

Degradation Kinetics of Manure-Derived Sulfadimethoxine in Amended Soil

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Spreading of contaminated manure into agricultural lands as fertilizer is one of the major routes through which veterinary antibiotics enter the environment. In this study, the degradation of manure-derived sulfadimethoxine, a widely used veterinary sulfonamide antibiotic, in manure-amended soil was investigated. A kinetic model, called the availability-adjusted first-order model based on the first-order kinetics and an assumption of the availability of target compound during the degradation process, was developed and was found to fit sulfadimethoxine degradation well. The effect of initial sulfadimethoxine concentration showed that the degradation rate constant increased with decreasing initial concentration, indicating that the bioactivity of the degrading microorganisms in manure-amended soil was sensitive to sulfadimethoxine concentration. Sulfadimethoxine degradation was accelerated with increasing manure content in amended soil. Degradation in nonamended soil was significantly slower than in manure-amended soil. This indicated that sulfadimethoxine may become more persistent once it reaches soil after leaching from manure and that storage of manure for a certain period before application is needed to diminish sulfadimethoxine contamination. Sulfadimethoxine degradation was effectively enhanced with increasing moisture of amended soil. No adverse effect was observed with manure storage on the degradation of manure-derived sulfadimethoxine in amended soil.

KEYWORDS: Sulfadimethoxine; sulfonamide; antibiotic; degradation; manure; soil

INTRODUCTION

In modern agriculture, veterinary antibiotics are administered to animals not only casually for therapeutical treatment but also routinely for growth promotion. It was estimated that >22 million pounds of antibiotics were used to treat farm animals and pets in the United States in 2002 (1). Contaminations of veterinary antibiotics in surface water, groundwater, and soil have been reported (2–5). Scientific and public concerns about the presence of veterinary antibiotics in the environment and its risk to human health and ecosystem safety are increasing (6, 7). Evidence has shown that antibiotic-resistant genes can be built up and widely transferred among microorganisms in the environment (8, 9). Pathogenic bacteria may become antibiotic resistant by adapting resistance-encoding genes. When resistant pathogens are transferred into humans and animals through drinking water or the food chain, the success of pharmaceutical therapies is greatly diminished.

The excretion of feces and urine from medicated animals and the subsequent application of the contaminated manure as

fertilizer into agricultural lands is among the major routes through which the veterinary antibiotics enter the environment (6, 10, 11). Veterinary antibiotics generally cannot be totally metabolized by physiological processes in animals. For some antibiotics, as much as 40–90% of the applied dose is excreted as parent compounds after treatment (12, 13). Some of the metabolites may still possess antibacterial activity (14, 15), and some can convert to their parent compounds in manure during storage and physical–chemical treatment (16). Although degradation of pharmaceuticals occurs in manure, readily detectable levels of veterinary antibiotic residues may remain in manure after composting and storage (10). Considerable amounts of various veterinary antibiotics are unintentionally introduced into soil with the application of animal manure in agricultural lands.

As a heavily used group of veterinary antibiotics, sulfonamides have been intensively studied with respect to their occurrence in the environment, as well as the sorption in soil with and without manure. It was found that the concentration of sulfadimethoxine, a sulfonamide antibiotic, in fresh feces from treated calves was as high as 300–900 mg kg⁻¹ (17). In soil fertilized with manure, the concentration of sulfadimidine, another sulfonamide antibiotic, was detected at 11 μg kg⁻¹ (18). Because of the low sorption affinity and high mobility in soil, sulfonamides have very high potential to leach into groundwater

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(19). Sulfadimidine concentration in groundwater below agricultural land was detected at 0.08–0.16 $\mu\text{g L}^{-1}$ (4). Sorption studies showed that all of the investigated sulfonamides, including sulfanilamide, sulfadimidine, sulfadiazine, sulfadimethoxine, sulfapyridine, and sulfachloropyridazine, could be characterized by low sorption potential and became less adsorptive in soil with the addition of manure (19, 20). The major metabolism pathway of sulfadimethoxine and sulfamonomethoxine in animals was found to be N^4 -acetylation (21, 22). The amino- N -substituted metabolites of sulfonamides generally possess greatly reduced antibacterial activity (20). During an incubation of 180 days in the laboratory, sulfadimethoxine was found to be degraded by $\sim 20\%$ in sediment, whereas ormethoprim and trimthorim, two miscellaneous antibiotics, disappeared within 60 days. It was proposed that demethylation might be the degradation pathway of sulfadimethoxine. No change was found in antibacterial activity of sulfadimethoxine-treated sediment during this incubation, indicating that the antibacterial activity of the degradation products was not significantly higher than that of sulfadimethoxine (23). However, little was known about the degradation kinetics of sulfonamides in soil, manure, and manure-amended soil. Effects of various environmental factors on the degradation of sulfonamides have been rarely investigated.

In the present study, sulfadimethoxine [4-amino- N -(2,6-dimethoxy-4-pyridinyl) benzenesulfonamide] was chosen as the target sulfonamide antibiotic. Sulfadimethoxine was spiked into manure first, and then the fortified manure was mixed with soil, imitating the application of contaminated manure into tilled soil. The degradation kinetics of sulfadimethoxine in manure-amended soil was studied. The effect of sulfadimethoxine concentration, manure amendment ratio, moisture of amended soil, and aging of the spiked manure on the degradation of sulfadimethoxine was investigated.

MATERIALS AND METHODS

Chemicals, Soil, and Manure. Sulfadimethoxine (>99%) was purchased from Sigma (St. Louis, MO). Acetonitrile (optima grade), acetic acid (HPLC grade), and methanol (HPLC grade) were purchased from Fisher (Fair Lawn, NJ). Acetone (HPLC grade) was purchased from Burdick & Jackson (Muskegon, MI).

Soil was obtained from the top layer (0–10 cm) of grassland in University Park, PA. After collection, soil was immediately transferred to the laboratory and air-dried. After manually sorting to remove gravel and plant residues, the soil was sieved to 1 mm. Soil texture was determined to be silt loam with clay 26.9%, silt 65.1%, and sand 8.0%. Soil pH (at soil/water = 1:2 by wet weight) was 5.54, organic carbon content was 1.44%, and moisture was 1.8%.

Steer manure was produced by Earthgro Inc. (Marysville, OH) and was purchased from K-mart at Riverside, CA. Manure was sieved to 4 mm. The moisture content was determined to be 83% and manure pH (at wet manure/water = 1:2 by weight) was 8.37. No sulfadimethoxine residue was detected in the manure.

Degradation Experiments. Sulfadimethoxine was dissolved in acetone at 2.0×10^3 , 5.0×10^3 , 1.0×10^4 , and 2.0×10^4 μM , respectively. Three milliliters of sulfadimethoxine solution at each concentration was added into a portion of 30.0 g (dry weight) of manure in different 150-mL beakers. The manure was thoroughly mixed in the beakers, and then the beakers were transferred into a vacuum hood for evaporation of acetone. After 4 h of evaporation, four portions of the spiked manure were transferred into four portions of 570 g (dry weight) of soil in four plastic zip bags, respectively. Soil and manure were thoroughly mixed. After the addition of water to bring the moisture of manure-amended soil to 20%, soil and manure were then thoroughly mixed a second time. The sulfadimethoxine concentration in manure-amended soil was 1.0×10^1 , 2.5×10^1 , 5.0×10^1 , and 1.0×10^2 $\mu\text{mol kg}^{-1}$ (dry weight), respectively.

Amended soil at each sulfadimethoxine concentration was then weighed into eight 150-mL glass jars at ~ 100 g (wet weight) per jar. After the weight of each jar had been recorded, they were loosely covered with aluminum foil and transferred into a constant-temperature room at 25 ± 0.5 $^\circ\text{C}$. Every other day, jars were weighed and water was added to compensate for any moisture loss. At days 0, 5, 10, 20, 30, 40, 55, and 70, one jar from each sulfadimethoxine concentration was taken out, sealed, and then put into a freezer at -21 $^\circ\text{C}$ until extraction for sulfadimethoxine concentration analysis. Storage period in the freezer for all samples was no longer than 80 days.

To investigate the effect of manure amendment ratio on the degradation of sulfadimethoxine, four portions of 3.0 mL of 1.0×10^4 μM sulfadimethoxine solution were spiked into 30 g (dry weight) of soil and 12, 30, and 60 g (dry weight) of manure, respectively. The fortified soil or manure was then mixed with 570, 588, 570, and 540 g (dry weight) of soil, respectively, following the procedure stated above. The sulfadimethoxine concentration in manure-amended soil was 5×10^1 $\mu\text{mol kg}^{-1}$ (dry weight), and the moisture was at 20%. The percentage of manure in the amended soil was 0, 2, 5, and 10% (in dry weight), respectively.

When the degradation of sulfadimethoxine in manure-amended soil with different moistures was investigated, sulfadimethoxine concentration was controlled at 5×10^1 $\mu\text{mol kg}^{-1}$ (dry weight) and manure percentage in the amended soil was controlled at 5% (in dry weight). Different amounts of water were added into the manure-amended soil, controlling the moisture at 15, 20, and 25%, respectively.

The aging effect of the spiked manure on the degradation of sulfadimethoxine in the amended soil was also studied. A portion of 30 g (dry weight) of manure was spiked with 3.0 mL of 1.0×10^4 μM sulfadimethoxine solution in a 150-mL glass jar. After mixing in the jar and the evaporation of acetone in a vacuum hood, the spiked manure was sealed and stored in a refrigerator at 4 $^\circ\text{C}$. Fifteen days later, the aged manure was mixed into 570 g (dry weight) of soil. Manure percentage in the amended soil was 5% (in dry weight), and the moisture was controlled at 20%.

Control samples were prepared in sterilized soil. Six hundred grams (dry weight) of soil was weighed into a Fisher plastic autoclave bag and then sterilized at 121 $^\circ\text{C}$ for 1 h. Sterilization was repeated for a total of three times. After the soil had completely cooled, 3 mL of 1.0×10^4 μM sulfadimethoxine solution and a certain weight of cool sterilized water were added into the soil in a laminar hood. The soil was then thoroughly mixed in the bag. Soil moisture was 20%, and sulfadimethoxine concentration was 5.0×10^1 $\mu\text{mol kg}^{-1}$. After the soil was transferred into glass jars in the laminar hood, jars were immediately sealed with caps and put into a constant-temperature room for incubation with other samples.

Sulfadimethoxine Concentration Analysis. After thawing at room temperature, the amended soil sample in each jar was thoroughly mixed. Three portions of 12.5 g (wet weight) of sample from each jar were weighed into three 40-mL polyethylene centrifuge tubes. Fifteen milliliters of methanol/acetic acid mixture (10:1 in volume) was immediately added into each tube. After being sealed with caps, tubes were vigorously shaken for 30 min in a reciprocating shaker (Eberbach Corp., Ann Arbor, MI). Tubes were then centrifuged at 11000 rpm for 10 min, and supernatants were transferred into 50-mL metric flasks. Extraction was repeated for a total of three times. Supernatants from the same centrifuge tube were combined and then diluted to 50 mL in each metric flask. One milliliter of extract from each flask was transferred into a 2-mL GC vial for sulfadimethoxine concentration analysis. The concentration of sulfadimethoxine in manure was calculated on the basis of the following equation

$$C_m = 50C_e/12.5 \quad (1)$$

where C_m ($\mu\text{mol kg}^{-1}$) and C_e ($\mu\text{mol L}^{-1}$) are sulfadimethoxine concentration in manure and extract, respectively.

A Hewlett-Packard series II 1090 high-performance liquid chromatograph (Wilmington, DE) was used for concentration analysis. An Agilent Hypersil ODS 5 μm 4.0 \times 250 mm column was used for separation. Mobile phase was composed of 75% water with 10 mM ammonium acetate and 10 mM acetic acid and 25% acetonitrile. The

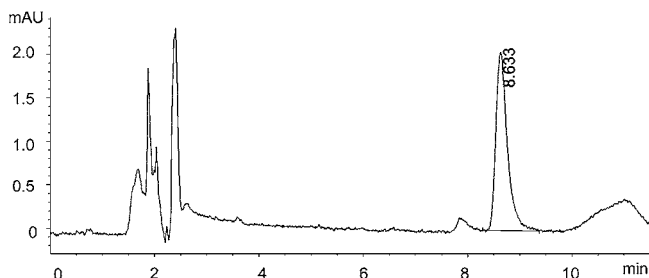


Figure 1. Typical HPLC spectrum of sulfadimethoxine in manure extract.

detection wavelength of the diode array detector was set at 270 ± 20 nm with reference at 450 ± 80 nm. The retention time of sulfadimethoxine was 8.6 min. A typical HPLC spectrum is shown in Figure 1.

The detection and quantification limits of this method were 0.8 and $1.7 \mu\text{mol kg}^{-1}$ (dry weight) of sulfadimethoxine in manure, respectively. The linear concentration range was determined to be from 1.7 to $4200 \mu\text{mol kg}^{-1}$ (dry weight). Sulfadimethoxine was quantified on the basis of external standards. The extraction recovery of sulfadimethoxine from soil containing 10% manure (in dry weight) was $92.7 \pm 0.5\%$. Data presented in this study have not been adjusted on the basis of the extraction recovery.

Kinetic Model. Degradation kinetics of many organic contaminants in the environment follows the pseudo-first-order model (24–28), which can be expressed as

$$dC/dt = -kC \quad (2)$$

where C ($\mu\text{mol kg}^{-1}$ or $\mu\text{mol L}^{-1}$) is the instant concentration of the target compound at time t (day) and k (day^{-1}) is the rate constant.

When a portion of the target compound is adsorbed in soil, manure, or other environmental media, the degradation can be reduced because the adsorbed species are unavailable to the degrading microorganisms (29). Assuming that the ratio of nonadsorbed concentration to the total concentration of the target compound at time t is λ , then eq 2 can be written as

$$dC/dt = -k\lambda C \quad (3)$$

If λ is a constant, then it could be combined with the rate constant, and eq 3 can be written as

$$dC/dt = -k' C \quad (4)$$

Then the overall kinetics should still obey the simple first-order model.

However, if λ is not a constant, the degradation kinetics will not follow the simple first-order model. We assume that

$$\lambda(t) = \xi e^{-at} \quad (5)$$

where ξ is the fraction of the nonadsorbed amount in the total amount of the target compound at $t = 0$ and a is a constant called the unavailability coefficient. ξ is between 0 and 1, and a is non-negative. A higher a indicates a quicker decrease of λ from ξ with time during the degradation. Substituting eq 5 into eq 3, we get

$$dC/dt = -k'' C e^{-at} \quad (6)$$

where $k'' = k\xi$. Integrating both sides of eq 6 results in a degradation kinetic model that accounts for the availability of the target compound for degradation

$$C_t = C_0 e^{-k''/a(1 - e^{-at})} \quad (7)$$

where C_0 and C_t are the concentration of the target compound at time

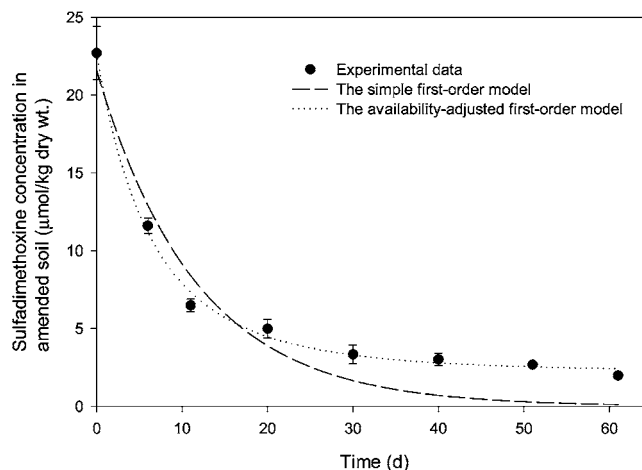


Figure 2. Fitting results of the degradation kinetics of manure-derived sulfadimethoxine in amended soil at the initial concentration of $22.7 \mu\text{mol kg}^{-1}$ using the simple first-order and availability-adjusted first-order models. Points are experimental data, and lines are fitting results.

0 and time t . Equation 7 is called the availability-adjusted first-order model and was used to fit the degradation kinetics of sulfadimethoxine in this study.

RESULTS AND DISCUSSION

Fitting the Experimental Data with the Availability-Adjusted Model. Both the simple first-order and the availability-adjusted first-order models were used to fit the degradation kinetics of manure-derived sulfadimethoxine in amended soil with an initial concentration of $22.7 \mu\text{mol/kg}$ (dry weight) (shown in Figure 2). The simple first-order model fitting result was slightly higher than the experimental data in the beginning and became lower than the experimental data afterward. The deviation of the fitting result from the experimental data indicates that the simple first-order model is not accurate enough to describe the degradation of manure-derived sulfadimethoxine in soil. This deviation also confirms that the fraction of nonadsorbed sulfadimethoxine in the total amount was not constant during the degradation.

Compared with the simple first-order model, the availability-adjusted first-order model fit the experimental data more accurately. A higher correlation coefficient, >0.99 , was obtained. Better fitting results with the availability-adjusted first-order model than with the simple first-order model were also obtained for all of the other initial concentrations. The successful fitting of the developed model implied a decreasing ratio of nonadsorbed sulfadimethoxine in the total remaining amount in the amended soil and greatly supported the assumption of eq 5.

Degradation Kinetics Affected by the Initial Concentration. Degradation of manure-derived sulfadimethoxine in amended soil with different initial concentrations of sulfadimethoxine is shown in Figure 3. All degradation kinetics obeyed the availability-adjusted first-order model well. The correlation coefficient, r , for the lowest initial concentration, that is, $8.6 \mu\text{mol/kg}$ (dry weight), was 0.98, and those for all of the other concentrations were >0.99 . Obtained values of the degradation rate constant, k'' , and the unavailability coefficient, a , are listed in Table 1. With the increase of the initial concentration of sulfadimethoxine concentration, both the degradation rate constant, k'' , and the unavailability coefficient, a , decreased.

As $k'' = k\xi$, the decrease of k'' with the increasing initial sulfadimethoxine concentration in amended soil might be attributed to the decrease of k and/or ξ . The sorption isotherms

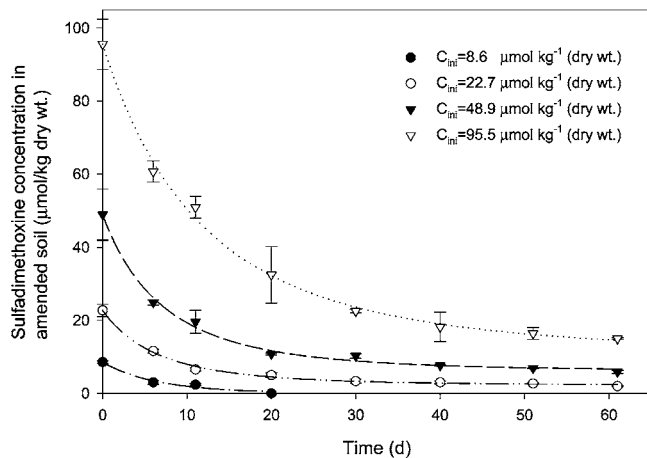


Figure 3. Degradation kinetics of manure-derived sulfadimethoxine in soil with different initial concentrations. Points are experimental data, and lines are fitting results using the availability-adjusted first-order model.

Table 1. Fitting Results of Manure-Derived Sulfadimethoxine Degradation in Amended Soil Using the Availability-Adjusted First-Order Model

initial concn in manure- amended soil ($\mu\text{mol/kg}$ of dry wt)	degradation rate constant, k (day^{-1})	unavailability coefficient, a	correlation coefficient, r	time to 50% degradation (day)
8.6	0.316 ^a	0.225 ^a	0.98	3.0
22.7	0.141 ± 0.008^b	0.0616 ± 0.0064^b	>0.99	5.8
48.9	0.124 ± 0.008^b	0.0608 ± 0.0064^b	>0.99	6.8
95.5	0.076 ± 0.004^b	0.0359 ± 0.0038^b	>0.99	11.0

^a Standard deviations and P values were not obtained. ^b P values were <0.0001.

of sulfadimethoxine and some other antibiotics in soil/manure was found to be L-shaped with a characteristic decreasing slope with increasing concentration (19, 20, 30–32), indicating that the ratio of nonadsorbed sulfadimethoxine in the total amount increases with the increase of the total concentration. It is evident that ξ increased with the increasing initial concentration of sulfadimethoxine in this study. Therefore, the decrease of k'' with increasing initial concentration of sulfadimethoxine resulted only from the decrease of k .

The first-order rate constant, k , is a pseudo rate constant, which accounts for the contributions of both chemical and biological processes in the degradation of the target compound. Microorganisms were found to be responsible for the major degradation of veterinary antibiotics in soil and manure (29, 33). It is well-known that the rate constant is independent of the reactant concentration if a chemical reaction obeys first-order kinetics (34). However, the kinetics of a biological reaction with microorganisms involved may be quite different from that of a chemical reaction. During the degradation, if the bioactivity of the microorganisms is constant, the overall degradation kinetics would probably follow the first order, but if the bioactivity is significantly altered from the initial concentration of the target compound, a higher initial concentration of the target compound may result in a lower bioactivity of the degrading microorganisms, which leads to a lower rate constant of the first-order kinetics.

Pharmaceutical antibiotics are designed to affect mainly microorganisms. There is no doubt that microorganisms are sensitive to the change of antibiotic concentration (14). With increasing initial concentration of sulfadimethoxine in manure-

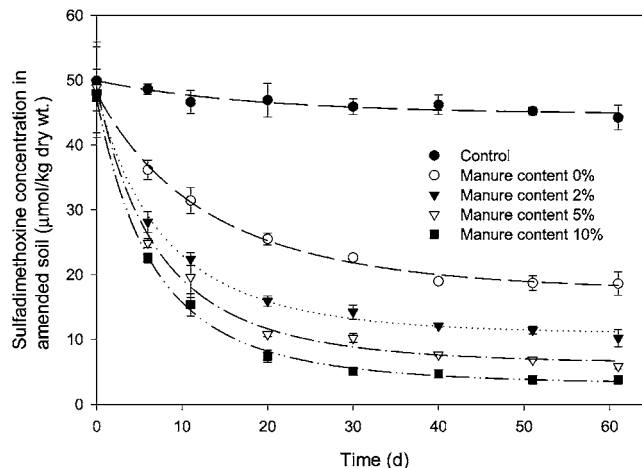


Figure 4. Degradation kinetics of sulfadimethoxine in amended soil with different contents of manure. Points are experimental data and lines are fitting results using the availability-adjusted first-order model.

amended soil, the bioactivity of the degrading microorganisms was surely weakened; thus, the contribution of the biodegradation to the overall degradation of sulfadimethoxine was lessened. Therefore, a reduction of k'' was observed with the increasing initial sulfadimethoxine concentration.

The decrease of a with the increase of sulfadimethoxine initial concentration might result from the decrease of k'' . A lower value of k'' means a lower percentage of sulfadimethoxine is degraded within a certain period of time. It is certain that the decline of the nonadsorbed sulfadimethoxine concentration in aqueous phase was slower at a lower k'' than at a higher one. If any desorption hysteresis existed, the instant ratio of non-adsorbed sulfadimethoxine in its total remaining amount in the soil declined absolutely more quickly (i.e., a higher a) at a higher k'' than at a lower one. Hence, the lower the degradation rate constant, k'' , the lower the unavailability of sulfadimethoxine, a .

Time for the degradation of 50% sulfadimethoxine in manure-amended soil was calculated on the basis of the following equation, which was derived from eq 7

$$t_{50\%} = -\frac{1}{a} \ln \left(1 - \frac{0.693a}{k''} \right) \quad (8)$$

The obtained values of $t_{50\%}$ for different initial concentrations are also listed in **Table 1**. Although a high degradation rate constant was found always to associate with a high unavailability coefficient, which slows the degradation, $t_{50\%}$ decreased with increasing rate constant. This implied that the rate constant dominated the degradation of manure-derived sulfadimethoxine in amended soil. Lowering the initial concentration of sulfadimethoxine in manure may result in a high degradation rate constant in amended soil, which helps to eliminate sulfadimethoxine contamination in the environment.

Effect of Manure Content. The degradation of manure-derived sulfadimethoxine in amended soil was accelerated with increasing manure content (shown in **Figure 4**). Degradation kinetics with different manure contents obeyed the availability-adjusted first-order model, and regression coefficients were >0.99 (data not shown). With the increase of manure content from 0 to 2, 5, and 10%, the rate constant, k'' , increased from 0.051 ± 0.002 to 0.102 ± 0.005 , 0.124 ± 0.008 , and 0.141 ± 0.004 (day^{-1}), and the unavailability coefficient, a , changed from 0.051 ± 0.004 to 0.069 ± 0.005 , 0.061 ± 0.006 , and 0.052 ± 0.003 , respectively. However, no significant degradation was

found in control samples (sterilized nonamended soil) during the incubation period. The remarkably faster degradation in nonsterilized soil than in sterilized soil indicated that microorganisms are responsible for the major degradation of sulfadimethoxine in soil. A similar phenomenon was also observed in sterilized and nonsterilized manure (results not presented in this study).

Compared with that in manure-amended soil, sulfadimethoxine degradation in nonamended soil was significantly slower. This difference in rate constant might result from the different pH values of soil and manure, which were 5.54 and 8.37, respectively. It was reported that many antibiotics hydrolyzed more rapidly in alkaline solutions than in acidic ones (33, 35, 36). However, the faster degradation in manure-amended soil than in nonamended soil might result mainly from the richer degrading microorganisms in manure than in soil (29, 33). It was reported that the measured bacterial populations in an experimental soil with 1 and 10% manure amendment were 0.7 and 2.6 times higher, respectively, than in the nonamended soil (37). This result implied that once sulfadimethoxine is introduced into the soil, it may persist for a longer time than in manure. Therefore, a certain period of storage for contaminated manure is recommended before its application into tilled soil, thus diminishing the contamination of manure-derived sulfadimethoxine or other veterinary antibiotics in the environment.

With the increase of manure content from 2 to 10%, the degradation of manure-derived sulfadimethoxine was enhanced. In this study, sulfadimethoxine was first spiked into manure and then the fortified manure was mixed with soil. Hence, the same concentration of sulfadimethoxine in the amended soil with different manure contents meant different initial concentrations of sulfadimethoxine in the manure. It might take some time for sulfadimethoxine to diffuse from manure into soil, and the major degradation could occur in the manure instead of the soil. As revealed in the section on the initial concentration effect, a lower initial concentration of sulfadimethoxine resulted in a lower inhibition on the bioactivity of the degrading microorganisms and thus a faster degradation. At this point, the effect of manure content is quite similar to that of the initial concentration.

With the increasing rate constant, k'' , the unavailability coefficient, a , was found to decrease, exhibiting a contrary phenomenon of a and k'' to what was observed in the effect of initial concentration of sulfadimethoxine. This unique observation of a and k'' might be caused by the change of the amended soil pH. When the manure content increased from 0 to 2, 5, and 10%, the soil pH (at amended soil/water = 1:2 in wet weight) increased from 5.54 to 6.01, 6.34, and 6.73, respectively. The increasing pH might have accelerated the desorption of sulfadimethoxine from the manure-amended soil (19, 20) and greatly enhanced the availability of sulfadimethoxine to the degrading microorganisms. Hence, the obtained unavailability coefficient decreased with the increase of manure content.

Degradation at Different Moisture Contents. The degradation of manure-derived sulfadimethoxine was further studied in amended soil with different moisture contents. Increasing moisture significantly accelerated the degradation of sulfadimethoxine (shown in Figure 5). Degradation kinetics at three investigated moistures obeyed the availability-adjusted first-order model, and correlation coefficients were >0.99 (data not shown). With the increase of moisture from 15 to 20 and 25%, the degradation rate constant, k'' , increased from 0.082 ± 0.004 to 0.122 ± 0.007 and 0.170 ± 0.010 (day^{-1}), and the unavailability coefficient, a , increased from 0.041 ± 0.003 to 0.060 ± 0.006 and 0.081 ± 0.007 . On the basis of eq 8, the

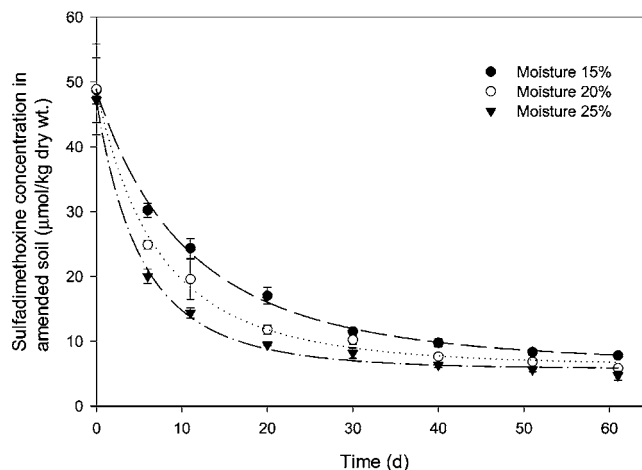


Figure 5. Degradation kinetics of manure-derived sulfadimethoxine in amended soil with different moistures. Points are experimental data, and lines are fitting results using the availability-adjusted first-order model.

times for 50% sulfadimethoxine degradation at different moistures were also calculated. They were 10.4, 6.9, and 4.9 days at moisture contents of 15, 20, and 25%, respectively. Increasing soil moisture effectively shortened the persistence of sulfadimethoxine in amended soil.

The enhanced degradation of sulfadimethoxine at high moisture of manure-amended soil might result from the change of the fraction of nonadsorbed sulfadimethoxine in the total amount in the amended soil, ξ . With the increase of moisture, ξ increased because more sulfadimethoxine was dissolved in the aqueous phase and became available for biochemical and/or chemical degradation. As $k'' = k\xi$, an increase of k'' was observed with increasing moisture. However, sulfonamides were found to have low sorption affinity and high mobility in soil (19, 29). Excessive moisture may lead to runoff and leaching of sulfadimethoxine from manure-amended soil, resulting in surface water and groundwater contamination.

Aging Effect of Manure. It was found that the sorption of some organic contaminants in soil increased and became hard to be desorbed with aging (38–40). The enhanced sorption may be attributed to diffusion of contaminants into less accessible sorption sites in adsorbents and stronger interaction between contaminants and adsorbents. As stated above, a certain storage period is recommended for contaminated manure to ultimately utilize manure-borne microorganisms to degrade sulfadimethoxine in the manure. However, long storage might enhance the sorption of sulfadimethoxine in the manure, thus impeding the degradation of sulfadimethoxine after the manure is spread into soil. To identify the aging effect, two kinds of sulfadimethoxine-spiked manure were amended with soil for experiments. One was the fresh sulfadimethoxine-spiked manure, and the other was aged spiked manure with an aging period of 15 days at 4 °C. The degradation kinetics of sulfadimethoxine in amended soil with two kinds of manure were compared (shown in Figure 6).

Both degradation kinetics fit the availability-adjusted first-order model with correlation coefficients >0.99 . Although the detected initial sulfadimethoxine concentration in amended soil with aged manure was significantly lower than that with fresh spiked manure, which resulted from the degradation during the aging period, the obtained values of degradation rate constant, k'' , as well as values of the unavailability coefficient, a , were almost the same. Values of k'' were 0.122 ± 0.007 and 0.122 ± 0.003 (days^{-1}), and those of a were 0.060 ± 0.006 and 0.065 ± 0.002 , for soil amended with fresh and aged spiked manure,

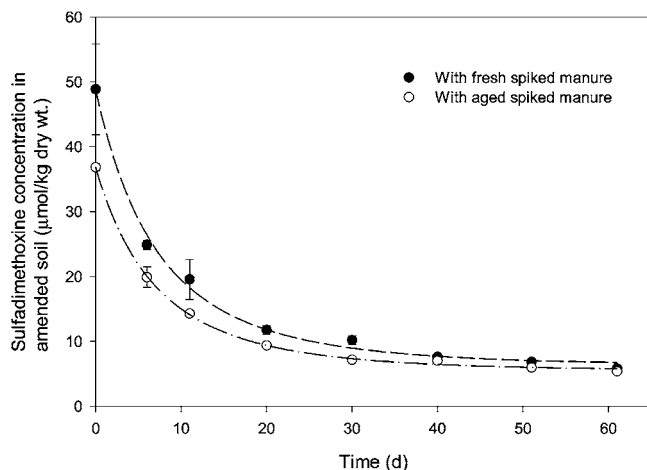


Figure 6. Degradation kinetics of sulfadimethoxine in soil amended with aged and fresh spiked manure. Points are experimental data, and lines are fitting results using the availability-adjusted first-order model.

respectively. Similar values of k'' , as well as those of a , indicated that the degradation of sulfadimethoxine from both aged and fresh manure shared the same degradation kinetics in the amended soil. The storage of manure did not create any enhanced interaction between sulfadimethoxine and manure, which impeded the degradation of sulfadimethoxine in amended soil.

Storage of manure before its application as fertilizer into tilled soil helps to eliminate the residue of sulfadimethoxine in manure and causes no adverse effect on the degradation of sulfadimethoxine after manure is amended into soil. Lowering the initial sulfadimethoxine concentration in manure and increasing the moisture content can effectively accelerate sulfadimethoxine degradation in manure-amended soil. Further study might be needed to investigate the degradation kinetics of sulfadimethoxine in manure and effects of various environmental factors.

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