isotherms.** Sorption isotherms were obtained for goethite and hematite using standard batch sorption experiments conducted at 21 °C. Duplicate batch polypro-
polyethylene tubes were set up by prewetting the sorbent in pH 5.5 PIPES buffer (10 mM). The 10 mM CaCl₂ solution suggested by the OECD guideline 106 for sorption measurements (41) was not used in these experiments because of possible complex formation between calcium and oxytetracycline (42). Instead, PIPES was chosen as a buffer compound because it does not complex metals (43) and thus was expected to not compete for sorption sites. After pre-wetting the solids, oxytetracycline was added from a stock solution to give final concentrations from 0.04 to 0.24 mM and a solid-to-water ratio of 10 g/L (±5%). The range of initial isotherm concentrations was of the same magnitude as the maximum concentration reported for the field (3). Tubes were wrapped with foil to prevent photodegradation and shaken end-over-end in the dark for 72 h. Control tubes containing no sorbent were assembled in the same manner to account for possible oxytetracycline losses, although no sorptive loss to polypropylene was expected, based on previous experiments (17). At the end of the equilibration time, the supernatant was filtered through 0.2-μm polyvinylidene fluoride (PVDF) syringe filters (Fisher) that were shown not to sorb oxytetracycline. Supernatant samples were analyzed by HPLC, and sorbed concentrations were calculated by difference according to

\[ C_s = \frac{(C_o - C_w)V}{MA} \]  

(1)

where \( C_s \) (mmol/m²) is the sorbed concentration, \( C_o \) (mmol/L) is the control tube concentration at the end of the experiment, \( C_w \) (mmol/L) is the aqueous phase concentration, \( V \) (L) is the volume of solution, \( M \) (kg) is the mass of solid sorbent, and \( A \) (m²/kg) is the sorbent specific surface area. Area-normalized concentrations were computed because oxytetracycline interactions were anticipated to occur by an adsorptive mechanism.

**Sorption Edge Experiments.** Sorption coefficients for oxytetracycline were measured as a function of pH. Duplicate batch tubes were prepared in a similar manner as for sorption isotherms; however, the initial oxytetracycline concentration was held constant at 0.083 mM, while the pH was varied from 4 to 9 in one-unit increments. Sorbents were pre-wet in 10 mM PIPES buffer, spiked with oxytetracycline from a stock solution, and pH-adjusted by adding small volumes of concentrated HCl or NaOH. The buffer solution in soil samples was amended with 1.5 mM sodium azide to inhibit biological activity. The final solid-to-water ratio was 10 g/L for oxide-containing tubes and 5 g/L for soil-containing tubes. Sorbent-free control tubes were assembled at each pH. Final pH values were measured at the end of the 72 h mixing time. Samples were filtered through PVDF syringe filters and analyzed by HPLC. Sorption coefficients, \( K_d \) (L/m²), were calculated as

\[ K_d = \frac{C_o}{C_w} \]  

(2)

where \( C_o \) was calculated by difference according to eq 1. Note that sorption coefficients on a volume per mass basis (i.e., L/kg) can be computed by multiplying reported values by the appropriate specific surface area given in Table 1.

**Mass Balance.** Desorption experiments were conducted to determine the reversibility of the sorption process and to verify solute recovery. Replicate tubes containing iron oxides at a final pH of 5 were prepared according to the sorption edge protocol, except that the PIPES buffer was omitted and the contact time was 24 h. Because the iron oxides were acidic, pre-wetting of goethite and hematite was done at pH 9.3 and 6.3, respectively, to give a final solution pH of 5. After mixing, tubes were centrifuged at 9000g for 60 min. A small sample of supernatant was removed for analysis while the remainder was decanted. Less than 1 mL of pore fluid retained accounted for an average of 7.5% of the oxytetracycline mass remaining in the tube.

Next, a desorption treatment was applied by adding either (i) 3 M NaCl at pH 8.5, (ii) 1 M MgCl₂ at pH 8.5, (iii) 0.25 M EDTA at pH 8.9, or (iv) methanol. Desorption solutions were mixed for 24 h in the dark before analysis for dissolved oxytetracycline content. The percentage of sorbed oxytetracycline desorbed by various treatments was calculated by

\[ \% \text{ desorbed} = \frac{M_{\text{dissolved}}}{M_{\text{initial}}} \times 100\% \]  

(3)

where \( M_{\text{dissolved}} \) (mmol) is the mass of oxytetracycline in the desorbing solution obtained by multiplying the final oxytetracycline concentration in the desorbing solution by the volume of the desorbing solution and \( M_{\text{initial}} \) (mmol) is the mass of oxytetracycline sorbed after 24 h calculated by computing \( C_o \) by difference (eq 1) and multiplying by the mass of sorbent. The divisor \( f \) is a factor to account for oxytetracycline losses in controls over the desorption time

\[ f = \frac{C_{o,d}}{C_{o,s}} \]  

(4)

where \( C_{o,d} \) (mmol/L) is the control concentration after the sorption step and \( C_{o,s} \) (mmol/L) is the control concentration after the desorption step. Formulation of the factor \( f \) assumed that the same fraction of oxytetracycline mass was degraded in the sample tube as was lost from the control tube over the duration of desorption. This assumption was valid because losses from the controls were slower (approximately days) than desorption rates (approximately hours). Values for \( f \) ranged from 0.74 to 0.95.

Mass balances were obtained for soils using the same procedure; however, 10 mM PIPES buffer + 1.5 mM sodium azide was used as the sorbing solution, mixing times (sorption and desorption) were increased to 72 h, and pH 8.5 deionized water was used as a desorbing solution in place of 0.25 M EDTA.

**Modeling of Oxytetracycline Sorption to Iron Oxides.** Goethite and hematite sorption edges were modeled using FITEQL (44) to identify possible oxytetracycline surface complexation reactions. The shape of the sorption edges—increased sorption with pH—was consistent with zwitterion, or anion species interacting with the oxide surfaces. Possible interaction stoichiometries were evaluated as shown in Table 4. The surface sites denoted by %=FeOH were all assumed to

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**TABLE 3. Percentage of Sorbed Oxytetracycline Mass Desorbed by Various Treatments**

<table>
<thead>
<tr>
<th>Sample</th>
<th>3 M NaCl (pH 8.5)</th>
<th>1 M MgCl₂ (pH 8.5)</th>
<th>0.25 M EDTA (pH 8.9)</th>
<th>Methanolb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>goethite</td>
<td>18</td>
<td>49</td>
<td>40</td>
<td>7</td>
</tr>
<tr>
<td>hematite</td>
<td>17</td>
<td>42</td>
<td>36</td>
<td>5</td>
</tr>
<tr>
<td>Soils</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Georgeville</td>
<td>0, 5</td>
<td>14</td>
<td>13</td>
<td>3</td>
</tr>
<tr>
<td>Orangeburg</td>
<td>15</td>
<td>30, 37</td>
<td>109</td>
<td>5</td>
</tr>
<tr>
<td>Digested Soils</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Georgeville</td>
<td>10</td>
<td>27</td>
<td>108</td>
<td>0</td>
</tr>
<tr>
<td>Orangeburg</td>
<td>13, 20</td>
<td>24, 26</td>
<td>115</td>
<td>0</td>
</tr>
</tbody>
</table>

* Duplicate measurements are presented unless <5% variation between two trials was observed. * Desorption values are based on the minimum detectable amount of oxytetracycline in the methanol phase. — denotes treatments not tested.
be identical. Best fits of these sorption reactions were obtained using the diffuse layer model that required the least number of input parameters. Model inputs included solid loading of 10 g/L, ionic strength of 10 mM and sorbent-specific surface area, and site density and surface acidity constants. The best-fit model was identified according to the minimum error parameter (WSOS/DF in FITEQL). An error parameter value <20 generally signifies a good model fit (44). In cases where several models satisfied this criterion, the model with the least error was chosen.

Results and Discussion

Aqueous phase oxytetracycline concentrations were always lower in iron oxide- or soil-containing tubes than in sorbent-free controls prepared at the same pH. Sorbed concentrations were calculated by difference from controls at 72 h (eq 1) because previous experiments had shown that a slow degradation reaction, possibly hydrolysis (45), yielded quantifiable oxytetracycline losses after 48 h. With the equilibration times of 72 h used in soil and oxide experiments, abiotic compound losses from controls ranged from 5 to 26% with greater values observed for alkaline pHs. Sorbed oxytetracycline concentrations were determined by difference from controls at 72 h (eq 1) and 72 h).

Desorption experiments were conducted to obtain insight into the mechanism of interaction between oxytetracycline and iron oxides (Table 3). The first treatment was the addition of methanol to determine the role of hydrophobicity in oxytetracycline sorption. Less than 7% of the sorbed oxytetracycline mass was recovered, based on the minimum detectable amount of oxytetracycline in the methanol phase. These results suggested that hydrophobic interactions between iron oxides and oxytetracycline were minor. The second treatment was ionic strength adjustment by the addition of 3 M NaCl. Only 18% of the sorbed oxytetracycline was desorbed by the introduction of competing ions, implying that the oxytetracycline sorption mechanism was stronger than nonspecific electrostatic interactions. The third treatment was 1 M MgCl₂, a solution with the same ionic strength as the NaCl solution but containing cations that are capable of forming solution phase complexes with oxytetracycline (42, 47). In this case, the amount of desorbed oxytetracycline increased to almost 50% of the sorbed mass, presumably due to competing oxytetracycline complexation with Mg²⁺ in the aqueous phase. Slightly less mass was recovered from the hematite than the goethite solids. Finally, EDTA, a strong chelating agent capable of forming an inner sphere complex with iron oxide surfaces (46), was used to competitively displace sorbed oxytetracycline. Less than half of the sorbed oxytetracycline was desorbed by EDTA addition, suggesting that the oxytetracycline—iron oxide interaction was stronger than the EDTA—iron interaction on both oxide types. Thus, results of the desorption treatments were also consistent with oxytetracycline forming surface complexes on oxide surfaces.

The iron oxide sorption edges were modeled using FITEQL to determine the magnitude of possible oxytetracycline surface complexes. Complexation reactions involving deprotonated oxytetracycline species (OTC⁰, OTC⁻, and OTC⁻²; Table 4) were chosen because Kᵣ values increased with pH when these species were dominant in the solution phase (Figure 1) and because anionic tetracycline forms are known to complex metals in solution (49). Modeling results for goethite gave better fits within pH edges than higher 20 for all reactions modeled, so no complexation constant nor best fit line was reported for goethite. Model results for hematite also showed that a reaction involving the divalent oxytetracycline anion was necessary to describe the oxytetracycline sorption edge.
the sorption edge of oxytetracycline. Better fits were obtained when reaction 4 was combined with any of the other three reactions, suggesting that more than one species could be interacting with the hematite surface sites. The best model fit for both hematite data sets (contact time of 24 and 72 h) was obtained using reactions 2 and 4 (error = 14), which was closely followed by a model using reactions 1 and 4 (error = 17), implying that anionic oxytetracycline species (OTC\(^{1-}\) and OTC\(^{2-}\)) tend to interact more with iron oxide surfaces than zwitterionic species. The computed complexation constants for the best model fit were \(10^{1.34}\) (reaction 4) and \(10^{5.30}\) (reaction 2) (Table 4). The modeling results suggest that the mechanism of oxytetracycline interaction with iron oxide surfaces was likely strong surface complexation of the most deprotonated species shown in Figure 1.

**Sorption Isotherms for Iron Oxides.** Sorption isotherms were obtained to evaluate the effect of sorbate concentration on oxytetracycline sorption to goethite and hematite. The pH conditions of 5.5, typical of groundwater or pure rainwater, were chosen to be consistent with prior studies of oxytetracycline sorption (17, 30). The oxytetracycline sorption isotherms for goethite and hematite were nonlinear over the range of sorbate concentrations tested (Figure 3). Isotherms were fit with the Langmuir model, assuming only one type of surface site (Table 5)

\[
C_s = \frac{QbC_w}{1 + bC_w} \tag{5}
\]

where \(Q\) (mmol/m\(^2\)) is the maximum adsorption capacity and \(b\) (L/mmol) is a measure of the energy of adsorption. The maximum adsorption capacities of goethite and hematite translated to 32 and 48% oxide coverage on a per area basis, respectively, when the projected surface area of oxytetracycline was assumed to be constant at 190 Å\(^2\) (20). The oxytetracycline adsorption capacity \((Q)\) and the adsorption constant \((b)\) for hematite were significantly greater than those for goethite (95% confidence level). The Langmuir fits indicated that the higher oxytetracycline sorption to hematite over the entire range of \(C_s\) values resulted from both the presence of more oxytetracycline sorption sites and a stronger interaction of oxytetracycline with the hematite surface.

Further inference regarding mineralogy effects is precluded by the absence of surface spectroscopic observations that could indicate surface complex stoichiometry (e.g., ref 46). Nevertheless, our results suggest that the mineralogy of the iron oxides should be considered when predicting oxytetracycline sorption in iron oxide-rich soils.

**Sorption of Oxytetracycline to Ultisol Soils.** Since oxytetracycline sorbed to model iron oxides and clays, we were interested to understand sorption interactions between oxytetracycline and whole soils that were aggregates of these sorbents. Two weathered soils from North Carolina were chosen for this investigation because they represented soil aggregates that were rich in iron oxides and clays (Table 2). Both of these soils were classified as Ultisols and described as acidic and kaolinitic (25, 30). The primary oxide constituents were iron and aluminum. Although soil parent materials were manganese poor, small amounts of secondary manganese oxides may have been present (50). Sorption interactions with other soil components, such as organic matter and quartz, were thought to be negligible. An organic matter sorption coefficient of 0.46 L/kg was estimated using the mass fraction of 0.23% organic carbon and a reported organic carbon partition coefficient of 200 for oxytetracycline (51). Methanol extractions recovered less than 5% of the sorbed oxytetracycline mass (Table 3), confirming minor contributions of organic matter partitioning to oxytetracycline sorption. Sorption coefficients for oxytetracycline and Ottawa sand ranged from 2.4 L/kg (pH 6) to 0.6 L/kg (pH 8.5) (52). Thus, we anticipated that surface complexation to oxide surfaces and/or cation exchange to clays would be the most important mechanisms of oxytetracycline sorption to the chosen soils.

Sorption edges for Georgeville and Orangeburg soils decreased with increasing pH (Figure 4). The similarity between these sorption edges and those observed for oxytetracycline sorption to clays (17) would suggest that clay interactions were dominating sorption to these soils. However, unlike model iron oxides that exhibited a \(K_d\) maxima at high pH interactions between oxytetracycline and oxide components of the whole soils would also decrease with pH due to charge effects. The net negative charge on the soil aggregates over most of the pH range tested (pHpzc < 4 for Ultisols; refs 53, 54) would cause electrostatic repulsion of anionic oxytetracycline species. Sorption coefficient trends with pH could not be used alone to elucidate clay versus oxide sorption contributions to overall \(K_d\) but were combined with digestion and desorption treatments to constrain possible interaction mechanisms.

The first treatment was a digestion step to assess the importance of soil oxide components on oxytetracycline sorption coefficients for the two soils. Sodium citrate—sodium dithionite was added to the soils to dissolve free amorphous and crystalline phases of iron and aluminum oxides. The effectiveness of this digestion technique was confirmed by the sharp color change observed after citrate—dithionite treatment of the soils. The Georgeville soil that had a uniform red—brown color in its undigested form was transformed to a white powder. Similarly, the treatment yielded coarse off-white solids from the natural yellowish-colored Orangeburg soil. The citrate—dithionite digested soil solids that presumably contained minimal iron and aluminum oxides were used in sorption edge experiments to quantify sorption coefficients for the clay and silicate components.

Comparison of sorption edges for the untreated and digested Georgeville and Orangeburg soils indicated that oxide components were important for oxytetracycline sorption interactions. In the case of Georgeville soil, the sorption coefficients for oxytetracycline decreased at all pH values when the oxide components were removed (Figure 4a). This observation suggested that about 50% of the oxytetracycline

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**TABLE 5. Langmuir Fits for Oxytetracycline Sorption to Iron Oxides**

<table>
<thead>
<tr>
<th>sorbent</th>
<th>(Q) (mmol/m(^2))</th>
<th>(b) (L/mmol)</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>(2.8 \times 10^{-4}) ± 0.16 (\times 10^{-4})</td>
<td>31 ± 7.4</td>
<td>0.98</td>
</tr>
<tr>
<td>Hematite</td>
<td>(4.2 \times 10^{-4}) ± 0.12 (\times 10^{-4})</td>
<td>90 ± 26.3</td>
<td>0.99</td>
</tr>
</tbody>
</table>

*Correlation coefficient from linearized isotherm: \(C_w/C_s = Q/C + 1/bQ\). Mean ± standard error (n = 12).*

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**FIGURE 3. Sorption isotherm of oxytetracycline using goethite and hematite as sorbents (T = 21 °C, pH = 5.5, and [PIPES buffer] = 10 mM). The solid lines are best fits obtained with the linearized form of the Langmuir isotherm (Table 5).**
sorption could be attributed to oxide interactions. For example, $K_d$ at pH 6 decreased from 0.054 to 0.026 L/m², and $K_d$ at pH 7 decreased from 0.017 to 0.006 L/m² after citrate–dithionite digestion. The true contribution of oxide interactions to the overall sorption coefficients of the undigested Georgeville soil could be greater because the sharp color change upon digestion was consistent with iron oxide coating of clay and silicate surfaces. Thus, the $K_d$ values measured for the digested soil could actually reflect sorption to new sites that were only exposed during the digestion treatment and that were not accessible for oxytetracycline interactions in untreated Georgeville soil. This explanation could also account for the observed increase in sorption coefficients of oxytetracycline at all pH values for the digested Orangeburg soil, as compared to the untreated form (Figure 4a); however, the minimum oxytetracycline–oxide sorption interaction could not be estimated in this case. Although component contributions to the overall oxytetracycline sorption to Georgeville and Orangeburg soils could not be quantified, it appeared that oxytetracycline–clay interactions were suppressed by oxide coatings when these two sorbent types were present in these test soils.

Soil oxide properties likely also accounted for differences in the sorption affinity of oxytetracycline to the Georgeville and Orangeburg soils. Even after normalizing to surface area, oxytetracycline sorption coefficients for untreated Georgeville soil were greater at all pH values than for untreated Orangeburg soil (Figure 4). Oxytetracycline sorption coefficients for the clay and silicate components of these soils were virtually identical when the amorphous and crystalline oxide fractions were removed (Figure 4a). Evident soil property differences between the two soils that could give greater oxytetracycline sorption to Georgeville soil were (Table 2) (i) texture, a gross indicator of total clay and oxide content; (ii) color, a gross indicator of iron oxide mineralogy; (iii) exchangeable Ca²⁺; and (iv) the mass fraction of amorphous and crystalline iron oxides. The Georgeville soil was the finer of the two and had less exchangeable Ca²⁺ and more amorphous (3.5x) and crystalline (2.2x) iron oxides than the Orangeburg soil. Of these soil properties, only the effects of exchangeable cations on oxytetracycline sorption (52) could be assessed by soil treatment. Sodium saturation of the soils indicated that exchangeable cations had little effect on oxytetracycline sorption coefficients, except for a 30% increase in Georgeville $K_d$ at pH 4 (Figure 4b). Consequently, sorption affinity differences between these two soils was ascribed to oxide properties, either because of differences in the amounts or the types of oxide coatings on Georgeville versus Orangeburg soil.

Soil oxytetracycline sorption coefficients were compared to those from model systems to gain insight into differences between environmental solids and high purity sorbents. Our previous studies had indicated that oxytetracycline sorption isotherms for clays and iron oxides were nonlinear. Thus, soil systems could only be compared to model systems with the same equilibrium aqueous oxytetracycline concentration, $C_w$, pH, and ionic strength. Isotherm relationships were available for all model sorbents at pH 5.5 and 10 mM ionic strength to account for variations in $C_w$ on sorption coefficients. Exponential fits were used to interpolate $C_w$ and $K_d$ values at pH 5.5 from each soil sorption edge study (Table 6). The interpolated $C_w$ values were used with the best fit parameters from kaolinite (17) and iron oxide (Table 5) isotherms to calculate $K_d$ values for each of the model sorbents. For example, Table 6, column 1, gives a $C_w$ value of 0.005 mmol/L at pH 5.5 for the Georgeville soil. This $C_w$ value was used to compute $K_d$ values of 0.0035 L/m² for kaolinite, 0.026 L/m² for goethite and hematite, and so forth for comparison with the soil $K_d$ of 0.07 L/m². For Georgeville and each of the other soil samples, the soil $K_d$ values were greater than the values calculated at the same $C_w$ for the individual model sorbents (Table 6). The oxytetracycline soil $K_d$ values for the untreated Georgeville and Orangeburg soils were of the same order of magnitude as the hematite $K_d$ values at pH 5.5. Since
oxide coatings contributed at least 50% of the oxytetracycline sorption to untreated Georgeville soil. It seemed that surface sorption properties of the oxides in this aggregate were similar to those of model sorbents.

The $K_d$ values for the digested soils were compared to only kaolinite and silicate solids since most oxide components had been removed. Assuming that the oxide-specific citrate–dithionite treatment did not chemically alter other soil mineral or organic matter phases, the $K_d$ values for the digested soils fell between the values obtained for model clay and quartz sorbents (Table 6). It was unlikely that the oxytetracycline sorption to the digested Georgeville or Orangeburg soil could be attributed entirely to quartz components. Although Ottawa sand has a higher surface area normalized $K_d$, the mass normalized $K_d$ was only 2.4 L/kg (pH 6). The mass normalized $K_d$ values for digested Georgeville and Orangeburg soils were 900 and 500 L/kg, respectively—orders of magnitude greater than expected for Ottawa sand and closer to those observed for clays (70 L/kg for kaolinite and 1500 L/kg for montmorillonite, ref 17). The surface areas of the digested soils were much greater than the 0.1 m²/g expected for fine sand of 20 μm diameter size (55), suggesting that the digested soil compositions were indeed more clay-rich than sand-rich. Assuming that most of the oxytetracycline sorption to the digested soils was through clay interactions, the digested soil $K_d$ values were about an order of magnitude greater than observed for the model kaolinite (Table 6). Although $K_d$ computations were somewhat insensitive to $C_m$ over the relevant range, actual experimental measures of $K_d$ for kaolinite were between 0.003 and 0.01 L/kg for oxytetracycline $C_m$ concentrations of 0.005–0.030 mmol/L. Thus, uncertainties in soil $C_m$ interpolations and model sorbent $K_d$ estimates could not account for the greater oxytetracycline sorption to digested Georgeville and Orangeburg soils. Surface properties of clay and silicate minerals in the soil aggregates had a greater number of sorption sites or greater oxytetracycline sorption affinities than did the model sorbents, although they were not manifest when oxide coatings were present.

Environmental Significance. The results of this research indicate that oxytetracycline interactions with soil oxide components must be considered when developing robust fate and transport models for this and similar ionogenic compounds. The sorption edge studies with model oxides suggest that initial application of oxytetracycline to oxidereic agricultural soils, such as by percolation of a manure lagoon slurry, would result in compound sorption to soils. Although the large oxide sorption coefficients for oxytetracycline favor sorbed over dissolved distributions of this compound, the presence of swamping concentrations of other soil ligands—phosphate in fertilizer, for example—may induce oxytetracycline desorption to soil pore waters, thereby increasing the mobility and bioavailability of this compound. Other pore water chemistry changes, including pH and complexing cation concentrations, will also affect sorption distributions and should be considered in fate models for ionogenic compounds, such as oxytetracycline.

This work has addressed some of the challenges arising from the need to predict sorption coefficients for sorbate molecules having multiple mechanisms of interaction with environmental matrices. The sorption edge and isotherm measurements with goethite and hematite validated Jones et al.’s (30) proposal that oxide, as well as clay, sorbents contributed to oxytetracycline sorption to soils. Thus, the key soil properties that govern sorbate interactions for large groups of soils can be broadly characterized using statistical approaches. Model sorbent studies were necessary to elucidate specific sorption mechanisms, thereby ensuring that quantitative predictors of $K_d$ capture the appropriate sorption interactions with individual soil/sediment components.

Although model sorbent studies can demonstrate sorption trends, for example, as a function of pH, ionic strength, etc., the model sorbent $K_d$ values may not be directly applicable to environmental solids because weathering can alter soil mineralogy. In the case of oxytetracycline, mineralogy differences between iron oxides in this study and clays in our previous work (17) accounted for differences in species-specific sorption coefficients of up to an order of magnitude. Finally, specific sorption interactions for individual soils/sediments can be strongly affected by surface coatings and soil aggregation; thus, predictive estimates of $K_d$ will likely need to be coupled with a calibrating experimental sorption measure for a specific sample.

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