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## Effects of Sorbate Speciation on Sorption of Selected Sulfonamides in Three Loamy Soils

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Sorption of sulfamethazine (SMN) and sulfathiazole (STZ) was investigated in three soils, a North Carolina loamy sand, an Iowa sandy loam, and a Missouri loam, under various pH conditions. A significant increase in the sorption coefficient ( $K_D$ ) was observed in all three soils, as the sulfonamides converted from an anionic form at higher pH to a neutral/cationic form at lower pH. Above pH 7.5, sulfonamides exist primarily in anionic form and have higher aqueous solubility and no cationic character, thereby consequently leading to lower sorption to soils. The effect of speciation on sorption is not the same for all sulfonamides; it is a function of the pH of the soil and the  $pK_a$  of the sulfonamides. The results indicate that, for the soils under investigation, SMN has comparatively lower  $K_D$  values than STZ. The pH-dependent sorption of sulfonamides was observed to be consistent in all three soils investigated. The  $K_D$  values for each speciated form—cationic, neutral, and anionic—were calculated using an empirical model in which the species-specific sorption coefficients ( $K_{D0}$ ,  $K_{D1}$ , and  $K_{D2}$ ) were weighted with their respective fractions present at any given pH.

**KEYWORDS:** Soil sorption; antimicrobials; sulfamethazine; sulfathiazole; sulfonamides; soil pH; speciation

### INTRODUCTION

Antimicrobials are routinely used in livestock operations or concentrated animal feed operations (CAFO) for therapeutic uses as well as for growth promotion (1). Key classes of antimicrobials used for veterinary purposes include sulfonamides, macrolides, tetracyclines, and  $\beta$ -lactams (2). A major concern regarding the use of antimicrobials at CAFOs is that animals often do not completely metabolize an antimicrobial prior to excretion. For example, up to 90% of sulfonamides are excreted within 1–2 days into a treatment system or the environment (3, 4), depending on factors such as the molecular structure of the antimicrobials, dosage level, animal age, means of administration, and other practices (5, 6). Animal excrement at CAFOs is commonly stored and/or partially treated in anaerobic lagoons prior to periodic field application of the lagoon slurry (7). It should be noted that some metabolites of sulfonamides can convert back to parent compounds during manure storage (8). As a result, antimicrobials are commonly found in lagoons at CAFOs as well as in drinking water sources (9).

Sulfonamides have relatively high water solubility that is dependent on pH due to speciation effects. For example, a rapid

increase in solubility with increasing pH has been reported for sulfamethazine (SMN) (10–12) due to a shift from neutral to anionic species. Although sulfonamides are not readily hydrolyzable (13) and are recalcitrant to anaerobic degradation (13), sulfonamides have been shown to be readily biodegradable under aerobic conditions (14). The mobility of a sulfonamide (or any compound) in soils is related, in part, to its propensity to sorb to the sediment solids. Laboratory and field studies have suggested that sulfachloropyridazine (a sulfonamide) is relatively weakly sorbed in soils and slurry-amended soils and is, thus, quite mobile in soil (15). Similar results were reported by Thiele-Bruhn and Aust (16), who observed lower sorption of sulfanilamide, sulfadimidine, sulfadiazine, sulfadimethoxine, and sulfapyridine in pure soil systems than in pig slurry and pig-slurry-amended soils. The authors attributed the higher sorption for pig slurry and soils amended with slurry to a resulting decrease in pH and an increase in organic carbon content.

Several studies have been conducted that examine the effects of chemical speciation on the transport of sulfonamides. Boxall et al. (15) observed an increase in adsorption of sulfachloropyridazine in soil with decrease in pH due to the relative predominance of cationic species. Lower sorption of sulfachloropyridazine in slurry/manure-amended soils was attributed to the increased pH resulting from the addition of swine manure (15). Gao and Pedersen (17) studied the sorption of three

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**Table 1.** Physical and Chemical Properties of Soil Material

| property                                   | soil sampling location |            |          |
|--|------------------------|------------|----------|
|  | North Carolina         | Iowa       | Missouri |
| soil texture                               | loamy sand             | sandy loam | loam     |
| pH   | 5.3                    | 7.5        | 4.9      |
| % organic carbon                           | 1.0                    | 2.1        | 1.1      |
| cation exchange capacity (cmol/kg)         | 6.8                    | 24         | 13       |
| % sand                                     | 77                     | 56         | 46       |
| % silt                                     | 18                     | 28         | 38       |
| % clay                                     | 5.2                    | 16         | 16       |
| soil particle density (g/cm <sup>3</sup> ) | 2.6                    | 2.5        | 2.6      |
| surface area (m <sup>2</sup> /g)           | 1.8                    | 4.0        | 28       |
| charge density (cmol/m <sup>2</sup> )      | 0.0039                 | 0.0059     | 0.00045  |

sulfonamides to pure montmorillonite and kaolinite clays and found that the clay surface charge was an important factor in partitioning behavior. Sassman and Lee (18) similarly studied the pH effects on sorption of tetracyclines on eight different soils. Figueroa et al. (19) also studied tetracycline adsorption on iron oxides in pure form and in soils. Furthermore, a review by Tolls (20) presented partition coefficients for a wide range of antimicrobials in various soils.

Other classes of antimicrobials, including tetracyclines, macrolides, and carbadox, are all reportedly less mobile due to strong interactions with soil components related to cation exchange and partitioning into organic carbon in soils with higher organic carbon content (21). Because of their common use, observed occurrence in the environment, and potentially significant mobility, it is important to understand the effects of pH on the transport of sulfonamides in soils.

The purpose of this research was to experimentally evaluate and model the effects of pH on the sorption of two common sulfonamides, sulfamethazine (SMN) and sulfathiazole (STZ), for three different soils from CAFO sites—North Carolina (NC), Iowa (IA), and Missouri (MO).

## MATERIALS AND METHODS

**Soils.** Sorption on three different soils obtained near CAFO sites in North Carolina, Iowa, and Missouri was examined in this study. The soils were collected from five locations per site, at two depths per location (0–15 and 15–30 cm), using a posthole digger that was washed with deionized water between samples. The global positioning system (GPS) coordinates of each sample borehole were determined using a portable meter (Garmin model GPS III Plus, Olathe, KS). The soil samples were air-dried, sieved through a sieve stack (10, 20, 40, and 100 mesh), and stored in plastic bags at room temperature until use. The 40 × 100 mesh fractions of 10 samples (five locations at two depths) for each soil were mixed in equal portions, homogenized, and used for the sorption experiments.

The Cornell Nutrient Analysis Laboratory (804 Bradfield Hall, Ithaca, NY) conducted physicochemical characterization of soils used for sorption experiments. Specifically, the soil pH was determined in a 1:1 (v/v) soil/water suspension using both deionized water and a 0.01 M CaCl<sub>2</sub> solution. Soil organic matter was determined using the loss-on-ignition method (22). Exchangeable acidity was determined by extraction with a barium chloride/triethanolamine solution, buffered at pH 8.0, followed by titration with excess base (22). Soil particle density was calculated using the standard procedure (23). The standard textural classification guide, adopted from the U.S. Department of Agriculture, Soils and Agricultural Engineering (24), was used to classify the soils as loamy sand, sandy loam, and loam for the NC, IA, and MO soils, respectively. The results of soil characterization are presented in **Table 1**. The BET surface area of the soil was measured by nitrogen adsorption techniques using an Autosorb-1 series surface area and pore size analyzer (Quantachrome, Pittsburgh, PA). Surface charge density was calculated using surface area and total cation exchange capacity (25).

Soil characterization is very essential because the sorption of individual species at any particular pH is dependent on the functional groups present on the soil surface. The acidity/basicity of soil functional groups affects whether the organic chemical may become mobile or retarded in the terrestrial environment (26).

**Chemicals.** Sulfathiazole (STZ) (CAS Registry No. 144-74-1; ≥99%) and sulfamethazine (SMN) (CAS Registry No. 1981-58-4; ≥99%) were purchased from Sigma Chemicals (St. Louis, MO) and used as received. The molecular structures of SMN and STZ are shown in **Figure 1**. Sodium hydroxide (ACS grade) was used for pH adjustment, and monobasic sodium phosphate (99.5%) was obtained from Fisher Scientific (Pittsburgh, PA) for use as buffer solution. Standards and solutions were prepared in distilled/deionized (DI) water with a resistivity of >18.2 MΩ-cm using a Milli-Q Simplicity 185 water purification system (Millipore, Bedford, MA). Antimicrobial solutions were freshly prepared and stored in the dark at 4 °C until use.

**Analytical Methods.** The pH was measured using a Corning 3-in-1 combination pH probe and a Corning 340 pH-meter (Corning, NY). Antimicrobial concentrations were measured using reverse-phase high-performance liquid chromatography (HPLC) with UV detection at 275 nm. This wavelength works well for a suite of sulfonamides including SMN and STZ, which have λ<sub>max</sub> at 272 and 288 nm, respectively. The HPLC model 6000 system (Waters, Milford, MA) included a 717+ autosampler, a 996 photodiode array detector (PDA), and a 600E quaternary pump and controller. Chromatographic separations were achieved using a Phenomenex Luna 3μ phenyl-hexyl 100A (150 × 3.0 mm) column with a binary gradient with solvents A and B. Solvent A was composed of 90% (v/v) 20 mM ammonium acetate, with pH adjustment to 5.7 with acetic acid and 10% acetonitrile; solvent B was composed of 20% (v/v) solvent A and 80% acetonitrile. The binary gradient ramped from 90% A to 100% B over an 18.5-min period. An injection volume of 30 μL was used. Standard curves always had regression coefficients of at least ≥0.999. The retention times for SMN and STZ were 6.3 and 4.2 min, respectively.

**Batch Sorption Studies.** Sorption of SMN and STZ was studied in three soils, at varied pH, using procedures in accordance with Organization for Economic Co-operation and Development (OECD) Test Guideline 106 (27). A sorption kinetic study was conducted with sampling at 0, 4, 8, 12, 24, 48, and 96 h, which showed that nearly 90% sorption was achieved in <24 h. On this basis, 24 h was chosen as the equilibration time for all sorption experiments.

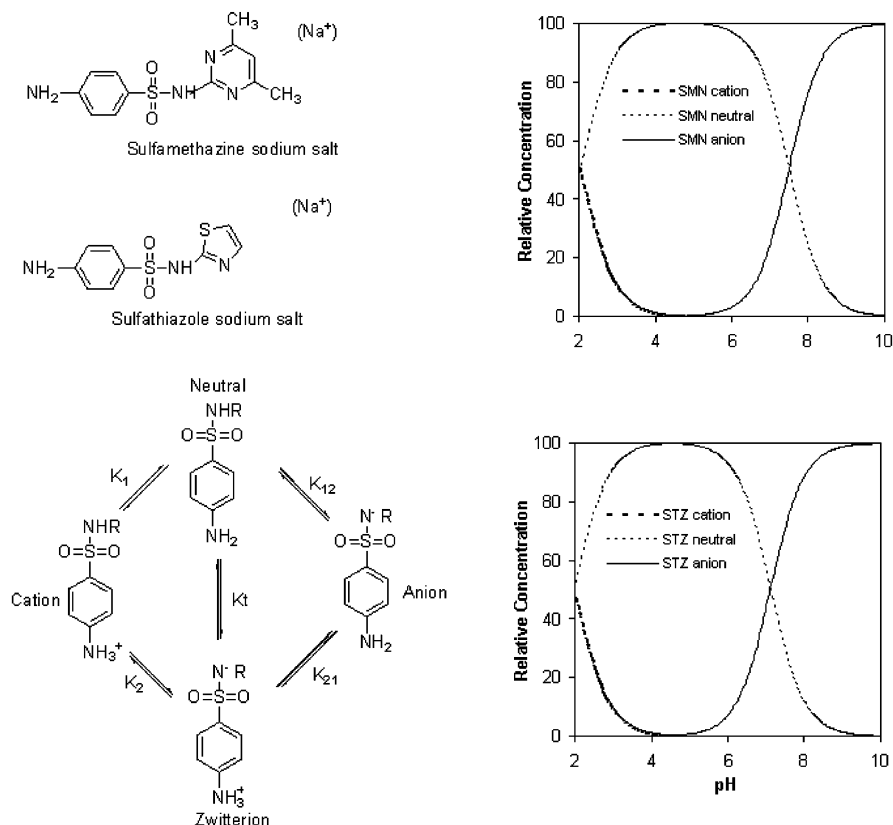
In the sorption experiments, 5 g of air-dried, homogenized soil was mixed with 20 mL of water, buffered with 10 mM monobasic sodium phosphate, and agitated in a tumbler for 24 h. The soil samples were then spiked with 5 mL of different concentrations of SMN or STZ to achieve final concentrations of 0, 0.25, 0.50, 1.0, 2.5, and 4.0 mg/L. The pH was adjusted using sulfuric acid or a sodium hydroxide solution. The antimicrobial-spiked, pH-adjusted suspensions were then agitated for an additional 24 h in the dark at 25 °C. A control sample, containing only aqueous-phase antimicrobials (no soil), was also included. All isotherm samples were prepared and analyzed in duplicate for each antibiotic and soil combination. After 24 h, the sample suspensions were centrifuged at 3000g for 10 min, followed by filtration of the supernatant with a 0.45-μm HV-Durapore membrane filter. The filtrate was transferred to a vial for HPLC analysis.

**Adsorption Isotherms.** Effective adsorption at a given pH was modeled in two different manners, with both linear partition coefficients (*K<sub>D</sub>*) and Freundlich isotherm parameters (*K<sub>F</sub>* and 1/*n*) being developed. The nonlinear form of the Freundlich adsorption model is represented by

$$q = K_F C_{aq}^{1/n} \quad (1)$$

where *q* is the equilibrium capacity (mg of compound adsorbed/kg of soil), *C<sub>aq</sub>* is the equilibrium aqueous-phase concentration (mg/L), *K<sub>F</sub>* is the Freundlich sorption coefficient, and 1/*n* is the Freundlich measure of nonlinearity. The linearized form of the Freundlich isotherm can be written as

$$\log q = \log K_F + (1/n) \log C_{aq} \quad (2)$$



**Figure 1.** Molecular structures, general ionization equilibria (Sakurai and Ishimitsu, 1980), and speciation diagrams of sulfamethazine (SMN) and sulfathiazole (STZ).

The isotherm coefficients were determined from linearized plots of  $\log C_{\text{aq}}$  versus  $\log q$ , as per eq 2.

The second approach used to model the sorption results involved using only the initial linear part of the isotherm plotted as  $C_{\text{aq}}$  and  $q$ . Specifically, for the linear portion of the isotherm (e.g., at low mass loading and lack of apparent sorption site saturation), the model may be represented as

$$q = K_{\text{D}} C_{\text{aq}} \quad (3)$$

At low concentration, such site saturation does not occur and a linear isotherm results. Thus, depending on the relative concentration of surface sites and adsorbate molecules, either a nonlinear (i.e., Freundlich) or a linear model may be more appropriate for modeling purposes. Both nonlinear and linear models are frequently used depending on the particular system of interest. One should note that for cases when the Freundlich  $1/n$  is unity, the Freundlich sorption constant ( $K_{\text{F}}$ ) becomes equal to the partition coefficient ( $K_{\text{D}}$ ).

**Speciation Modeling.** In this work, the effective sorption coefficient ( $K_{\text{D,eff}}$ ) was modeled as the weighted average of individual  $K_{\text{D}}$  values for the neutral and anion species (as well as the cation species where possible), as originally proposed by Schwarzenbach et al. (28). Specifically, the  $K_{\text{D,eff}}$  was represented by

$$K_{\text{D,eff}} = K_{\text{D}0}\alpha_0 + K_{\text{D}1}\alpha_1 + K_{\text{D}2}\alpha_2 \quad (4)$$

where  $K_{\text{D}0}$ ,  $K_{\text{D}1}$ , and  $K_{\text{D}2}$  and  $\alpha_0$ ,  $\alpha_1$ , and  $\alpha_2$  represent the individual  $K_{\text{D}}$  and fractions of the cationic, neutral, and anionic species, respectively. The proportion of speciated forms is dependent on the  $\text{p}K_{\text{a}}$  of the compound and the pH of the solution. The fractions of each ionic form of SMN and STZ can be expressed as a function of pH and  $\text{p}K_{\text{a}}$  as

$$\alpha_0 = \frac{1}{1 + 10^{(\text{pH}-\text{p}K_1)} + 10^{(2\text{pH}-\text{p}K_1-\text{p}K_2)}} \quad (5)$$

$$\alpha_1 = \frac{1}{1 + 10^{(\text{p}K_1-\text{pH})} + 10^{(\text{pH}-\text{p}K_2)}} \quad (6)$$

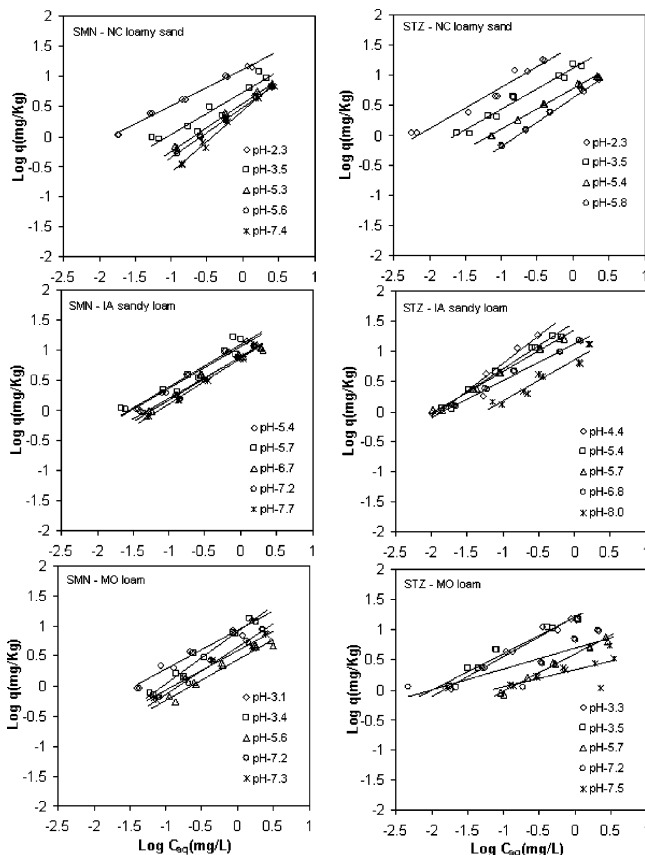
$$\alpha_2 = \frac{1}{1 + 10^{(\text{p}K_2-\text{pH})} + 10^{(\text{p}K_1+\text{p}K_2-2\text{pH})}} \quad (7)$$

where  $\text{p}K_1$  and  $\text{p}K_2$  for SMN are  $2.07 \pm 0.30$  and  $7.49 \pm 0.13$ , respectively, and those for STZ are  $2.01 \pm 0.30$  and  $7.11 \pm 0.09$ , respectively (29). Individual sorption coefficients for different forms (cationic, neutral, and anionic) of sulfonamides were determined using nonlinear regression analysis of experimental versus modeled  $K_{\text{D}}$  values using MS Excel 2003 (Microsoft).

## RESULTS AND DISCUSSION

**Isotherms.** Only negligible losses were observed in control (no soil) samples. The linear adsorption isotherms for SMN and STZ for the three soils investigated are shown in **Figure 2**. The sorption isotherms were well described by the Freundlich model ( $0.65 \leq R^2 \leq 1.0$ ). The calculated values of Freundlich constants  $K_{\text{F}}$  and  $1/n$  for SMN and STZ are given in **Tables 2** and **3**, respectively. Over the entire concentration range studied, all Freundlich isotherms were observed to be nonlinear with  $1/n$  coefficients of less than unity (except for SMN at pH 7.4, for which  $1/n$  is unity). These isotherms suggest that, as the concentration of sorbate (i.e., antimicrobial) in aqueous phase increased, the sorption sites became increasingly saturated and, hence, less able to sorb additional sorbate molecules (30).

**Partition Coefficient.** Experimental partition coefficients ( $K_{\text{D}}$ ) were calculated for SMN and STZ using eq 3. Partition coefficients were calculated, using the linear part of the isotherm existing at low concentration, where  $1/n$  is unity. Representative plots showing the use of this approach are shown in **Figure 3**, and the resultant  $K_{\text{D}}$  values for SMN and STZ are given in **Tables 2** and **3**, respectively. The highest  $K_{\text{D}}$  value was observed



**Figure 2.** Freundlich sorption isotherms ( $K_F$ ,  $1/n$ ) for SMN and STZ at various pH values for three loamy soils.

**Table 2.** Mean Sorption Coefficients ( $K_D$ ) and Freundlich Coefficients ( $K_F$  and  $1/n$ ) for Sulfamethazine (SMN) at Various pH Values

| pH                             | linear |                          |       | Freundlich |                          |       |       |
|--------------------------------|--------|--------------------------|-------|------------|--------------------------|-------|-------|
|                                | $K_D$  | relative SD <sup>a</sup> | $R^2$ | $K_F$      | relative SD <sup>a</sup> | $1/n$ | $R^2$ |
| North Carolina (NC) Loamy Sand |        |                          |       |            |                          |       |       |
| 2.3                            | 30     | 2.3                      | 0.89  | 13         | 0.32                     | 0.61  | 1.0   |
| 3.5                            | 7.4    | 2.4                      | 0.71  | 5.6        | 1.4                      | 0.71  | 0.93  |
| 5.3                            | 4.6    | 0.071                    | 0.97  | 3.6        | 0.074                    | 0.81  | 1.0   |
| 5.6                            | 3.9    | 0.13                     | 0.99  | 3.1        | 0.035                    | 0.84  | 1.0   |
| 7.4                            | 2.5    | 0.42                     | 0.98  | 2.7        | 0.13                     | 1.0   | 0.99  |
| Iowa (IA) Sandy Loam           |        |                          |       |            |                          |       |       |
| 5.4                            | 22     | 0.88                     | 0.99  | 12         | 1.9                      | 0.71  | 0.99  |
| 5.7                            | 17     | 2.9                      | 0.85  | 13         | 0.20                     | 0.71  | 0.94  |
| 6.7                            | 14     | 0.59                     | 1.0   | 7.6        | 0.00                     | 0.69  | 0.98  |
| 7.2                            | 10     | 0.23                     | 0.95  | 7.7        | 0.27                     | 0.72  | 0.99  |
| 7.7                            | 9.8    | 0.86                     | 0.97  | 7.4        | 0.66                     | 0.77  | 1.0   |
| Missouri (MO) Loam             |        |                          |       |            |                          |       |       |
| 3.1                            | 17     | 0.35                     | 0.95  | 8.7        | 0.47                     | 0.66  | 0.97  |
| 3.4                            | 10     | 1.9                      | 0.93  | 8.3        | 0.74                     | 0.88  | 0.98  |
| 5.6                            | 4.5    | 0.62                     | 0.99  | 2.8        | 0.24                     | 0.68  | 0.98  |
| 7.2                            | 4.0    | 0.057                    | 0.98  | 4.4        | 0.15                     | 0.80  | 0.99  |
| 7.3                            | 3.1    | 0.049                    | 0.92  | 3.9        | 0.070                    | 0.66  | 0.98  |

<sup>a</sup> SD, standard deviation.

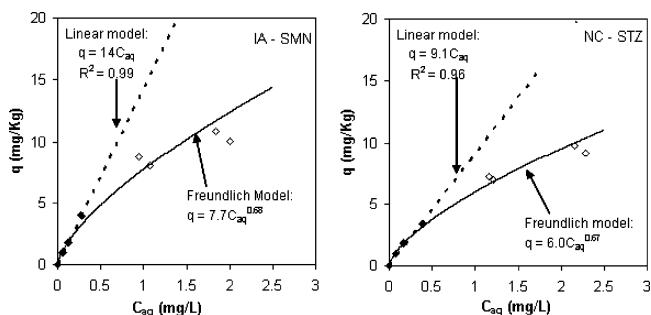
for Iowa sandy loam, followed by North Carolina loamy sand and Missouri loam. The  $K_D$  value obtained for North Carolina loamy sand at pH 5.6 is within the range of reported literature  $K_D$  values at identical pH and percent organic carbon content (20). There are no values of  $K_D$  reported for the other two soils for SMN and STZ.

Sulfonamides are amphoteric in nature and rapidly undergo dissociation/protonation according to the general ionization equilibria shown in **Figure 1**. At soil pH closer to the isoelectric

**Table 3.** Mean Sorption Coefficients ( $K_D$ ) and Freundlich Coefficients ( $K_F$  and  $1/n$ ) for Sulfathiazole (STZ) at Various pH Values

| pH                             | linear |                          |       | Freundlich |                          |       |       |
|--------------------------------|--------|--------------------------|-------|------------|--------------------------|-------|-------|
|                                | $K_D$  | relative SD <sup>a</sup> | $R^2$ | $K_F$      | relative SD <sup>a</sup> | $1/n$ | $R^2$ |
| North Carolina (NC) Loamy Sand |        |                          |       |            |                          |       |       |
| 2.3                            | 48     | 0.078                    | 0.94  | 31         | 3.0                      | 0.70  | 0.96  |
| 3.5                            | 29     | 1.4                      | 0.99  | 13         | 0.95                     | 0.69  | 0.98  |
| 5.4                            | 9.1    | 0.085                    | 0.97  | 6.0        | 0.075                    | 0.68  | 1.0   |
| 5.8                            | 5.1    | 0.042                    | 0.99  | 4.2        | 0.19                     | 0.82  | 1.0   |
| Iowa (IA) Sandy Loam           |        |                          |       |            |                          |       |       |
| 4.4                            | 65     | NA                       | 0.98  | 52         | 0.0                      | 0.92  | 0.92  |
| 5.4                            | 44     | 3.3                      | 0.98  | 29         | 1.5                      | 0.78  | 1.0   |
| 5.7                            | 35     | 0.69                     | 0.96  | 23         | 2.2                      | 0.70  | 1.0   |
| 6.8                            | 33     | 0.36                     | 0.96  | 13         | 0.22                     | 0.61  | 1.0   |
| 8.0                            | 11     | 1.5                      | 0.96  | 7.3        | 0.34                     | 0.70  | 0.93  |
| Missouri (MO) Loam             |        |                          |       |            |                          |       |       |
| 3.3                            | 33     | 1.1                      | 0.97  | 17         | 3.1                      | 0.67  | 1.0   |
| 3.5                            | 25     | 3.9                      | 0.86  | 16         | 0.39                     | 0.61  | 0.96  |
| 5.7                            | 7.7    | 0.0071                   | 0.98  | 3.9        | 0.26                     | 0.62  | 1.0   |
| 7.2                            | 7.7    | 0.18                     | 0.67  | 5.0        | 0.14                     | 0.35  | 0.68  |
| 7.5                            | 6.1    | 0.40                     | 0.89  | 2.2        | 0.15                     | 0.29  | 0.65  |

<sup>a</sup> SD, standard deviation.



**Figure 3.** Representative linear sorption isotherms for calculating the  $K_D$  values for SMN and STZ at various pH values (dark symbols represent the low concentration used for calculation of  $K_D$  values).

point of sulfonamides [i.e.,  $(pK_1 + pK_2)/2$ ], sulfonamides exist in transient equilibrium between neutral and zwitterionic form. Previous research has shown that the zwitterionic form constitutes <2% of the net neutral species and, hence, is negligible (31). Thus, at neutral or slightly acidic pH levels, sulfonamides will be in the neutral form that can partition into the soil organic carbon and be significantly retarded with respect to mobility (26).

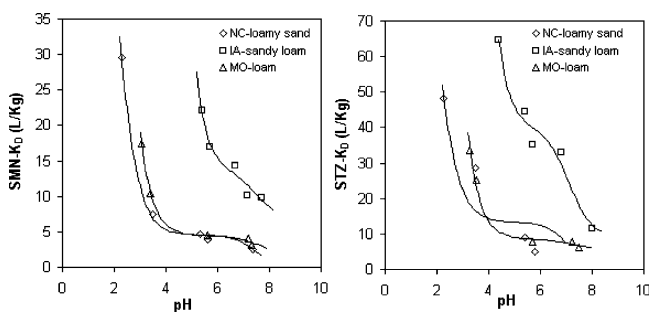
To assess the relative contribution of each of the speciated forms to sorption, theoretical  $K_D$  values were extrapolated from the experimental batch  $K_D$  values.  $K_{D0}$ ,  $K_{D1}$ , and  $K_{D2}$  values for each of the individual species were calculated on the basis of the fraction of the speciated form existing at a given pH. **Table 4** shows the  $K_D$  values obtained for cationic, neutral, and anionic forms, respectively.

In general, the partition coefficients for the anionic species ( $K_{D2}$ ) was lowest as compared with the neutral ( $K_{D1}$ ) or cationic species ( $K_{D0}$ ) (**Table 4**). The reason for this relates to a cation's ability to adsorb through a cation exchange mechanism with anionic moieties associated with the clay and related fractions. Similarly, the neutral species may partition readily into the organic carbon fraction of the soils. With the higher water solubility of the anionic species and the general lack of anionic exchange sites on soils, the sorption of the anionic species was seen to be the lowest (**Table 4**). It is believed that the modeled  $K_{D0}$  values for the cationic form of SMN and STZ in the IA sandy loam are effective values and potentially higher than

**Table 4.** Batch Sorption Coefficients for Cationic ( $K_{D0}$ ), Neutral ( $K_{D1}$ ), and Anionic ( $K_{D2}$ ) Forms of Sulfamethazine (SMN) and Sulfathiazole (STZ)

| soil texture  | sulfonamide | pH range | $K_{D0}$ (L/kg)    | $K_{D1}$ (L/kg) | $K_{D2}$ (L/kg) |
|---------------|-------------|----------|--------------------|-----------------|-----------------|
| NC loamy sand | SMN         | 2.3–7.4  | 70                 | 4.8             | ~0              |
| IA sandy loam | SMN         | 5.4–7.7  | 18000 <sup>a</sup> | 13              | 6.9             |
| MO loam       | SMN         | 3.1–7.3  | 140                | 4.3             | 2.2             |
| NC loamy sand | STZ         | 2.3–5.8  | 94                 | 23              | ~0              |
| IA sandy loam | STZ         | 4.4–8.0  | 6200 <sup>a</sup>  | 40              | 8.9             |
| MO loam       | STZ         | 3.3–7.5  | 490                | 8.5             | 5.9             |

<sup>a</sup> High values were due potentially to lack of  $\alpha_0$  dominating (due to strong soil buffering). Ignoring  $\alpha_0$  (cation), however, does not allow good fit of data. Thus, model use should be strictly limited to the pH range of the experiments.

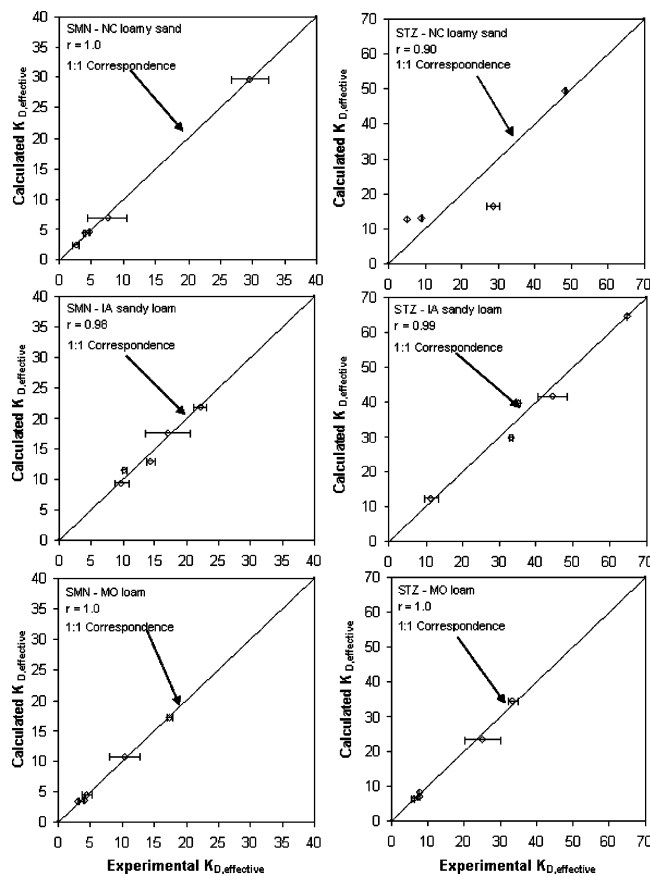
**Figure 4.** Experimental and modeled sorption coefficients ( $K_D$  values) for SMN and STZ: pH-dependent behavior.

“true” values. The reason for this is the inability to reduce the pH of the highly buffered soil sufficiently to establish sorption data in the pH region where the cationic form significantly predominates.

Sorption of STZ and SMN greatly increased as the pH of the aqueous phase decreased for the pH range studied for all three soils investigated. Sulfonamides are speciating compounds (Figure 1). They are characterized by two acid dissociation constants ( $pK_a$ ), indicating protonation and deprotonation, based on the pH of the aqueous phase.  $pK_{a1}$  pertains to the dissociation of the ammonium group ( $-\text{NH}_3^+$ ), which normally occurs at low pH (pH 2–3), and  $pK_{a2}$  refers to the dissociation of a proton from the sulfonamide group ( $-\text{SO}_2\text{NH}-$ ), occurring at higher pH values (pH 5–11) (2, 30). As a result of rapid dissociation of sulfonamides with pH, significant changes in  $K_D$  values were observed. The dependence of  $K_D$  on the pH of the suspension is clearly illustrated by the gradual decrease in  $K_D$  observed for both SMN and STZ for the three different soils (Figure 4).

In general, at a lower pH, sorption of sulfonamides is enhanced primarily due to cation exchange of predominantly cationic forms of the adsorbate (17). Conversely, the observed reduction in the  $K_D$  values at high pH could be attributed to the shift from cationic to anionic species of the sulfonamides, which are unavailable for cationic exchange or neutral adsorption into soil organic matter. The decrease in  $K_D$  at high pH was observed to be more pronounced for SMN than for STZ, potentially due mainly to greater solubility of SMN at high pH (10) and no cationic character. Aqueous solubilities of SMN and STZ are reported as 1500 mg/L (at 29 °C) and 600 mg/L (at 26 °C), respectively (12).

It should be noted that sulfonamides can form salts in strongly acidic or basic solutions (2); hence,  $K_D$  values obtained at extreme pH ranges need to be carefully studied. Additionally, speciation significantly affects the ability of sulfonamides to form complexes with metal ions, thereby affecting the sorption coefficient (29).

**Figure 5.** Experimental and modeled sorption coefficient ( $K_{D,eff}$ ) for SMN and STZ in three soils.

**Net Antimicrobial Sorption.** The modeled effective sorption coefficient ( $K_{D,eff}$ ) was calculated using the weighted sorption coefficient using eq 4 and compared with experimental values. This approach was originally proposed by Schwarzenbach et al. (28) and further developed by Figueroa et al. (19). A significant correlation ( $\alpha = 0.05$ ) existed between all sets of experimental versus model (calculated)  $K_D$  values, with the exception of STZ in NC loamy sand for which the correlation was only significant at  $\alpha = 0.10$  (Figure 5). These experiments demonstrate the application of the simple three-species model for sorption of sulfonamides.

Specifically, the  $K_{D,eff}$  values were observed to be higher at lower pH, which is consistent with the lower sorption of anionic sulfonamides with the soil material. Gao and Pederson (17) studied sorption of SMN and STZ in two pure clay minerals, montmorillonite and kaolinite. This study indicated that sorption of sulfonamide antimicrobials depended on pH and that sorption of cationic SMN to montmorillonite was 100–200% greater than that of the neutral SMN. They attributed increased sorption of SMN to montmorillonite to cation exchange. The desorption experiments performed by Gao and Pederson (17) suggested that the anionic species generally did not participate in sorption interactions and, furthermore, that inclusion of zwitterionic species does not improve the model. Consequently, both the anionic and zwitterionic species were not considered by Gao and Pederson (17) for modeling purposes. In our study, however, all three species (cationic, neutral, and anionic) were considered as part of the overall model.

**Implications of Speciation on Transport Mechanism.** These results show that speciation of the sulfonamides significantly affects the sorption (and transport by inference) of sulfonamides. Hence, sorption and transport phenomena should

be considered with reference to the pH. In highly acidic soils, sulfonamides can be expected to partially occur in the cationic form and become attached to the clay surface by cation exchange. On the other hand, in alkaline soils with pH levels well above the isoelectric point of the sulfonamides, the sulfonamides will speciate to the anionic form and can be expected to be much more mobile. The pH (alkalinity or acidity) of a soil is only one of the important factors that could increase mobility, and its role must be judged in combination with other soil properties that may affect sorption and mobility. For example, the highest sorption noted in this study was for the Iowa sandy loam. This is consistent with the high charge density (contributing to cationic exchange) and higher percent organic carbon content (**Table 1**) (contributing to partitioning into organic carbon) relative to the other two soils studied.

**Environmental Significance.** Occurrence of pharmaceutical compounds in the aquatic environment has been widely reported in scientific journals. Land application of antimicrobial-containing manure from livestock operations could potentially endanger the environment and affect human health if drinking water supplies are affected. The results of this work demonstrate the effect of pH on sorption of antimicrobials to soils. Transport modeling of these antimicrobials has also been conducted and will be reported elsewhere as a function of pH and pH-based sorption coefficients. This study provides quantitative determination and modeling of SMN and STZ in real soils and demonstrates the significant variation of sorption with pH.

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