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ENVIRONMENTAL BENEFITS OF BIOCHAR

Effect of Biochar Amendment on Tylosin Adsorption–Desorption and Transport in Two Different Soils

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The role of biochar as a soil amendment on the adsorption–desorption and transport of tylosin, a macrolide class of veterinary antibiotic, is little known. In this study, batch and column experiments were conducted to investigate the adsorption kinetics and transport of tylosin in forest and agricultural corn field soils amended with hardwood and softwood biochars. Tylosin adsorption was rapid at initial stages, followed by slow and continued adsorption. Amounts of adsorption increased as the biochar amendment rate increased from 1 to 10%. For soils with the hardwood biochar, tylosin adsorption was 10 to 18% higher than that when using the softwood biochar. Adsorption kinetics was well described by Elovich equation ($r^2 \geq 0.921$). As the percent of biochar was increased, the rates of initial reactions were generally increased, as indicated by increasing α value at low initial tylosin concentration, whereas the rates during extended reaction times were generally increased, as indicated by decreasing β value at high initial tylosin concentration. A considerably higher amount of tylosin remained after desorption in the corn field soil than in the forest soil regardless of the rate of biochar amendment, which was attributed to the high pH and silt content of the former. The breakthrough curves of tylosin showed that the two soils with biochar amendment had much greater retardation than those of soils without biochar. The CXTFIT model for the miscible displacement column study described well the peak arrival time as well as the maximum concentration of tylosin breakthrough curves but showed some underestimation at advanced stages of tylosin leaching, especially in the corn field soil. Overall, the results indicate that biochar amendments enhance the retention and reduce the transport of tylosin in soils.

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Veterinary antibiotics are widely used as feed additives in intensive livestock production, and studies have shown that as much as 90% of these antibiotics can be excreted, primarily through the feces (Sarmah et al., 2006). This has raised concern over the ecological risks associated with antibiotic compounds in the environment because animal manure is widely applied on agricultural lands as fertilizer (Boxall et al., 2004; Hu et al., 2010). Antibiotics may be released into the aquatic environment through surface runoff (Chefetz et al., 2008; Topp et al., 2008) and leaching into ground water (Blackwell et al., 2009). Therefore, antibiotic compounds can enter the food chain, imposing potentially adverse impacts on human health (Boxall et al., 2006).

Tylosin, a macrolide class antibiotic, has been used for disease prevention and growth promotion in swine, beef cattle, and poultry production (Sarmah et al., 2006). The compound was first isolated from a strain of *Streptomycetes fradiae* found in soil from Thailand (McGuire et al., 1961) and is produced by fermentation. The veterinary formulation of tylosin is often a mixture of tylosin A (tylosin), tylosin B (desmycosin), tylosin C (macrosin), and tylosin D (relomycin), with tylosin A being the primary component (>90%) (Loke et al., 2000). This natural product exhibits antibacterial activity against numerous gram-positive bacteria and mycoplasma species by binding to ribosomes and inhibiting bacterial protein synthesis (Elanco, 1982). Tylosin likely behaves as a cation in soils that are below neutral pH because it has a pK_a of 7.4 (O'Neil et al., 2001). It has been proposed that the protonated form of tylosin is primarily bound on anionic components of soil and manure matrices through ionic bonds; however, it can also bind with cationic components of manure through Van der Waals dipole interactions (Loke et al., 2002).

Fate and transport studies are often conducted to assess the behaviors of contaminants in the soil environment. Accurate predictions for the transport of the contaminants are dependent on an understanding of their adsorption–desorption characteristics (Unold et al., 2009). The adsorption–desorption process is affected by the physical and chemical properties of the contaminants and of the soil. Previous studies have

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Abbreviations: BTCs, breakthrough curves; CEC, cation exchange capacity.

demonstrated that soil properties, such as organic matter, clay content, pH, Fe oxide, and cation exchange capacity (CEC), can have significant effects on the behavior of chemicals in soils (Rabølle and Spliid, 2000; Loke et al., 2002).

Recently, the application of biochars as soil amendments to agricultural lands has been proposed for soil carbon (C) sequestration and to increase plant growth through enhancing nutrient and water-use efficiency (Laird et al., 2010). Biochar refers to biologically active charcoal resulting from the pyrolysis of biomass. Mikan and Abrams (1995) reported that soil near a charcoal hearth increased the CEC by up to 40% and soil pH by up to one unit. Because of enhanced CEC, biochar was also proposed for remediation of contaminated lands (Beesley et al., 2010). Hossain et al. (2010) investigated the effectiveness of waste sludge biochars for promoting cherry tomato growth and found that biochar application increased yields by 64% and reduced the uptake of bioavailable metals. In addition, Yu et al. (2009) reported that biochar addition to soils reduced the bioavailability of soil-applied pesticides to spring onions due to the high affinity of biochar for pesticides. Evidence from direct burning of plant residues and natural forest fires have further suggested a role for biochars in enhancing the retention of contaminants in soils (Young et al., 2005; Lehmann et al., 2006). For example, Yang and Sheng (2003) showed that the soil adsorption of diuron after a residue burn was 400 to 2500 times more effective than that without the residue burn. They concluded that black C remaining after the burn was primarily responsible for the enhanced adsorptive characteristics of soils. Clearly, biochar has the potential to reduce pollutant mobility and nutrient leaching. Biochar also improves overall soil physical properties and benefits plant growth through better recycling of soil nutrients and increasing soil organic C (Lehmann et al., 2006).

Despite widespread interest in biochars as soil amendments, there is very little information in the literature on the effects of biochar amendments on the release or transport of antibiotics in soils. The objectives of this study were therefore to investigate the effects of two different biochars on tylosin adsorption–desorption behavior in two soils with contrasting properties and to determine the influence of a biochar on tylosin transport characteristics in these soils.

Materials and Methods

Biochars and Soils

The biochars used in this study were produced from pulp-grade hardwood and softwood chips. The hardwood chips were composed mostly of sweetgum and oak. The softwood chips were a mix of southern yellow pines, with loblolly pine being the predominant species. Briefly, air-dried wood chips were processed through a 25-kW pilot-scale gasification plant (BioMax 25; Community Power Corp., Littleton, CO) using standard operating procedures. The maximum process temperature within the downdraft gasifier was 850°C for the hardwood chips and 900°C for the softwood chips. The high efficiency of this bioenergy system resulted in biochar yields that were approximately 1% the weight of the feedstock consumed. The two biochars were ground in a grinder and roller to pass through a 200-μm sieve before analysis. Their physical and chemical properties are shown in Table 1. The specific surface area of the biochars was measured using the ethylene glycol monoethyl ether method (Cerato and Lutenegger, 2002). The two biochars were generally alkaline in nature (pH 9.85 and 9.86) and low in total N (2.1 and 2.3%).

The two soils used for this study were a Malbis sandy loam soil (fine-loamy, siliceous, subactive, thermic Plinthic Paleudults) from the Kisatchie National Forest, Pineville, Louisiana, and a Norwood silt soil (fine silty, mixed, superactive, hyperthermic Fluventic Eutrudepts) from a corn field at the Dean Lee Research Station, LSU Agricultural Center, Alexandria, Louisiana. The corn field had been subjected to past applications of animal manures. The collected soils were air-dried, ground, and passed through a 2-mm mesh before use. Selected physical and chemical properties of the soils are listed in Table 2.

Biochar-amended soil samples were prepared by thoroughly mixing the soil with biochar on a rotary shaker for 7 d, and the final biochar contents in the amended soils were made at 0, 1, 3, 5, and 10% (w/w), respectively.

Adsorption–Desorption: Batch Experiments

Tylosin A, the primary component in a veterinary tylosin formulation, was obtained from Sigma-Aldrich (Milwaukee, WI). Adsorption experiments were conducted at two levels

Table 1. Selected physical and chemical properties of biochars used in the study.

Parameter	Hardwood biochar	Softwood biochar
pH	9.86	9.85
Ash contents, g kg^{-1}	388.3	596.3
Total C, g kg^{-1}	552.6	287.0
Total N, g kg^{-1}	2.1	2.3
C/N ratio	263.15	124.78
Specific surface area, m^2 g^{-1}	242	159
Other elements, g kg^{-1}		
Al	0.62	7.09
Ca	82.26	103.20
Fe	6.22	9.64
K	118.90	92.10
Mg	135.80	103.40
Mn	5.72	7.23
Na	1.93	2.19
P	3.18	3.60
Si	0.17	0.28

Table 2. Selected physical and chemical properties of the studied soils.

Parameter	Forest soil (Malbis)	Corn field soil (Norwood)
pH	4.26	7.80
OM† contents, g kg^{-1}	29.7	19.6
CEC,‡ cmol kg^{-1}	2.30	2.60
Particle size distribution, g kg^{-1}		
Sand	456.0	27.8
Silt	494.0	916.0
Clay	50.0	55.6

† Organic matter.

‡ Cation exchange capacity.

of initial tylosin concentrations (250 and 500 mg L^{-1}) using a batch equilibrium method. For the adsorption experiment, 3 g of soil or biochar-amended soil samples were weighed into a Teflon centrifuge tube containing 30 mL of 0.005 mol L^{-1} $CaCl_2$ solution with one of the two initial concentrations (C_i) of tylosin. The mixture slurries were shaken for 4, 24, 48, 144, and 240 h of reaction time followed by centrifuging at 5000 × *g* for 15 min. At each reaction time, a 1.5-mL aliquot was removed from the supernatant for tylosin analysis. The slurries were then resuspended using a vortex mixer and shaken for the next reaction time.

Tylosin was desorbed from the soil after the adsorption step by replacing the supernatant with a 0.005 mol L^{-1} $CaCl_2$ background solution (containing no tylosin). A total of five desorption steps included three 0.005 mol L^{-1} $CaCl_2$ extractions followed by two methanol extractions, each lasting 48 h. Extraction supernatants were collected for tylosin analysis. All adsorption–desorption experiments were performed in duplicate. Tylosin in supernatants was analyzed using an Agilent 1100 Series high-performance liquid chromatograph (Agilent Technologies, Santa Clara, CA) equipped with an octadecylsilane (silica based) column (250 × 460 mm i.d.). The mobile phase consisted of sodium perchlorate (2.25% m/v) at pH 2.7 and acetonitrile (60:40 v/v). The flow rate was 1.2 mL min^{-1}. The column was operated at 35°C. The injection volume of the samples was 25 μL. Tylosin was detected with a UV absorbance detector at a wavelength of 290 nm (Loke et al., 2000). All experiments were performed at room temperature.

The kinetic data of tylosin adsorption was fitted with Elovich equation as follows:

$$q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t \quad [1]$$

where q_t represents the amount of adsorption (mg kg^{-1}) at time t (h), α is the initial adsorption rate (mg kg^{-1} h^{-1}), and β is related to the extent of surface coverage and activation energy for chemisorption (kg mg^{-1}).

Transport: Column Experiments

A series of miscible displacement column experiments were conducted to investigate the influence of biochar on tylosin transport in soils, based on a procedure described by Selim et al. (2010). Before packing the soil columns, biochar-amended soils (5% hardwood biochar [w/w]) were incubated for 5 wk under periodically wet-dry cycles at 20°C in a dark room. Acrylic columns (5-cm length, 6.2-cm i.d.) were uniformly packed with soil with or without biochar-amendment and were slowly saturated with 0.005 mol L^{-1} $CaCl_2$ background solution with an upward flow direction being maintained. After saturation, a constant flux was maintained by a piston pump. Each soil column received pulses of 0.005 mol L^{-1} $CaCl_2$ solution between 10 and 20 pore volumes before the introduction of tylosin pulses.

Four different miscible displacement column experiments were performed. The volume of each tylosin pulse and the soil parameters associated with each column are listed in Table 3. Before a tylosin pulse application, the dispersion coefficient (D) was estimated using bromide as a nonreactive tracer (Rabølle and Spliid, 2000). For this purpose, pulses of 45 mg L^{-1} bromide solution were applied to the column for 4 to 5 h (corresponding pore volumes are listed in Table 3). Bromide concentrations in the outflow samples were measured using a Dionex ICS-2000 ion chromatography system with suppressed conductivity (ASRS Ultra II 4mm; Dionex, Sunnyvale, CA). Bromide breakthrough curves (BTCs) were constructed using relative concentration (C/C_o) as a function of pore volume (V/V_o).

The one-dimensional convection-dispersion equation was used to describe solute transport under steady state flow in a homogeneous soil condition (please see Supplemental Information). In doing so, the CXTFIT code (Toride et al., 1999) was used to solve the convection-dispersion equation for appropriate boundary conditions. The parameter D for the bromide BTCs was estimated using a nonlinear regression based on the Levenberg-Marquardt algorithm (Press et al., 1992; Jeong and Selim, 2010) and was adapted for subsequent tylosin transport simulation.

Statistics

Tylosin adsorption by the biochar-amended soils was compared using the Student's t test with a significance level of $p < 0.05$. The JMP 5.0.1 statistical program was used in all analyses (SAS Institute, 2002).

Results and Discussion

Adsorption and Desorption

Tylosin adsorption for corn field and forest soils was generally increased by increasing the biochar amendment rate (Fig. 1 and 2). For example, tylosin adsorption in the forest soil with hardwood biochar increased from 12 to 66%, as compared with the control treatment, when the amendment rate was increased from 1 to 10%. Tylosin adsorption exhibited clear kinetic behavior in biochar-amended corn field and forest soils. Overall, the amount of tylosin adsorbed in biochar-amended soil rapidly increased during the initial stages of adsorption, followed by slow and continued adsorption. Tylosin adsorption in soils amended with hardwood biochar was significantly higher ($p < 0.05$) than those

Table 3. Soil physical parameters and experimental conditions in the miscible displacement column experiments for tylosin.

Sample	Bulk density	Moisture content	Pore water velocity	Pulse input		Dispersion coefficient
				Bromide	Tylosin	
	Mg m^{-3}	m^3 m^{-3}	m h^{-1}	PV†		m^2 h^{-1}
Forest soil	1.558	0.412	9.10×10^{-3}	1.51	3.42	7.48×10^{-5}
Forest soil + hardwood biochar	1.557	0.413	1.21×10^{-2}	1.98	13.02	8.44×10^{-5}
Corn field soil	1.475	0.443	1.20×10^{-2}	2.01	5.69	9.35×10^{-5}
Corn field soil + hardwood biochar	1.395	0.474	1.06×10^{-2}	2.02	13.72	8.56×10^{-5}

† Pore volume.

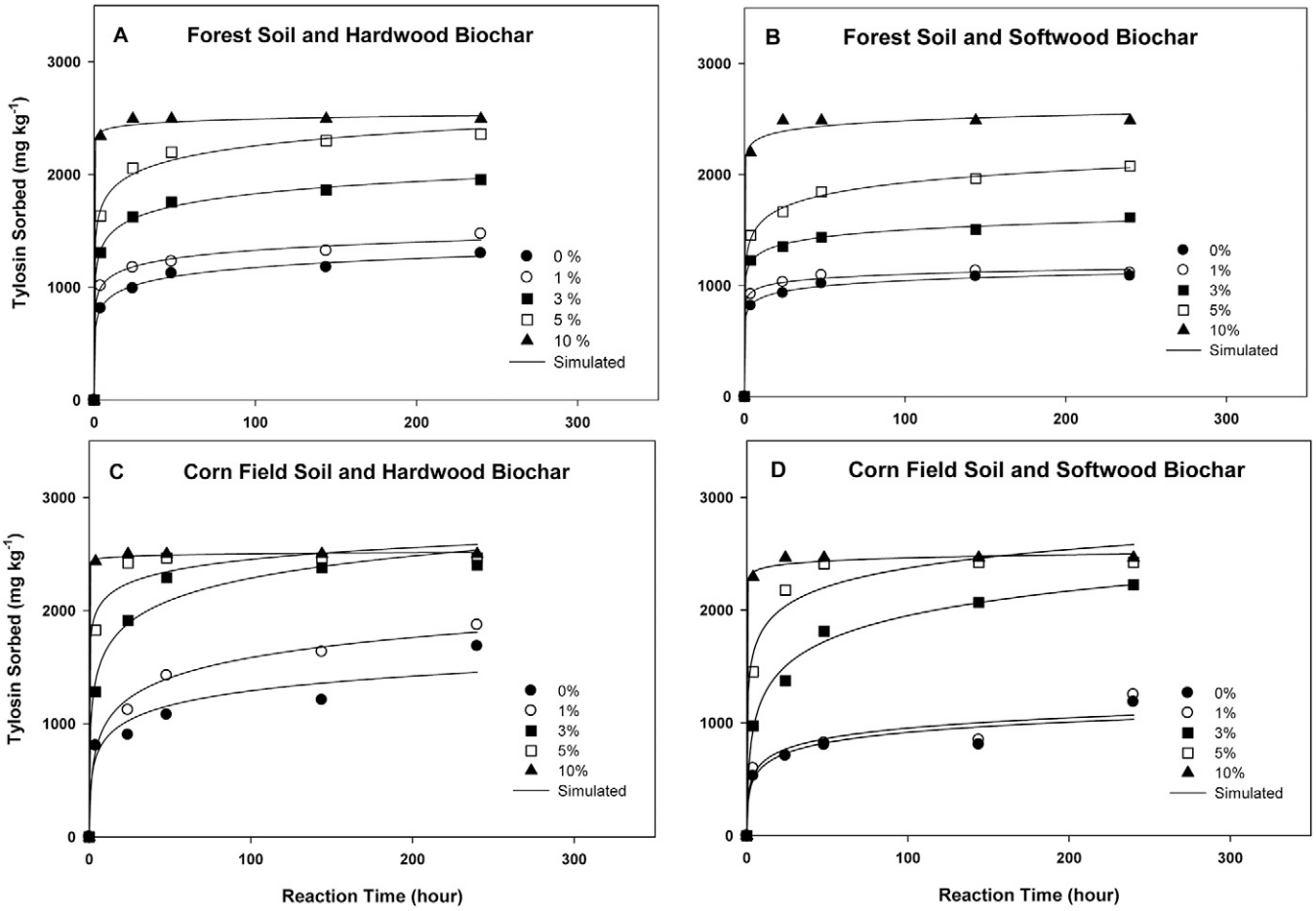

Fig. 1. Tylosin adsorption kinetics in the forest and corn field soils amended with various rates of two different biochars at initial tylosin concentration of 250 mg L^{-1}. Solid curves depict results of curve fitting with the Elovich equation.

amended with softwood biochar, especially when using higher biochar amendment rates or lower initial tylosin concentration (Supplemental Table S1). This may be due to the higher C content and specific surface area of the hardwood biochar than the softwood biochar (Table 1).

The kinetics of tylosin adsorption were generally well described by the Elovich equation, with r^2 values ranging from 0.921 to 0.999 (Fig. 1 and 2; Supplemental Tables S2 and S3). The Elovich equation has been used to estimate sorption rates of various cations and anions binding onto organic matter and soils (Wu et al., 2009; Özacar and Şengil, 2009). According to the assumption of the Elovich equation, the constant α may be regarded as the rate of initial instantaneous rapid reaction not governed by exponential law (Wu et al., 2009). The higher α value represents the fast reaction of tylosin in soils, whereas the lower β value suggests an increased rate in adsorption reaction during extended reaction times (in terms of the extent of surface coverage) (Özacar and Şengil, 2009). The resolved α value from the Elovich equation ranged from 8.67×10^2 to 5.77×10^{70}, and the β value ranged from 0.0013 to 0.0659 for tylosin adsorption by the two biochar-amended soils. The specific effects of biochar on tylosin adsorption kinetics appeared to relate to the initial tylosin concentrations. In general, there were increasing trends in α value along with an increasing biochar amendment rate when the soil was reacted with low initial tylosin concentration (250 mg L^{-1}). This suggests that the initial reaction rates were elevated as the level of biochar addition was increased. On the other hand, β values were generally decreased along with increasing percent biochar addition at high initial tylosin concentration (500 mg L^{-1}), indicating that the reaction rates during extended reaction times were enhanced. The Elovich equation has been considered as a semiempirical model because the rates of α and β are often changed with solution-to-soil ratios (Sparks, 1999). Nonetheless, our data clearly showed that the Elovich model accurately described the kinetic data of tylosin adsorption.

Total percentage of tylosin desorbed was generally decreased in the two soils with increasing biochar amendment rate (Fig. 3). The average percent tylosin desorption was 32.5% with no biochar and 9.7% with the biochar amendment rate at 10% for the forest and corn field soils, respectively. The residual tylosin, which was nonextractable after the methanol treatment, likely represented the fraction that was strongly retained by the soil matrix due to irreversible mechanisms of chemical entrapment in biochar-amended soils (Spokas et al., 2009). This observed hysteresis was likely due to the integrated influence from the characteristics of biochar and soils. Besides the reduction in total amount of tylosin desorbed, the percentage of tylosin recovered from methanol extractions became dominant as the biochar amendment rate was increased. The $CaCl_2$ salt solution extracts the tylosin present in loosely bound forms, presumably ionically bonded, whereas methanol can extract tylosin in less

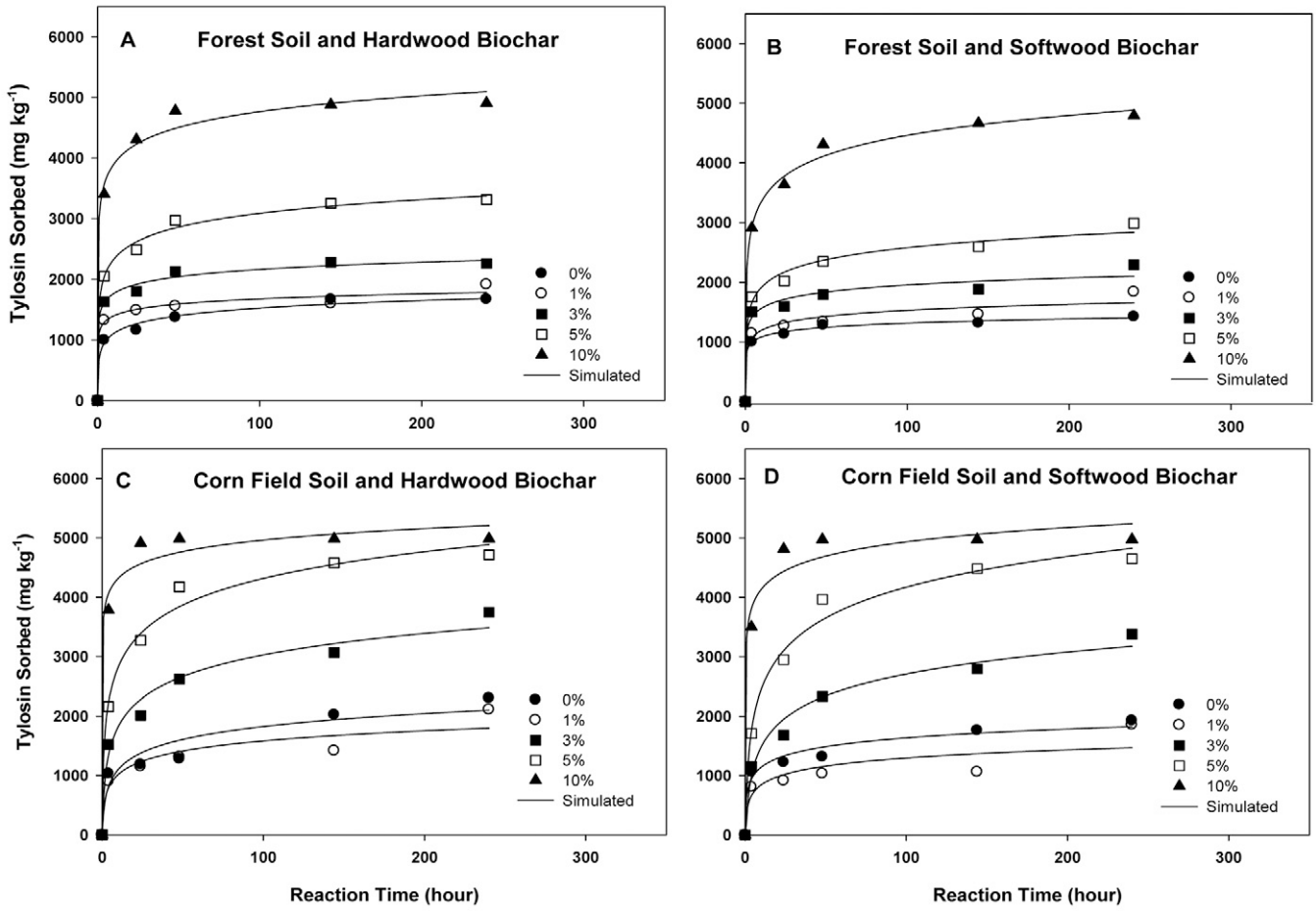

Fig. 2. Tylosin adsorption kinetics in the forest and corn field soils amended with various rates of two different biochars at initial tylosin concentration of 500 mg L^{-1}. Solid curves depict results of curve fitting with the Elovich equation.

mobile forms, such as that bound to organic matter through hydrophobic–hydrophobic interactions. Together, the results clearly demonstrate an important role for biochars in tylosin retention.

Considerably less tylosin was desorbed from the corn field soil than from the forest soil, regardless of the biochar amendment rate. For the corn field soil, the majority of tylosin desorbed was by $CaCl_2$ extraction, whereas for the forest soil it was from $CaCl_2$ and methanol extractions, with similar contributions without biochar or at low biochar amendment rates. This difference was likely due to the high organic matter content in the forest soil compared with the corn field soil (Table 2). Soil organic matter has been reported to strongly affect the adsorption of tylosin (Zhou, 2008). The corn field soil had a much higher pH than the forest soil (pH 7.80 vs. 4.26); thus, the strong adsorption of tylosin was likely due to its high pKa (7.4). Because the dominant fraction of tylosin desorbed from the corn field soil was obtained by $CaCl_2$ extraction, other mechanisms rather than electrostatic attraction may be important in tylosin retention, and soil pH also plays a strong role in this process. Rabølle and Spliid (2000) studied sorption and mobility of several veterinary antibiotics in soil and reported that oxytetracycline and tylosin had a much lower mobility compared with metronidazole and olaquindox. They showed that tylosin adsorption was positively correlated with soil clay content. In the present study, the two soils had very similar clay contents (50.0 vs. 55.6 g kg^{-1}); however, the corn field soil had much greater silt content than the forest soil (916 vs. 494 g kg^{-1}). Our results could suggest that the silt fraction plays a role in tylosin retention.

We did not control microbial activities in these experiments because the half-life of tylosin was reported to be as long as 79 to 82 d in soils (Halling-Sørensen et al., 2005). Although we could not exclude the possibility that some of unrecovered tylosin by methanol extraction could be due to transformation to other metabolites, we did observe unidentified peaks in chromatograms for desorption samples, especially from the corn field soils. Nonetheless, total percent peak areas for these unidentified substances were generally much smaller (≤14.2%) than total tylosin A peak area (≥85.8%).

Transport Characteristics

For this part of the study, only the forest and corn field soils treated at 5% hardwood biochar were examined. The choice of only one biochar for this experiment was based on basically similar kinetic retention mechanisms of the two biochars, as shown in Fig. 1 and 2. In general, the shapes of all bromide BTCs were mostly symmetrical, except for the forest soil, which showed only slight asymmetrical shape in the end of tailing part of the BTC (Fig. 4). The latter indicates physical nonequilibrium or hysteresis of the bromide tracer, which was likely due to the interaction with immobile water or intraparticle diffusion in

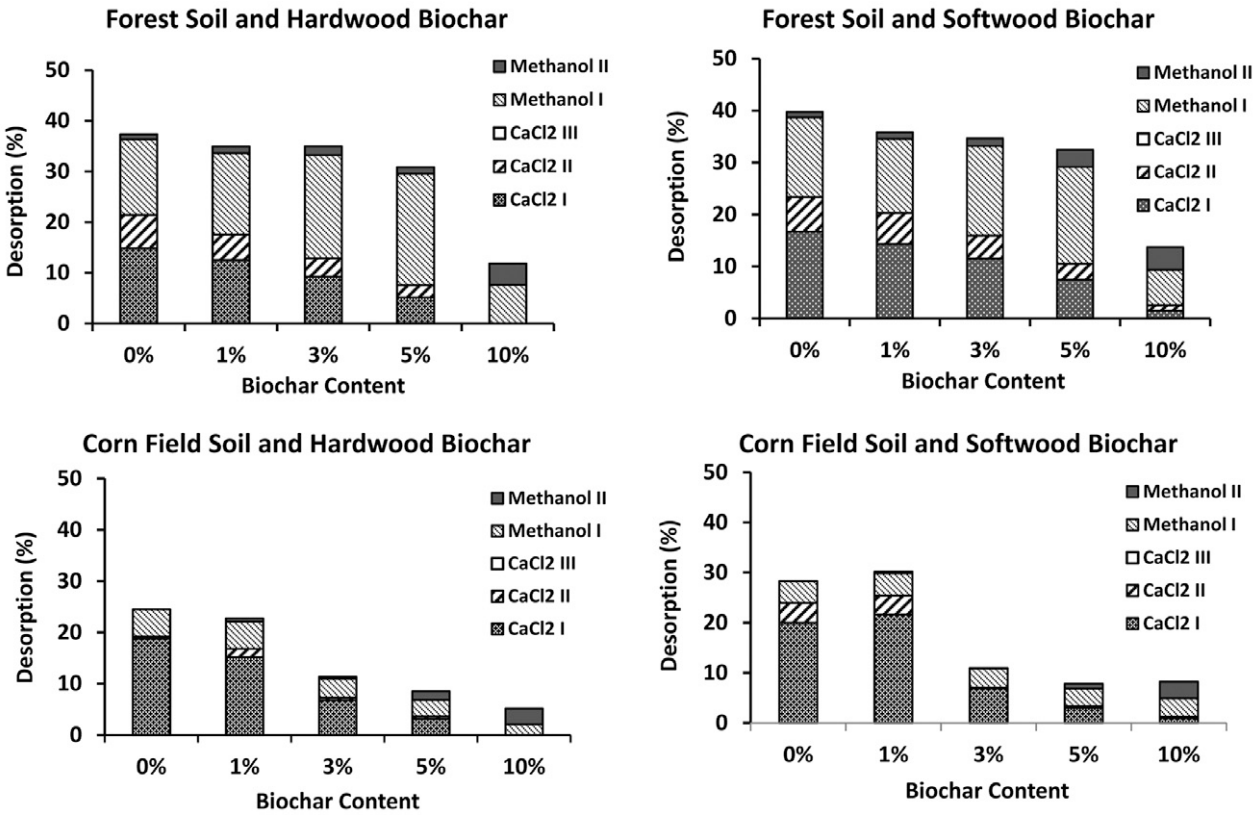

Fig. 3. Tylosin desorption with three steps of 0.005 mol L^{-1} $CaCl_2$ extractions followed by two steps of methanol extractions from the forest and corn field soils amended with different biochars.

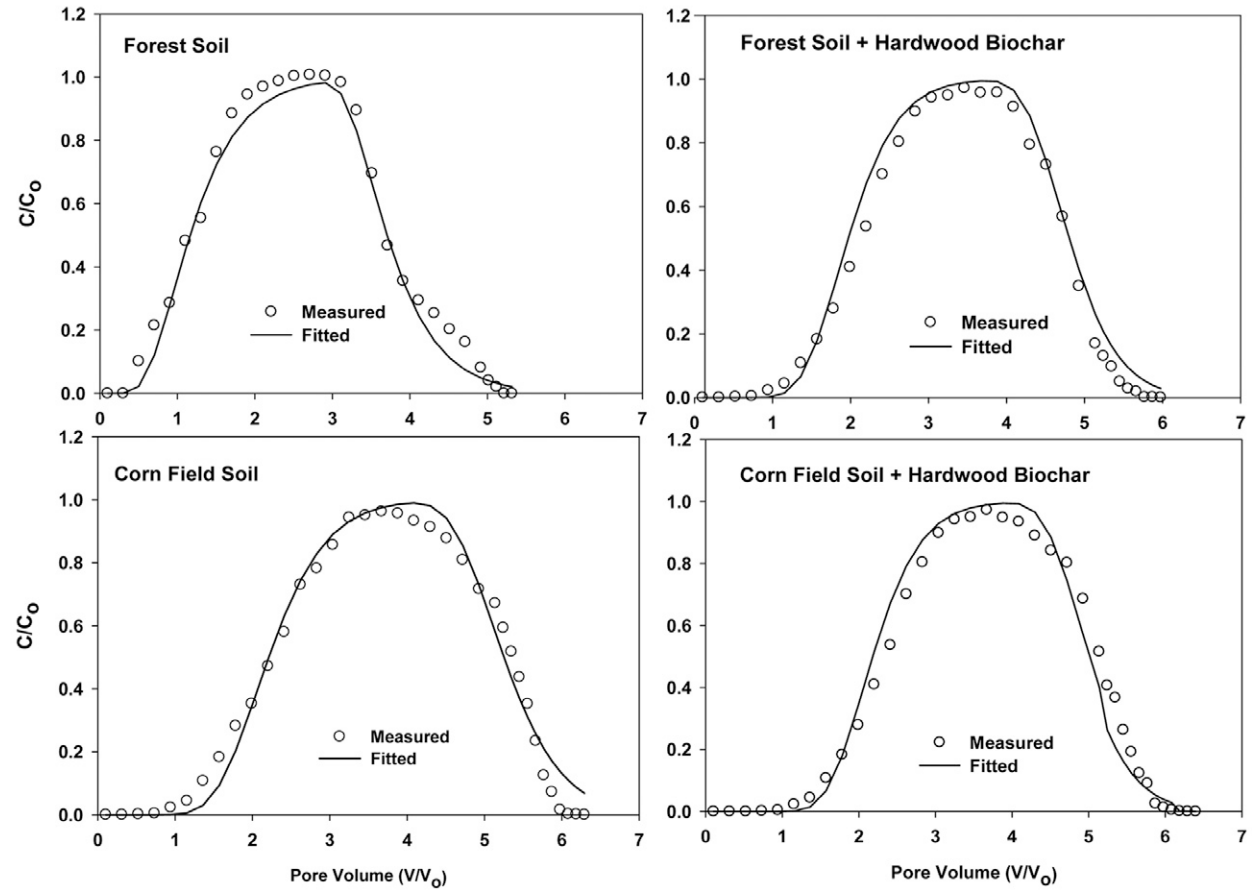

Fig. 4. Bromide breakthrough curves for the forest and corn field soils with and without hardwood biochar amendment at 5%. Solids curves are simulations using CXTFIT model.

the soil column (Brusseau, 1993). The front sides of the BTCs were not generally affected by hysteresis because they were determined by the adsorption isotherm only, whereas the tailing likely happened during the elution. Nonetheless, the bromide BTCs were very close to the ideal symmetrical shapes, as expected for a nonreactive solute. The soil physical properties and experimental conditions in the miscible displacement column studies are listed in Table 3.

Breakthrough curves of tylosin showed extensive asymmetry in the shape of the effluent side during the leaching phase, compared with the front side (retention side) (Fig. 5 and 6). This asymmetry was unlikely due to the hydrodynamics of the soil columns because the bromide tracer exhibited relatively ideal BTCs. The clear tailing during eluting with the $CaCl_2$ solution, as compared with those with bromide as tracer, suggested that tylosin transport in both soils was considerably retarded (Fig. 4 vs. Fig. 5 and 6). It was also evident that the BTCs of tylosin for the forest and corn field soils with biochar amendment (at 5%) had much delayed peaks and longer tailing than those of the two soils without biochar amendment (Fig. 5 and 6). In fact, the resolved retardation factor (*R*) values with the CXTFIT model were 10.81 vs. 3.87 and 12.08 vs. 6.53 for the forest and corn field soils, respectively (Table 4). Such relatively high retardation in biochar-amended soils indicated that the biochar amendments increased the adsorption capacity of tylosin and slowed the release of tylosin to soil solution. In addition, between the forest soil and the corn field soil, there were relatively higher peaks of relative concentration (C/C_o) observed in the forest soil with and without biochar amendment, as compared with the corn field soil with and without biochar amendment (Fig. 5 and 6). This result, along with longer tailing and resolved higher retardation *R* values (Table 4), further confirmed the stronger retention of tylosin in the corn field soil, which has higher pH and silt content than the forest soil.

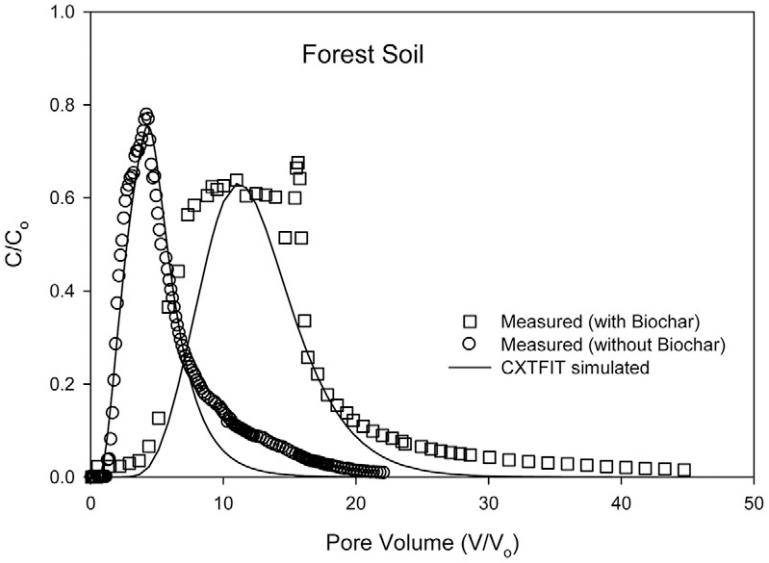

Fig. 5. Tylosin breakthrough curves for the forest soil with and without hardwood biochar amendment at 5%. Solids curves are simulations using CXTFIT model.

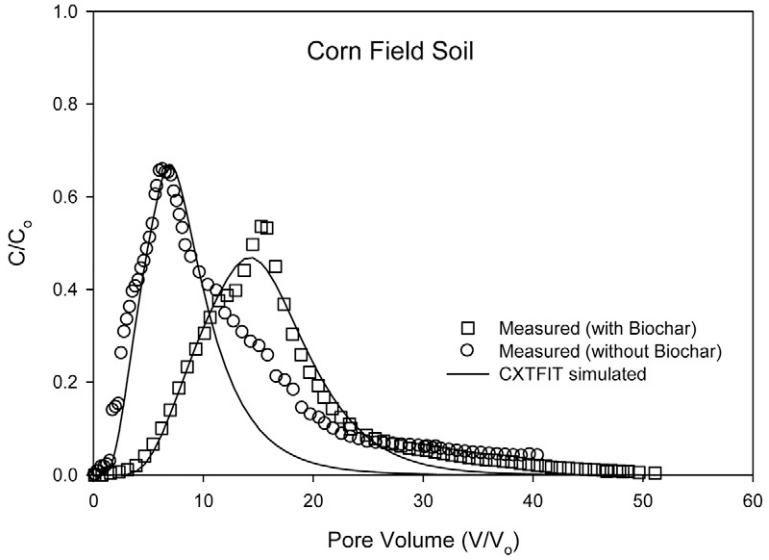

Fig. 6. Tylosin breakthrough curves for the corn field soil with and without hardwood biochar amendment at 5%. Solids curves are simulations using CXTFIT model.

The measured BTCs of tylosin for both soils, with their contrasting properties, were generally adequately described by the CXTFIT model. Overall, the CXTFIT model described well the peak arrival time as well as the maximum concentration of tylosin in the effluent. However, the CXTFIT model underestimated tylosin leaching at the advanced stage of BTCs. For instance, in the corn field soil, the CXTFIT predicted a sharp drop in tylosin concentration in the effluent after 10 pore volumes, whereas the tylosin leaching was slow (Fig. 6). Nonetheless, the mean squared errors and r^2 values ranged from 0.000668 to 0.01432 and 0.7782 to 0.9712, respectively, generally suggesting good fits of the BTCs (Table 4). Higher retardation

Table 4. Goodness of fit of CXTFIT model for the studied soils and biochar amended soils.

Sample	MSE†	r^2	*R*‡	μ, §
				h^{-1}
Forest soil	0.00293	0.9466	3.87 ± 0.0587	0.00100 ± 0.0004900
Forest soil + harwood biochar	0.01432	0.7782	10.81 ± 0.6080	0.00100 ± 0.0002828
Corn field soil	0.006326	0.8655	6.53 ± 0.0797	0.00100 ± 0.0004561
Corn field soil + hardwood biochar	0.000668	0.9712	12.08 ± 0.1580	0.00145 ± 0.0005323

† Mean squared error.

‡ Retardation factor.

§ Decay factor (see the supplemental information for detail explanation).

factors in the biochar-amended soils, as compared with the nonamended soils, were predicted by the CXTFIT model. The model also predicted a particularly higher decay factor, an irreversible parameter as a chemical sink for tylosin in the biochar-amended corn field soil. This suggests that the strong retention of tylosin occurred during transport in the biochar-amended corn field soil, which is consistent with the previously discussed desorption experiments (Fig. 3). Other studies have shown that the addition of biochar to soil increased the sorption of herbicides and reduced the bioavailability of insecticides (Yu et al., 2009). Our results clearly demonstrate that the application of biochar can enhance the retention of veterinary antibiotics such as tylosin.

Conclusion

This study demonstrated that a biochar amendment had a significant effect on tylosin adsorption–desorption and transport in soils. Adsorption of tylosin was increased with increasing percent biochar content in soils. The hardwood biochar had slightly higher tylosin adsorption and lower tylosin desorption than the softwood biochar. In the column transport experiments, hardwood biochar–amended forest and corn field soils yielded much higher retardation compared with control (no biochar) soils, and the corn field soil had less tylosin mobility than the forest soil. Overall, the results of this study suggest the potential of biochar as an amendment to control the field transport of tylosin antibiotics in soils, a problem caused by the widespread application of contaminated animal manures.

Reference

Beesley, L., E. Moreno-Jiménez, and J. L. Gomez-Eyles. 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environ. Pollut. 158:2282–2287. doi:10.1016/j.envpol.2010.02.003

Blackwell, P.A., P. Kay, R. Ashauer, and A.B.A. Boxall. 2009. Effects of agricultural conditions on the leaching behavior of veterinary antibiotics in soils. Chemosphere 75:13–19. doi:10.1016/j.chemosphere.2008.11.070

Boxall, A.B.A., L.A. Fogg, P. Kay, P.A. Blackwell, E.J. Pemberton, and A. Croxford. 2004. Veterinary medicines in the environment. Rev. Environ. Contam. Toxicol. 180:1–91. doi:10.1007/0-387-21729-0_1

Boxall, A.B.A., P. Johnson, E.J. Smith, C.J. Sinclair, E. Stutt, and L. Levy. 2006. Uptake of veterinary medicines from soils into plants. J. Agr. Food Chem. 54:2288–2297. doi:10.1021/jf053041t

Brusseau, M.L. 1993. The influence of solute size, pore water velocity, and intraparticle porosity on solute dispersion and transport in soils. Water Resour. Res. 29:1071–1080. doi:10.1029/92WR02595

Cerato, A.B., and A. J. Lutenegger. 2002. Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method. Geotech. Test. J. 25:1–7.

Chefetz, B., T. Mualem, and J. Ben-Ari. 2008. Sorption and mobility of soils irrigated with reclaimed wastewater. Chemosphere 73:1335–1343. doi:10.1016/j.chemosphere.2008.06.070

Elanco, C. 1982. Tylan injection veterinarian's technical handbook. Elanco Products Company, Indianapolis, IN.

Halling-Sørensen, B., A. Jacobsen, J. Jensen, G. Sengelov, E. Vaclavik, and F. Ingerslev. 2005. Dissipation and effects of chlortetracycline and tylosin in two agricultural soils: A field-scale study in southern Denmark. Environ. Toxicol. Chem. 24:802–810. doi:10.1897/03-576.1

Hossain, M.K., V. Strezov, K.Y. Chan, and P. F. Nelson. 2010. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*). Chemosphere 78:1167–1171. doi:10.1016/j.chemosphere.2010.01.009

Hu, X., Q. Zhou, and Y. Luo. 2010. Occurrence and source analysis of typical veterinary antibiotics in manure, soil, vegetables and groundwater from organic vegetable bases, northern China. Environ. Pollut. 158:2992–2998. doi:10.1016/j.envpol.2010.05.023

Jeong, C.Y., and H.M. Selim. 2010. Modeling adsorption-desorption kinetics of imidacloprid in soils. Soil Sci. 175:214–222. doi:10.1097/SS.0b013e3181e055e1

Laird, D.A., P. Fleming, D.D. Davis, R. Horton, B. Wang, and D.L. Karlen. 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158:443–449. doi:10.1016/j.geoderma.2010.05.013

Lehmann, J., J. Gaunt, and M. Rondon. 2006. Bio-char sequestration in terrestrial ecosystems: A review. Mitig. Adapt. Strategy Global Change 11: 403–427.

Loke, M.L., F. Ingerslev, B. Halling-Sorensen, and D.J. Tjornelun. 2000. Stability of tylosin A in manure containing test systems determined by high performance liquid chromatography. Chemosphere 40:759–765. doi:10.1016/S0045-6535(99)00450-6

Loke, M.L., J. Tjørnelund, and B. Halling-Sørensen. 2002. Determination of the distribution coefficient (logKd) of oxytetracycline, tylosin A, olaquindox and metronidazole in manure. Chemosphere 48:351–361. doi:10.1016/S0045-6535(02)00078-4

McGuire, J.M., W.S. Boniece, C.E. Higgens, M.M. Hoehn, W.M. Stark, J. Westhead, and R.N. Wolfe. 1961. Tylosin, a new antibiotic: I. Microbiological studies. Antibiot. Chemother. 11: 320–327.

Mikan, C.E., and M.D. Abrams. 1995. Altered forest composition and soil properties of historic charcoal hearths in southeastern Pennsylvania. Can. J. Forest Res. 25:687–696. doi:10.1139/x95-076

O'Neil, M.J., A. Smith, and P.E. Heckelman (ed.) 2001. The Merck index. 13th ed. Merck, Whitehouse Station, NJ.

Özacar, M., and I. A. Şengil, 2009. A kinetic study of metal complex dye sorption onto pine sawdust. Proc. Biochem. 40:563–572.

Press, W.H., S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery. 1992. Numerical recipes in FORTRAN. 2nd ed. Cambridge Univ. Press, New York.

Rabølle, M., and N.H. Spliid. 2000. Sorption and mobility of metronidazole, olaquindox, oxytetracycline and tylosin in soil. Chemosphere 40:715–722. doi:10.1016/S0045-6535(99)00442-7

Sarmah, A.K., M.T. Meyer, and A.B.A. Boxall. 2006. A global perspective on the use, sales, exposure pathways, fate and effects of veterinary antibiotics (VAs) in the environment. Chemosphere 65:725–759. doi:10.1016/j.chemosphere.2006.03.026

SAS Institute Inc. 2002. JMP statistics and graphics guide, Version 5. Cary, NC.

Selim, H.M., C.Y. Jeong, and T.A. Elbana. 2010. Transport of imidacloprid in soils: Miscible displacement experiments. Soil Sci. 175:375–381. doi:10.1097/SS.0b013e3181ebc9a2

Sparks, D. L. 1999. Kinetics and mechanisms of chemical reactions at the soil mineral/water interface. p. 135–191. *In* D.L. Sparks (ed.) Soil physical chemistry. CRC Press, Washington, DC.

Spokas, K.A., W.C. Koskinen, J.M. Baker, and D.C. Reicosky. 2009. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77:574–581. doi:10.1016/j.chemosphere.2009.06.053

Topp, E., S.C. Monteiro, A. Beck, B. Ball Coelho, A.B.A. Boxall, P.W. Duenk, S. Kleywegt, D.R. Lapen, M. Payne, L. Sabourin, and C.D. Metcalfe. 2008. Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. Sci. Total Environ. 396:52–59. doi:10.1016/j.scitotenv.2008.02.011

Toride, T., F.J. Leij, and M.T. van Genuchten. 1999. The CXTFIT code for estimating transport parameters from laboratory or fields tracer experiments. Version 2.1. Res Rep. 137. U.S. Salinity Lab., Riverside, CA.

Unold, M., R. Kasteel, J. Groeneweg, and H. Vereecken. 2009. Transport and transformation of sulfadiazine in soil columns packed with a silty loam and a loamy sand. J. Contamin. Hydro. 103: 38–47. doi:10.1016/j.jconhyd.2008.09.002

Wu, F.C., R.L. Tseng, and R.S. Juang. 2009. Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. Chem. Eng. J. 150:366–373. doi:10.1016/j.cej.2009.01.014

Yang, Y., and G. Sheng. 2003. Enhanced pesticide sorption by soils containing particulate matter from crop residue burns Environ. Sci. Technol. 37: 3635–3639. doi:10.1021/es034006a

Young, R., B.R. Wilson, M. Mcleod, and C. Alston. 2005. Carbon storage in the soils and vegetation of contrasting land uses in northern New South Wales, Australia. Aust. J. Soil Res. 43:21–31. doi:10.1071/SR04032

Yu, X.Y., G.G. Ying, and R.S. Kookana. 2009. Reduced plant uptake of pesticides with biochar additions to soil. Chemosphere 76:665–671. doi:10.1016/j.chemosphere.2009.04.001

Zhou, Z. 2008. Sorption and desorption characteristics of tylosin in three Louisiana soils and clay minerals. M.S. thesis, Louisiana State Univ., Baton Rouge.