5-2006

Characterizing the Fate and Transport of Solutes in Soil

Youngho Seo
University of Tennessee - Knoxville

Recommended Citation

Seo, Youngho, "Characterizing the Fate and Transport of Solutes in Soil. " PhD diss., University of Tennessee, 2006.
https://trace.tennessee.edu/utk_graddiss/1858

To the Graduate Council:

I am submitting herewith a dissertation written by Youngho Seo entitled "Characterizing the Fate and Transport of Solutes in Soil." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Plants, Soils, and Insects.

Jaehoon Lee, Major Professor

We have read this dissertation and recommend its acceptance:

Michael E. Essington, Daniel C. Yoder, H. Paul Denton, Ed Perfect

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a dissertation written by Youngho Seo entitled "Characterizing the Fate and Transport of Solutes in Soil." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Plants, Soils, and Insects.

Jaehoon Lee

Major professor

We have read this dissertation
and recommend its acceptance:

Michael E. Essington

Daniel C. Yoder

H. Paul Denton

Ed Perfect

Accepted for the Council:

Anne Mayhew
Vice Chancellor and
Dean of Graduate Studies

(Original signatures are on file with official student records.)

Characterizing the Fate and Transport of Solutes in Soil

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Youngho Seo

May 2006

DEDICATION

This dissertation is dedicated to my three girls: my wife Boohyun Ahn, and two daughters Whimin Seo and Jimin Seo. They provided me with love, encouragement, stability, and affection. I would like to express special thanks to my parents, Jeomseok Seo and Gapsun Lee, and parents-in-law, Dongkyoo An and Mija Chung. This dissertation would not have been completed without their steady support and love. My appreciation is also expressed to my brothers, sister, brothers-in-law, all my uncles and aunts, and other relatives.

ACKNOWLEDGMENTS

Many people have contributed their help and support to complete this dissertation. I would like to express sincere appreciation to my major professor, Dr. Jaehoon Lee for his consistent guidance, supervision, and mentorship. I also would like to express special thanks to Dr. Michael Essington, Dr. Daniel Yoder, Dr. Paul Denton, and Dr. Ed Perfect for serving on my committee and providing valuable suggestions, assistances, and guidance throughout my doctoral program.

I also appreciate the faculties and staffs in the Biosystems Engineering and Soil Science Department for their generous support, especially Dr. John Ammons, Dr. Hart William, Dr. John Wilkerson, Ms. Galina Melnichenko, Mr. Wesley Wright, Mr. Craig Wagoner, Mr. David Smith, Mr. Jeff Sowders, Ms. Margaret Taylor, Ms. Melanie Stewart, Ms. Lucille Carleton, Ms. Lois Stinnett, and Ms. Darla O'Neill. I thank the staff of the Plant Science Farm for my field experiments, especially Mr. Fred Ellis. I would like to thank my fellows, especially Dr. Soul Chun, Mr. Jason Wight, Mr. Justin Fisher, Mr. Paul Seger, Mr. Stacy Clark, Mr. Rob Anderson, Ms. Jessica Journey, Ms. Tara Garrett, Ms. Christa Davis, Ms. Heather Hart, and Mr. Aaron Peacock during my doctoral program.

I am expressing special appreciation to Dr. Yeongsang Jung for his encouragement and steady support, and Dr. Sunuk Lim for introducing me to soil science. I am thankful to the Gangwon-do Agricultural Research and Extension Services, Republic of Korea for providing me a long study leave to pursue my PhD degree. Finally, all who helped me to make comfortable stay at Knoxville are also thanked.

ABSTRACT

Increasing concerns about contamination of soil and aquatic environments have emphasized the importance of information about the fate and transport of agricultural chemicals in soil. The objective of this research was to provide an improved understanding of the behavior of reactive chemicals including nitrate, phosphate, and antibiotics in soil through leaching and surface runoff in order to develop appropriate technologies that can prevent or minimize contamination of soil and water by agricultural activity. In a first experiment, a time domain reflectometry (TDR) method was tested for its ability to measure preferential flow of nitrate and phosphate in soil. Saturated miscible displacement experiments were conducted using three undisturbed soil cores and tracer solution containing chloride, phosphate, and nitrate. Predicted breakthrough curves (BTCs) obtained from the mobile-immobile model parameters fitted to the TDR data were comparable to the measured effluent nitrate BTCs. Phosphate BTCs distinctly differed from chloride and nitrate BTCs, thus the TDR method did not work for phosphate. The vertical TDR probe technique proved to be a practical method for a first approximation of nitrate preferential flow in soil. The second experiment used a localized compaction and doming (LCD) applicator that was developed to reduce nitrate leaching and increase nitrogen use efficiency. During a two-year period, sediment and nutrient losses from plots prepared using the LCD were compared to those prepared using conventional no-till broadcast (NTB) and no-till coulter injection (NTC). Concentrations of nitrogen and bromide in the soil profile were also determined to quantify anion movement. Total sediment loss for LCD was significantly greater than sediment loss for NTC and NTB. Masses of bromide, nitrate, phosphate, total nitrogen, and total phosphorus in runoff for LCD were significantly less than the corresponding masses for NTB and NTC in 2004. Residual concentration profile values implied that nitrate applied by the LCD applicator was transported more slowly through soil compared with the other methods. Therefore, the LCD method can reduce phosphorus loss in runoff, although on sloping fields it appears to result in more soil erosion. In the third and final experiment, the effects of soil properties on the fate and transport of chlortetracycline (CTC), tylosin

(TYL), and sulfamethazine (SMT) were examined by conducting batch and column experiments. Sorption of CTC and TYL to montmorillonite and kaolinite generally decreased with increasing pH and ionic strength. Decreased retention of CTC and TYL to clays and soils was observed in the presence of Ca^{2+} compared with Na^{+}. Greater SMT sorption was observed for surface soils having higher soil organic matter compared with subsurface soils, indicating that SMT mainly binds to soil organic matter in soils. Addition of dissolved organic carbon (DOC) derived from dairy manure resulted in decreased sorption and increased mobility of CTC and TYL, while increasing sorption of SMT. Changes in pH, ionic strength, DOC level, and background electrolyte cation type in soil solution caused by concomitant application of animal manure can influence fate and transport of agricultural antibiotics in soils. Therefore, failure to take the animal manure application effects into account can lead to conclusions that have little relevance to real situations.

TABLE OF CONTENTS

General Introduction..1

Part 1: **Characterizing Preferential Flow of Nitrate and Phosphate in Soil using Time Domain Reflectometry**

Abstract..7
Introduction..8
Materials and Methods..9
Results and Discussion..13
Conclusions..17
References..18
Appendix..21

Part 2: **Sediment Loss and Nutrient Runoff from Three Fertilizer Application Methods**

Abstract..26
Introduction..27
Materials and Methods..28
Results and Discussion..31
Conclusions..36
References..38
Appendix..42

Part 3: **Influence of Soil Chemical Properties on Sorption and Mobility of Antibiotics in Soil**

Abstract..50
Introduction..51

Literature Review 54
Materials and Methods 62
Results and Discussion 73
Conclusions 87
References 89
Appendix 104

Vita 127

LIST OF TABLES

Table Page

1.1. Chemical and physical properties of the soil used in this study. 21

1.2. Mobile-immobile model parameters determined from measured effluent chloride and TDR data. 21

1.3. Peak of measured effluent and TDR-predicted BTCs. 22

1.4. Root mean square errors (RMSEs) and coefficients of determination (r^2) between TDR-predicted and effluent BTCs. 22

2.1. Chemical and physical properties of the soils located at the study site. 42

2.2. Runoff and sediment loss in 2003. 42

2.3. Runoff and sediment loss in 2004. 43

2.4. Masses (g ha^{-1}) of NO_3-N, PO_4-P, TN, and TP in runoff in 2003. 43

2.5. Masses (g ha^{-1}) of Br, NO_3-N, and PO_4-P in runoff in 2004. 44

2.6. Masses (g ha^{-1}) of TN and TP in runoff in 2004. 45

3.1. Macroscopic acidity constant (pK_a) for CTC. 104

3.2. Chemical and physical properties of the clay and soils used in this study. 105

3.3. HPLC conditions for the analysis of antibiotics. 105

3.4. Intrinsic acidity constants of the surface protolysis reactions. 106

3.5. Experimental conditions of the soil column studies for DOC effect on mobility of antibiotics. 106

3.6. Estimated partitioning coefficient (β) and mass transfer coefficient (ω)................. 107

3.7. Freundlich coefficient (K_F) and exponent (N) of chlortetracycline (CTC)............. 108

3.8. Freundlich coefficient (K_F) and exponent (N) of tylosin (TYL)............................. 109

3.9. Cooperative sorption model parameters for sulfamethazine (SMT)........................ 110

3.10. Freundlich coefficient (K_F) and exponent (N) for sulfamethazine (SMT)............. 111

3.11. Column transport parameter estimates obtained from CXTFIT program for chlortetracycline (CTC). 112

3.12. Column transport parameter estimates obtained from CXTFIT program for tylosin (TYL). 113

3.13. Column transport parameter estimates obtained from CXTFIT program for sulfamethazine (SMT). 114

LIST OF FIGURES

Figure Page

1.1. Measured effluent chloride and nitrate BTCs along with TDR-predicted BTCs. 23

1.2. Observed effluent phosphate BTCs. 24

2.1. Normal precipitation (1971-2000) at the Plant Science Farm in Knoxville, Tennessee. 46

2.2. Rainfall data during growing season in (a) 2003 and (b) 2004................................ 46

2.3. Concentrations of (a) Br, (b) NO_3-N, and (c) PO_4-P in runoff in 2004. Error bars indicate standard error.. 47

2.4. Residual concentration profiles for (a) Br and (b) NO_3-N in LCD, NTC, and NTB, 30 days after fertilizers were applied. 48

3.1. Chemical structure of (a) chlortetracycline (CTC), (b) tylosin (TYL), and (c) sulfamethazine (SMT). 115

3.2. Solution speciation of (a) chlortetracycline (CTC), (b) tylosin (TYL), and (c) sulfamethazine (SMT). 115

3.3. Two conformations of chlortetracycline (CTC). 115

3.4. Effect of pH on chlortetracycline (CTC) sorption. 116

3.5. Ionic strength effect on chlortetracycline (CTC) sorption. 116

3.6. Effect of pH on tylosin (TYL) sorption. 117

3.7. Ionic strength effect on tylosin (TYL) sorption. 117

3.8. Effect of pH on sulfamethazine (SMT) sorption. 118

3.9. Ionic strength effect on sulfamethazine (SMT) sorption. 118

3.10. Effect of background electrolyte cation type on chlortetracycline (CTC) sorption. 119

3.11. Effect of background electrolyte cation type on tylosin (TYL) sorption.............. 120

3.12. Effect of background electrolyte cation type on sulfamethazine (SMT) sorption. 121

3.13. Dissolved organic carbon (DOC) effect on chlortetracycline (CTC) sorption...... 122

3.14. Dissolved organic carbon (DOC) effect on tylosin (TYL) sorption. 123
3.15. Dissolved organic carbon (DOC) effect on sulfamethazine (SMT) sorption. 124
3.16. Dissolved organic carbon (DOC) effect on chlortetracycline (CTC) mobility...... 125
3.17. Dissolved organic carbon (DOC) effect on tylosin (TYL) mobility for Captina sandy loam. 126
3.18. Dissolved organic carbon (DOC) effect on sulfamethazine (SMT) mobility for Captina sandy loam. 126

General Introduction

Increasing concerns about environmental contamination have emphasized the importance of information about the fate and transport of chemicals in soil. When agricultural chemicals are applied to cultivated land to increase crop yield, they can move to the surrounding environment through volatilization, leaching, and surface runoff. Among them, leaching through the soil profile and surface runoff from sloping fields may be the primary processes of ground and surface water contamination. The pollutants of concern include nitrate, phosphate, pesticides, pathogens, and agricultural antibiotics from animal wastes. Movement of some of the pollutants is extremely complicated due to the chemicals' properties and interactions with soil (e.g. sorption, desorption, transformation, and degradation).

Nitrate is highly mobile in soil and can readily move downward to the subsoil, and then to groundwater. Phosphorus has been considered to be immobile in soil because of its strong sorption to soil particles. However, significant quantities of chemicals may move very rapidly by preferential flow. The fate and mobility of agricultural antibiotics in soil depend on their chemical properties and the soil environment. Land application of animal waste can change the soil chemical properties, thus affecting the fate and movement of agricultural antibiotics in soil. Therefore, solutes including nitrate, phosphorus, and antibiotics can reach groundwater and surface water, causing human health and other water quality problems.

The fate and behavior of antibiotics in soil was examined by batch equilibration and column transport experiments in this dissertation. All soil particle surfaces may be exposed to antibiotics in a closed system with constant agitation for batch studies, while all surfaces may not be exposed to antibiotics in an open system for column experiments. Batch studies cannot take soil structural effects into account for the behavior of antibiotics in soil. In column studies, pretreatment with background solution can change soil properties and soil surface chemistry. Desorption of applied antibiotics from the solid phase is reduced by continuous application of the antibiotic until the sorption sites are saturated with the antibiotic in column transport experiments while adsorbate-adsorptive equilibrium is attained in batch systems. In column studies, desorbed antibiotics can be constantly flushed out by continuously applying background solution while they can rebind to soil particles or precipitate in batch studies. The results obtained from batch studies may be more representative for reactions occurring in the soil matrix, while column studies may more closely represent the behavior of antibiotics in spatial-heterogeneous systems.

Surface runoff occurs when the rainfall intensity exceeds the infiltration capacity of the soil and the interception and depression storages are filled. Runoff from fields may be an important contributor to non-point source pollution of surface water. Plant nutrients from farmland may cause severe problems of eutrophication of rivers and lakes. In addition to dissolved solutes in runoff, soil erosion is also a significant process of water contamination because chemicals can move along with sediments. The soils in Eastern Tennessee are mainly Ultisols, which are very susceptible to erosion. Furthermore, many fields in this area are located on steep slopes, where soil erosion can be significant. In addition to soil properties, intense storms occur frequently in the spring and summer when cultivated land is exposed to raindrop impact.

According to the revised universal soil loss equation (RUSLE), soil erosion is functions of rainfall-runoff erosivity factor (R), soil erodibility factor (K), slope length factor (L), slope steepness factor (S), cover-management factor (C), and support practice factor (P). Fertilizer application methods may influence C, which depends on prior land use, canopy-cover, surface-cover and surface-roughness, and soil moisture. A localized compaction and doming (LCD) method can change the surface-roughness subfactor, since as the surface roughness increases, the transport capacity and runoff detachment decreases because of flow velocity reduction. Additionally, fertilizer application methods may indirectly affect the canopy-cover subfactor through corn growth differences. The canopy-cover effect depends on the fraction of land surface covered by canopy and raindrop fall height after striking the canopy. The influence of the LCD method on soil erosion and nutrient runoff was determined in this dissertation.

The dissertation is composed of three journal-style papers. Part 1 is entitled "Characterizing preferential flow of nitrate and phosphate in soil using time domain reflectometry," which is focused on leaching of nitrate and phosphate through preferential movement. A time domain reflectometry (TDR) technique has been used to determine water content and the bulk electrical conductivity of soil. The TDR method has the advantage in that it is less destructive and more labor- and cost-effective compared to conventional methods. TDR is portable, so it is easy to install, use, and maintain in the field. Using an automated TDR system, solute transport data can be continuously obtained at the same location without additional sampling works and chemical analysis. Moreover, spatial variability of chemical transport through soil can be determined by establishing a multiplexed TDR system. The hypothesis was that the TDR method can be used to determine the time of the peak of nitrate and phosphate breakthrough curves (BTCs) when preferential flow is predominant, although the absolute concentrations may not be determined. The main objective of this study was to test if the vertical TDR method along with a conservative tracer can be used as a first approximation to characterize preferential flow of nitrate and phosphate in soil. Miscible displacement experiments were done using undisturbed soil columns with TDR in the laboratory. The part 1 is a lightly revised version of a paper by the same name published in the journal *Soil Science* in 2005.

Part 2 is entitled “Sediment loss and nutrient runoff from three fertilizer application methods,” which reports the results from a field study evaluating three fertilizer application methods in a sloping field. An LCD applicator was developed to improve nitrogen efficiency and to reduce groundwater contamination. The LCD applicator consists of a modified knife to smear the soil and close macropores below the nitrogen injection slot, a cone disk guide wheel to fill the knife slit and compact the injection band, and a covering disk to cover the compacted soil layer with a surface dome. However, this method has not been tested on sloping fields. The objective of the study was to determine the effects of LCD on soil erosion, nutrient runoff and leaching in a sloping field compared with the other conventional fertilizer application methods, and to decide the applicability of LCD application method in sloping fields. The part 2 is a lightly revised version of a paper by the same name published in the journal *Trans. ASAE* in 2005.

Part 3 is entitled “Influence of Soil Chemical Properties on Sorption and Mobility of Antibiotics in Soil.” This paper reports the results of laboratory experiments that were conducted to investigate the fate and transport of agricultural antibiotics in soil. Veterinary antibiotics have been used to improve animal productivity by prevention and treatment of disease and by promotion of growth. Land application of animal manure as an organic fertilizer is one of the most common sources of agricultural antibiotics that can adversely affect the soil and water environment. Animal manure amendment can change the soil chemical properties, thus affecting fate and mobility of agricultural antibiotics in soil. The objective of the study was to determine the influence of soil chemical properties on the fate and transport of antibiotics in soil by conducting batch and column experiments in order to improve our ability to predict fate and behavior of antibiotics in the soil system and aid the development of management strategies that minimize and prevent the potentially adverse effects caused by agricultural antibiotics in the soil and aquatic environment.

Part 1

Characterizing Preferential Flow of Nitrate and Phosphate in Soil using Time Domain Reflectometry

This part is a lightly revised version of a paper by the same name published in the journal *Soil Science* in 2005 by Youngho Seo and Jaehoon Lee:

Seo, Y and Lee, J. Characterizing preferential flow of nitrate and phosphate in soil using time domain reflectometry. *Soil Science* 170(1): 47-54.

My primary contributions to this paper include (1) sampling of soil cores and conducting experiments, (2) most of the gathering and interpretation of literature, and (3) most of the writing.

ABSTRACT

Significant quantities of agricultural chemicals can rapidly be transported through preferential flow pathways in soil. Time domain reflectometry (TDR) has been used to characterize solute transport in soil. However, previous TDR studies have scarcely addressed preferential flow of reactive solutes. A TDR method was tested for its ability to measure preferential flow of nitrate and phosphate in soil. Saturated miscible displacement experiments were conducted using three undisturbed soil cores and tracer solution containing chloride, phosphate, and nitrate. An inverse curve fitting method (CXTFIT) was used to estimate mobile-immobile model (MIM) parameters using the TDR and observed effluent data. The parameters fitted to the time varying TDR-determined relative resident concentration were similar to the estimates from measured effluent chloride breakthrough curves (BTCs). Predicted BTCs were obtained from the parameters fitted to the TDR data. The predicted BTCs were comparable to the measured effluent nitrate BTCs with root mean square error (RMSE) being 0.0054. The times of the peaks were 0.18, 0.16, and 0.12 pore volumes for the predicted BTCs, as compared to 0.26, 0.19, and 0.21 pore volumes for the effluent nitrate BTCs. Phosphate BTCs distinctly differed from chloride and nitrate BTCs in our study, thus the TDR method did not work for phosphate. The vertical TDR probe technique proved to be a practical method for a first approximation of nitrate preferential flow in soil.

INTRODUCTION

Increasing concerns about environmental contamination have emphasized the need for information about the fate and transport of agricultural chemicals in soil. When chemicals are applied to cultivated land to enhance crop yield and quality, they can move below the root zone through preferential flow pathways and eventually contaminate groundwater. One of the mechanistic models used to describe preferential flow is the mobile-immobile model (MIM). In this model, volumetric water content is divided into a mobile region where solute transport is by convection and dispersion, and an immobile region where solute moves by diffusion only. Nitrate has been considered to be highly mobile in soil and can readily move downward to subsoil and then to groundwater. In contrast to nitrate, phosphorus has been considered to be fairly immobile because of strong adsorption to soil particles such as clay minerals, aluminum and iron oxides, and organic matter. However, James et al. (1996) showed an increase in extractable inorganic phosphorus concentration in subsoil as deep as 210 cm after long-term manure disposal. Scott et al. (1998) monitored phosphorus in New York State watersheds and concluded that 37% of the soluble phosphorus was exported from manure-applied fields via subsurface drains.

Time domain reflectometry (TDR) has been widely used to simultaneously determine water content and bulk soil electrical conductivity. Time domain reflectometry is less disruptive to soil than other methods to characterize solute transport in the field such as lysimeters and solution samplers. In addition, a multiplexed TDR system enables us to automatically monitor solute concentration at multiple locations. Topp et al. (1980) proposed a calibration function to measure water content of various soils using TDR, and Dalton et al. (1984) reported that the attenuation of electromagnetic wave could be used to measure the bulk electrical conductivity of soil. Kachanoski et al. (1992) reported that the change in bulk electrical conductivity with time was linearly related to solute mass flux past the TDR probes, thus field solute breakthrough curves (BTCs) can be determined using vertically installed TDR probes under steady-state conditions. Later, Lee et al. (2001) applied the vertical TDR probe method to characterize preferential flow. They showed that MIM parameters fitted to the time varying TDR-determined relative resident concentration corresponded well with those obtained using effluent data, and predicted BTCs obtained from the parameters were similar to the observed effluent BTCs. They concluded that the vertical TDR probe method can be used to delineate preferential flow of a conservative solute in undisturbed structured soil columns. However, previous studies have scarcely addressed preferential flow of reactive solutes such as nitrate and phosphate using the vertical TDR method.

Nissen et al. (1998) reported excellent agreement between the resident concentration measured with the horizontal TDR probe and the sum of chloride and nitrate concentrations measured with the solution sampler in soil fertilized with cattle slurry. They suggested that TDR measurements could be used to analyze transport of nitrate in soil. Note that the horizontal TDR method needs a separate calibration experiment (Ward et al., 1994; Mallants et al., 1996) and causes more physical disturbance during installation than vertical TDR probes.

The main objective of this study was to test if the vertical TDR method along with a conservative tracer can be used as a first approximation to characterize preferential flow of nitrate and phosphate in soil. Our hypothesis is that, when preferential flow, especially due to micro-scale immobile water, is predominant, the vertical TDR method can be used to determine the time of the peak of nitrate and phosphate BTCs, although the absolute concentrations may not be determined. Predicted BTCs obtained from the parameters fitted to the TDR data were compared with the observed effluent BTCs of chloride, nitrate, and phosphate.

MATERIALS AND METHODS

Undisturbed soil core samples were collected from a tomato field located on the Knoxville Experiment Station at the University of Tennessee using polyvinyl chloride (PVC) plastic pipe. Soil cores were obtained by forcing the pipes into the soil with a geotechnical drill rig and carefully excavating the surrounding soil. Distinct soil aggregates and macropores were observed at the time of core sampling. Core samples were covered with plastic to prevent evaporation during transport to the laboratory and stored at 4ºC before the miscible displacement experiments. The soil is classified as a Sequatchie fine sandy loam (mixed, superactive, thermic, Typic Hapludults).

Miscible displacement experiments were conducted with three undisturbed soil columns: Column A, Column B, and Column C. Selected chemical and physical properties of the soil are shown in Table 1.1[1]. The soil columns (150 mm long and 100 mm diameter) were saturated from the bottom with a background solution of 0.005 M $CaCl_2$. TDR probes were inserted vertically at the center of the soil column after saturation. The three-rod probes had a length of 150 mm, a diameter of 3 mm, and spacing between the center and outer rods of 30 mm. The pore volume of the soil column was obtained from TDR by measuring the water content with a calibration curve empirically determined by Topp et al. (1980). Preliminary data revealed that the deviation between the water content obtained from the Topp et al. (1980) equation and gravimetrically determined water content was not greater than 0.01 $m^3\ m^{-3}$. A constant water head of 1 cm on top of the soil column was maintained using a mariotte system. More than 10 pore volumes of background solution were leached before applying tracers. The application of background solution was then stopped, letting the ponding solution infiltrate. Input solution was made to contain chloride, nitrate, and phosphate. The concentrations of chloride, nitrate, and phosphate were 2, 0.036, and 0.048 M, respectively. High concentration of chloride was used as a conservative tracer to get corresponding TDR data. Note that the concentration of chloride is considerably higher than the concentrations of nitrate and phosphate, thus TDR data in this study mainly represent the presence and movement of chloride in the soil cores. We used the TDR data to determine preferential flow and time of the peaks of BTCs for nitrate and phosphate. The concentration of phosphate is comparable to the concentration found in animal wastes, though the composition of such wastes is highly variable. The contents of water-soluble phosphorus in animal manures were 2,500-6,600 mg kg^{-1} (Siddique and Robinson, 2003). Twenty milliliters of tracer consisting of chloride, phosphate, and nitrate was applied to the top of the column. The background solution was then applied again to the soil column shortly after the tracers infiltrated the soil surface. Effluent samples were

---

[1] All tables and figures located in the appendix.

collected at intervals of 0.05 pore volume using a fraction collector at the bottom of the column. The chloride concentrations were measured with a digital chloridometer (Labconco Corporation, Kansas, MO). The concentrations of nitrate and phosphate were determined using an ion chromatograph (DIONEX Corporation, Sunnyvale, CA).

The TDR100 and CR10X data-logger along with PCTDR and PC208W programs (Campbell Scientific INC, Logan, UT) were used to obtain impedance load (Z) as a function of time. The soil bulk electrical conductivity, ECa, can be determined using TDR by measuring Z (Nadler et al., 1991):

$$ECa = k \times Z^{-1} \qquad [1.1]$$

where k is a calibration constant.

A linear relationship was reported between ECa and average pore water electrical conductivity, ECw, at constant water content, θ (Rhoades et al., 1989), and ECw is linearly related to the solute concentration in soil water (Marion and Babcock, 1976). For constant water content, resident solute concentration (C) can be obtained from ECa (Ward et al., 1994):

$$C = a + b \times ECa \qquad [1.2]$$

where a and b are empirical constants.

The total specific mass per unit area (kg m^{-2}), M_L, for a particular depth of L, can be measured by a vertical TDR probe with a length of L (Kachanoski et al., 1992):

$$M_L = C_L \times \theta_L \times L \qquad [1.3]$$

where C_L and θ_L are the average resident concentration and average soil water content over depth L. When a pulse of solute is applied under steady state conditions, the relative specific mass at time t, $M_R(t)$, remaining within the depth L can be obtained by:

$$M_R(t) = \frac{ECa(t) - ECa_i}{ECa_0 - ECa_i} = \frac{Z(t)^{-1} - Z_i^{-1}}{Z_0^{-1} - Z_i^{-1}} \qquad [1.4]$$

where *ECa(t)* is TDR-measured *ECa* at time *t*, ECa_i is TDR-measured *ECa* before pulse application, ECa_0 is TDR-measured *ECa* after the solute pulse has been applied, but before any of the applied solute moves past *L*, *Z(t)* is impedance load at time *t*, Z_i is impedance load before pulse application, and Z_0 is the measured impedance load after the solute pulse has been applied, but before any has moved past *L*. Both empirical constants and calibration constants are not required for this equation, because all constants are dropped out. It has been reported that TDR-measured *Z* values are not affected by distribution of electrolyte within depth *L* when θ is constant over *L* (Nadler et al., 1991; Kachanoski et al., 1992; Lee et al., 2001).

The relative specific mass, $M_R(t)$, was computed from measured *Z(t)*, Z_0, and Z_i values using Eq. [1.4], and then the relative solute mass flux was obtained by taking the first derivative of $M_R(t)$ with respect to time. This derivative was converted to the mass flux by multiplying by the mass of chloride applied. Flux-averaged concentrations were obtained based on the mass flux. Relative concentrations were computed by dividing flux-averaged concentrations by the concentration of applied solution (Lee et al., 2001).

For steady and one-dimensional flow of non-sorbing solutes, the MIM can be written as:

$$\theta = \theta_m + \theta_{im} \qquad [1.5]$$

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \qquad [1.6]$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = a(C_m - C_{im}) \qquad [1.7]$$

where θ is volumetric water content, θ_m and θ_{im} are mobile and immobile water contents, respectively, C_m and C_{im} are concentrations in mobile and immobile domains, respectively, *t* is time, D_m is dispersion coefficient, *q* is water flux, *x* is depth, and α is a first-order mass transfer coefficient between mobile and immobile domains (van Genuchten and Wierenga, 1976).

In order to quantify preferential flow, a conventional inverse curve fitting method (CXTFIT) was used to estimate the MIM solute transport parameters: D_m, θ_{im}/θ, and α (Toride et al., 1999). The parameters fitted to the time varying TDR-determined relative resident concentration were compared with the parameters obtained from effluent breakthrough data. The estimated model parameters from TDR data were then used to obtain predicted BTCs which were compared with the observed effluent BTCs of chloride, nitrate and phosphate. The time of peak for the predicted BTCs was compared with the peak time for the effluent BTCs. For quantitative analysis, root mean square errors (RMSEs) between predicted and measured nitrate and phosphate BTCs were computed (Willmott et al., 1985). Coefficients of determination, r^2, of relationship between predicted and measured BTCs were also calculated.

RESULTS AND DISCUSSION

The effluent BTCs of chloride and nitrate showed an early breakthrough and tailing (Fig. 1.1) which is representative of preferential flow or physical nonequilibrium (Nkedi-Kizza et al., 1983). The immobile water fractions (θ_{im}/θ) for the effluent chloride BTCs ranged from 0.39 to 0.83, indicating preferential flow (Table 1.2). Previous studies reported similar results; θ_{im}/θ ranged from 0.39 to 0.95 for a ridge-till corn field (Casey et al., 1997) and from 0.42 to 0.82 for undisturbed soil cores (Lee et al., 2001). The mass recovery of chloride for column A, B, and C was 93.5, 78.5, and 92.9%, respectively. The relatively low recovery in column B resulted from tailing of the chloride BTC (Fig. 1.1) which is an indication of physical nonequilibrium of the chloride transport. The mass recovery of nitrate for column A, B, and C was 95.9, 53.1, and 78.5%, respectively. Preferential flow of nitrate has been reported both in laboratory and field studies. Clay et al. (2004) reported macropore bypass flow of nitrate in undisturbed soil columns, and Kelly and Pomes (1998) showed that substantial quantities of nitrate were transported to groundwater through preferential flow pathways in a claypan soil. All of the nitrate BTCs were very similar to chloride BTCs (Fig. 1.1).

Table 1.2 shows the estimated MIM parameters obtained from the measured effluent chloride BTCs and TDR data using an inverse curve fitting method (CXTFIT). A positive relationship between dispersion coefficient and pore water velocity is consistent with the results of others (Nkedi-Kizza et al., 1983; Chen et al., 2002). The MIM parameters obtained from TDR measurements were generally within the 95% confidence intervals of effluent BTCs. As a consequence, the predicted BTCs obtained from the parameters fitted to the time varying TDR-determined relative resident concentration ("TDR-predicted BTCs" hereafter) were comparable to the measured effluent chloride and nitrate BTCs (Fig. 1.1).

The time of the peak for the TDR-predicted BTCs was earlier than the measured effluent BTCs for all three soil columns (Table 1.3). The peak time for the predicted BTCs ranged from 0.12 to 0.18 pore volumes, while the peak time for the effluent chloride and nitrate BTCs ranged from 0.26 to 0.28 and from 0.19 to 0.26, respectively. Discussion on the discrepancy is provided later in this section. Table 1.4 shows root mean square errors (RMSEs) and coefficients of determination (r^2) between the TDR-predicted and the measured effluent BTCs. The average RMSEs for the observed effluent chloride and nitrate BTCs were 0.0043 and 0.0054, respectively. The values of r^2 for chloride and nitrate BTCs ranged from 0.85 to 0.94 and from 0.84 to 0.93, respectively.

The observed BTCs of phosphate are shown in Fig. 1.2. Phosphate BTCs distinctly differed from chloride and nitrate BTCs, and the concentrations were several orders of magnitude lower than chloride and nitrate BTCs. Only a small portion of phosphate was collected in effluent, presumably due to high sorption affinity to soil. Mass recovery of phosphate for column A, B, and C was 23.7, 2.2, and 12.8%, respectively. Column A showed more phosphate leaching than other soil columns, implying a certain degree of preferential flow of phosphate. Geohring et al. (2001) reported that soluble phosphorus was transported through macropores, and Gächter et al. (1998) showed that total phosphorus concentrations around macropores were higher than in the rest of the soil matrix.

Although most of the applied phosphate was presumably retained in the uppermost layer of the soil (Jensen et al., 1998; Stamm et al., 1998), preferential flow can be a potential mechanism for phosphorus transport. Garrido et al. (2001) reported a conceptual model that has two flow zones in the soil profile of a heterogeneous field, a distribution flow zone where lateral spreading of the solute occurred at the surface, followed by convergence into preferential flow pathways in the preferential flow zone. Jensen et al. (1998) reported that phosphorus was transported into the soil profile through a few, larger macropores only, while dye solution infiltrated soil matrix through all size of macropores. They suggested that macropores with greater than 3-mm diameter were responsible for the long distance transport of soluble phosphate in a structured clayey subsoil. Potential for phosphate leaching may be correlated to the diameter distribution of macropores and the total number of vertically oriented macropores. In addition, Stamm et al. (1998) showed positive correlation between the flow rate and soluble-reactive phosphorus in drainage effluent. The different size and orientation of macropores in soil and different flow rate may explain the difference among effluent phosphate BTCs shown in Fig. 1.2.

One of the limitations of our proposed TDR method is that it may not be suitable for a layered soil, because the vertical TDR measurement can be influenced by non-uniform water content with depth. Ferre et al. (2000) suggested that TDR may not be used to determine solute concentrations when θ varies along the TDR probes. When θ is spatially variable but the spatial distribution is constant over time, solute concentrations can be inferred from TDR measurements if the solute concentration is spatially uniform throughout the sample volume. Curvilinear relationship between *ECa* and soil solution concentration at a very low and high salinity level can also cause inaccurate calculation of relative mass BTCs. Vogeler et al. (2001) reported that the concentrations of conservative tracers measured by TDR was under- or overestimated by up to 50% in the field under transient water flow, depending on the *θ-ECa-ECw* relationships used. Ferre et al. (1998) defined the sample volume of TDR probe as the region of the porous medium that contributes to the TDR measurement. Although Zegelin et al. (1989) reported that a three-rod TDR probe gives more reliable and accurate measurement of θ

and *ECa* than a two-rod probe, a three-rod TDR probe has a smaller sampling volume in the plane perpendicular to the TDR rods than a two-rod probe with the same rod thickness and spacing (Knight et al., 1994; Ferre et al., 1998). Since it is difficult to obtain the spatial weighting function describing the sensitivity of three-rod probes, Knight et al. (1994) presented a relative spatial sensitivity function which is a normalized weighting function. For a TDR probe with a distance between the center and outer rods of 3 cm installed in a soil column of 10-cm diameter as in this study, the minimum relative spatial sensitivity is about 4.7×10^{-3} (see Eq. [21] of Knight et al. (1994)) with maximum sensitivity in the immediate vicinity of the probe rods. Furthermore, the TDR sample volume for water content and electrical conductivity may be different if *ECw* varies in the transverse plane because the *ECw* distribution can affect the weighting of electrical conductivity within the sample volume (Ferre et al., 2001). Therefore, TDR-predicted BTCs could be influenced by the position of preferential flow pathways such as macropores.

Because TDR is not able to distinguish one solute from another, it is impossible to determine the concentrations of each chemical using TDR method when soil solution consists of various ions. However, chloride and nitrate are likely to be the dominating anions in the soil solution in our study as shown in effluent BTCs (Fig. 1.1 and 1.2), and they have similar equivalent electrical conductivity. In spite of its potential shortcomings, the vertical TDR probe method provided representative BTCs and solute transport model parameters that can be used as a first approximation to characterize some type of preferential flow of nitrate in soil. The TDR method was shown to have good potential for measuring nitrate transport in soil, where direct soil solution sampling techniques are not available.

From an instrumentation standpoint, this research is believed to be a pioneering work as few studies on using vertical TDR method for monitoring reactive solute transport have been documented. Research efforts geared towards the use of vertical TDR for monitoring reactive solute transport in soils could be considered to be an important research strategy towards fulfilling the overall goal of investigating and characterizing chemical transport in soil, particularly for preferential flow.

CONCLUSIONS

A vertical TDR method was evaluated for its ability to measure preferential flow of nitrate and phosphate in soil. Nitrate BTCs were very similar to chloride BTCs in our study, both being indicative of significant preferential flow. The MIM parameters fitted to the TDR data were similar to the estimates obtained from measured effluent BTCs, and TDR-predicted BTCs were comparable to the measured effluent chloride and nitrate BTCs. Because the vertical TDR method responded well to the preferential transport of nitrate as well as chloride, the TDR method can be used as a first approximation of nitrate preferential flow in soil. Phosphate BTCs distinctly differed from chloride and nitrate BTCs in our study, thus the TDR method did not work. A small portion of phosphate was collected in effluents, indicating significant nonequilibrium sorption of phosphorus to soil. Further study is needed for application of the vertical TDR method to various soil situations such as a layered soil.

REFERENCES

Casey, F.X.M., S.D. Logsdon, R. Horton, and D.B. Jaynes. 1997. Immobile water content and Mass Exchange Coefficient of field soil. Soil Sci. Soc. Am. J. 61:1030-1036.

Chen, X., M. Vanclooster and G. Pan. 2002. Impact of soil water flux on vadoze zone solute transport parameters. Commun. Soil Sci. Plant Anal. 33:479-492.

Clay, D.E., Z. Zheng, Z. Liu, S.A. Clay, and T.P. Trooien. 2004. Bromide and nitrate movement through undisturbed soil columns. J. Environ. Qual. 33:338-342.

Dalton, F.N., W.N. Herkelrath, D.S. Rawlins, and J.D. Rhoades. 1984. Time domain reflectometry. Simultaneous measurement of soil water and electrical conductivities with a single probe. Science (Washington, DC) 224:989-990.

Ferre, P.A., J.H. Knight, D.L. Rudolph, and R.G. Kachanoski. 1998. The sample area of conventional and alternative time domain reflectometry probes. Water Resour. Res. 34:2971-2979.

Ferre, P.A., D.L. Rudolph, and R.G. Kachanoski. 2000. Identifying the conditions amenable to the determination of solute concentrations with time domain reflectometry. Water Resour. Res. 36:633-636.

Ferre, P.A., H.H. Nissen, P. Moldrup, and R.G. Kachanoski. 2001. The sensitivity of time domain reflectometry probes to spatially heterogeneous electrical conductivities. p. 210-224. *In* C.H. Dowding (ed.) Proc. Int. Symp. and Workshop on Time Domain Reflectometry for Innovative Geotechnical Applications, 2nd. Infrastructure Technology Institute, Northwestern University, Evanston, IL.

Gächter, R., J.M. Ngatiah, and C. Stamm. 1998. Transport of phosphate from soil to surface waters by preferential flow. Environ. Sci. Technol. 32:1865-1869.

Garrido, F., M. Ghodrati, C.G. Campbell, and M. Chendorain. 2001. Detailed characterization of solute transport in a heterogeneous field soil. J. Environ. Qual. 30:573-583.

Geohring, L.D., O.V. McHugh, M.T. Walter, T.S. Steenhuis, M.S. Akhtar, and M.F. Walter. 2001. Phosphorus transport into subsurface drains by macropores after manure applications: Implications for best manure management practices. Soil Sci. 166:896-909.

James, D.W., J. Jotuby-Amacher, G.L. Anderson, and D.A. Huber. 1996. Phosphorus mobility in calcareous soils under heavy manuring. J. Environ. Qual. 25:770-775.

Jensen, M.B., P.R. Jorgensen, H.C.B. Hansen, and N.E. Nielsen. 1998. Biopore mediated subsurface transport of dissolved orthophosphate. J. Environ. Qual. 27:1130-1137.

Kachanoski, R.G., E. Pringle, and A. Ward. 1992. Field measurement of solute travel times using time domain reflectometry. Soil Sci. Soc. Am. J. 56:47-52.

Kelly, B.P. and M.L. Pomes. 1998. Preferential flow and transport of nitrate and bromide in claypan soil. Ground Water 36:484-494.

Knight, J.H., I. White, and S.J. Zegelin. 1994. Sampling volume of TDR probes used for water content monitoring. p. 93-104. *In* Proc. Symp. Workshop. Time domain reflectometry in environmental infrastructure, and mining applications, Evanston, IL. 7-9 Sept. 1994. Spec. Publ. SP 19-94. U.S. Dep. Of Interior, Bureau of Mines, Washington, DC.

Lee, J., R. Horton, K. Noborio, and D.B. Jaynes. 2001. Characterization of preferential flow in undisturbed, structured soil columns using a vertical TDR probe. J. Contam. Hydrol. 51:131-144.

Mallants, D., M. Vanclooster, N. Toride, J. Vanderborght, M.Th. van Genuchten, and J. Feyen. 1996. Comparison of three methods to calibrate TDR for monitoring solute movement in undisturbed soil. Soil Sci. Soc. Am. J. 60: 747-754.

Marion, G.M. and K.L. Babcock. 1976. Predicting specific conductance and salt concentration in dilute aqueous solutions. Soil Sci. 122:181-187.

Nadler, A., S. Dasberg, and I. Lapid. 1991. Time domain reflectometry measurements of water content and electrical conductivity of layered soil columns. Soil Sci. Soc. Am. J. 55:938-943.

Nissen, H.H., P. Moldrup, and K. Henriksen. 1998. Time domain reflectometry measurements of nitrate transport in manure-amended soil. Soil Sci. Soc. Am. J. 62:99-109.

Nkedi-Kizza, P., J.W. Biggar, M.Th. van Genuchten, P.J. Wierenga, H.M. Selim, J.M. Davidson, and D.R. Nielsen. 1983. Modeling tritium and chloride 36 transport through an aggregated oxisol. Water Resour. Res. 19:691-700.

Rhoades, J.D., N.A. Manteghi, P.J. Shouse, and W.J. Alves. 1989. Soil electrical conductivity and soil salinity: New formulations and calibrations. Soil Sci. Soc. Am. J. 53:433-439.

Scott, C., L.D. Geohring, and M.F. Walter. 1998. Water quality impacts of tile drains in shallow, sloping, structured soils as affected by manure applications. Appl. Eng. Agric. 14:599-603.

Siddique, M.T. and J.S. Robinson. 2003. Phosphorus sorption and availability in soils amended with animal manures and sewage sludge. J. Environ. Qual. 32:1114-1121.

Stamm, C., H. Fluhler, R. Gachter, J. Leuenberger, and H. Wunderli. 1998. Preferential transport of phosphorus in drained grassland soils. J. Environ. Qual. 27:515-522.

Topp, G.C., J.L. Davis, and A.P. Annan. 1980. Electromagnetic determination of soil water content: Measurements in coaxial transmission lines. Water Resour. Res. 16:574-582.

Toride, N., F.J. Leij, and M.Th. van Genuchten. 1999. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.1. Research report No. 137. U.S. Salinity Laboratory. ARS-USDA, Riverside, CA.

van Genuchten, M.Th. and P.J. Wierenga. 1976. Mass transfer studies in sorbing porous media: I. Analytical solutions. Soil Sci. Soc. Am. J. 40:473-480.

Vogeler, I., G. Green, A. Nadler, and C. Duwig. 2001. Measuring transient solute transport through the vadoze zone using time domain reflectometry. Aust. J. Soil Res. 39:1359-1369.

Ward, A.L., R.G. Kachanoski, and D.E. Elrick. 1994. Laboratory measurements of solute transport using time domain reflectometry. Soil Sci. Soc. Am. J. 58:1031-1039.

Willmott, C.J., S.G. Ackleson, R.E. Davis, J.J. Feddema, K.M. Klink, D.R. Legates, and C.M. Rowe. 1985. Statistics for the evaluation and comparison of models. J. Geophys. Res. 90:8995-9005.

Zegelin, S.J., I. White, and D.R. Jenkins. 1989. Improved field probes for soil water content and electrical conductivity measurement using time domain reflectometry. Water Resour. Res. 25:2367-2376.

APPENDIX

Table 1.1. Chemical and physical properties of the soil used in this study.

Column	Sand/silt/clay fractions	Total C	pH (H_2O)	Water content	Pore water velocity
	%	%		m^3 m^{-3}	m h^{-1}
A	71/19/10	0.89	5.7	0.40	0.034
B					0.015
C					0.035

Table 1.2. Mobile-immobile model parameters determined from measured effluent chloride and TDR data.

Column	Parameter	Effluent Chloride	TDR
A	D_m, cm^2 h^{-1}	30.7 (±3.8)†	36.1 (±5.1)
	θ_{im}/θ	0.39 (±0.04)	0.45 (±0.06)
	α, h^{-1}	8.6×10^{-4} ($\pm4.0\times10^{-3}$)	1.0×10^{-7} ($\pm4.1\times10^{-4}$)
B	D_m, cm^2 h^{-1}	5.1 (±2.1)	3.7 (±2.7)
	θ_{im}/θ	0.83 (±0.05)	0.79 (±0.09)
	α, h^{-1}	0.19 (±0.05)	0.11 (±0.02)
C	D_m, cm^2 h^{-1}	33.8 (±0.9)	40.4 (±2.7)
	θ_{im}/θ	0.71 (±0.13)	0.74 (±0.02)
	α, h^{-1}	2.4 (±1.0)	0.8 (±0.1)

† Values in parentheses are 95% confidence intervals.

Table 1.3. Peak of measured effluent and TDR-predicted BTCs.

Column	Cl^-	NO_3-N	TDR
		Pore volumes	
A	0.26	0.26	0.18
B	0.28	0.19	0.16
C	0.26	0.21	0.12

Table 1.4. Root mean square errors (RMSEs) and coefficients of determination (r^2) between TDR-predicted and effluent BTCs.

Column	RMSE		r^2	
	Cl^-	NO_3-N	Cl^-	NO_3-N
A	0.0046	0.0046	0.94	0.93
B	0.0044	0.0067	0.85	0.84
C	0.0039	0.0050	0.88	0.88

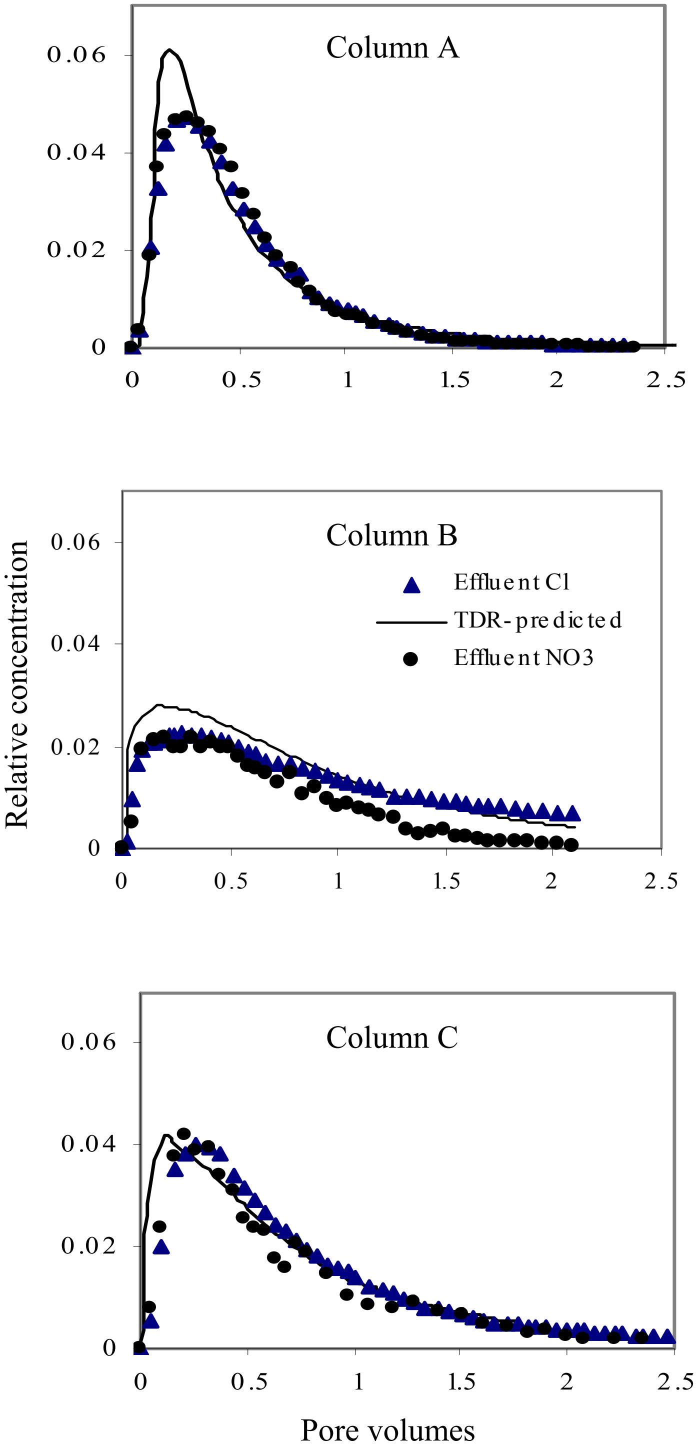

Figure 1.1. Measured effluent chloride and nitrate BTCs along with TDR-predicted BTCs. The "TDR-predicted" BTCs were obtained using TDR data and the CXTFIT program.

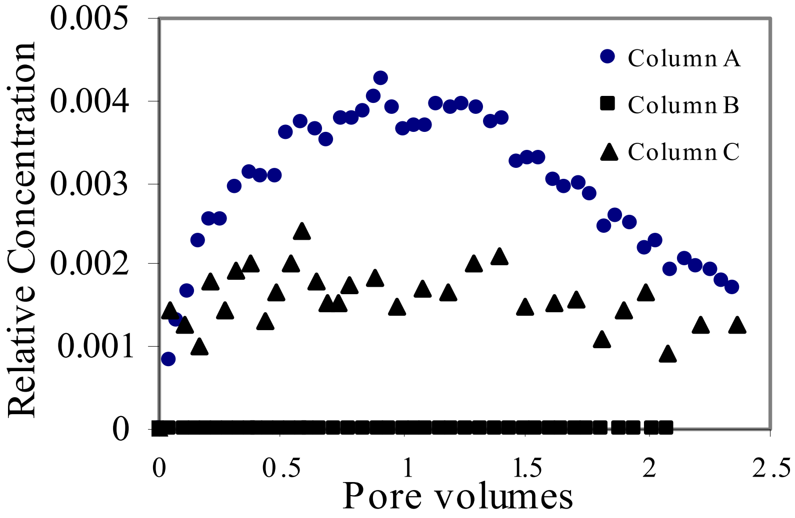

Figure 1.2. Observed effluent phosphate BTCs.

Part 2

Sediment Loss and Nutrient Runoff from Three Fertilizer Application Methods

This part is a lightly revised version of a manuscript by the same name published in the journal *Trans. ASAE* in 2005 by Youngho Seo, Jaehoon Lee, William Hart, Paul Denton, Daniel Yoder, Michael Essington, and Ed Perfect:

Seo, Y., Lee, J., Hart, W. E., Denton, H. P., Yoder, D. C., Essington, M. E., and Perfect, E. Sediment loss and nutrient runoff from three fertilizer application methods. *Trans. ASAE* 48(6): 2155-2162.

My primary contributions to this paper include (1) conducting field and laboratory experiments, (2) most of the gathering and interpretation of literature, and (3) most of the writing.

ABSTRACT

A localized compaction and doming (LCD) applicator has been shown to reduce nitrate leaching and increase nitrogen use efficiency in corn. The effects of LCD on sediment and nutrient losses in sloping fields are not well understood. During a two-year period (2003-2004), sediment and nutrient losses for each significant runoff event from corn plots were measured. A study was designed to compare losses from plots prepared using the LCD to those prepared using conventional no-till broadcast (NTB) and no-till coulter injection (NTC). These devices were used to apply recommended fertilizer rates ($N-P_2O_5-K_2O$ = 143-116-67 kg ha^{-1}) as well as a bromide tracer. Concentrations of nitrogen and bromide in the soil profile were also determined to quantify anion movement. For early rainfall events, there were significantly less runoff and soil erosion from LCD compared to the other treatments, but there was more sediment loss for later events in 2004. Total sediment loss for LCD was 1.6 Mg ha^{-1}, which was significantly greater than sediment loss for NTC (0.1 Mg ha^{-1}) and NTB (0.2 Mg ha^{-1}). Masses of bromide, nitrate, phosphate, total nitrogen, and total phosphorus in runoff for LCD were significantly less than the corresponding masses for NTB and NTC in 2004. Residual concentration profile values implied that nitrate applied by the LCD applicator was

transported more slowly through soil compared with the other methods. These results showed that the LCD method can reduce phosphorus loss in runoff, although on sloping fields it appears to result in more soil erosion.

INTRODUCTION

A localized compaction and doming (LCD) applicator was developed to improve nitrogen efficiency and reduce groundwater contamination (Ressler et al., 1997). The LCD applicator consists of a modified knife to smear the soil and close macropores below the nitrogen injection slot, a cone disk guide wheel to fill the knife slit and compact the injection band, and a covering disk to cover the compacted soil layer with a surface dome. Ressler et al. (1997) suggested that water movement was reduced through the LCD-injected fertilizer band. As a result, the LCD method reduced nitrate movement by about 40% compared with a conventional knife-injection method. Ressler et al. (1998b) showed that anion leaching through the soil profile could be reduced by LCD application. Only 1% of fluorobenzoate tracers applied by LCD leached to the subsurface drains, compared to 5% applied by a conventional knife shank and 4% applied as broadcast. Additionally, Ressler et al. (1998c) reported that LCD fertilizer injector increased corn yield by about 0.48 Mg ha^{-1} compared with the conventional knife method. These tests were all performed on nearly level plots or lysimeters. Little is known, however, about the effects of LCD on sediment and nutrient losses in sloping fields, where plant nutrients may contaminate the surface water through surface runoff, fertile topsoil may be lost from the farmland through soil erosion, and/or the buried fertilizers may be exposed by that erosion.

Soil erosion may reduce soil productivity through reductions in essential nutrients for plants, available water holding capacity, water infiltration rate, root penetration depth, and soil aggregation (National Soil Erosion - Soil Productivity Research Planning Committee, 1981). Furthermore, runoff of plant nutrients may be an important contributor to nonpoint-source pollution by nitrogen and phosphorus. Sixty percent of river impairment and 50% of lake impairment is a direct result of agricultural nonpoint-source pollution (Parry, 1998). Algal growth can be stimulated by 0.01 mg L^{-1} of phosphate-phosphorus and 0.3 mg L^{-1} of nitrate-nitrogen (Vollenweider, 1968).

Conservation tillage or no tillage can decrease runoff and sediment loss in sloping fields (Johnson et al., 1979b; McGregor and Mutchler, 1992; Soileau et al., 1994). In Tennessee, because of the high erosion hazard on many fields, no-till is practiced on 60% to 70% of the corn areas. The typical fertilization method is surface broadcast solid fertilizer. Surface broadcasting fertilization under no-till conditions can be similar to or better than soil incorporation for increasing corn yield (Hargrove, 1985; Howard and Tyler, 1987), but it may cause more nutrient loss in runoff (Soileau et al., 1994). Water-extractable phosphorus in the soil can be concentrated in the uppermost layer of the profile (Stamm et al., 1998) when phosphorus is applied to the soil surface. Dissolved phosphorus in runoff can be directly related to the level of soil P at the 0 to 5 cm depth (Pote et al., 1996; Torbert et al., 2002). Sharpley (2003) reported that dissolved P concentration in surface runoff was reduced from 2.9 to 0.3 mg L^{-1} by mixing surface soil having a high P level with subsoil through plowing.

The soils in eastern Tennessee are mainly Ultisols, in which the clay minerals are primarily nonexpanding amorphous silicates. Most Ultisols are extremely susceptible to soil erosion. Many arable lands in this area are located on sloping fields, where soil erosion can be significant. In addition to the highly erodible soils, intense storms occur frequently in the spring and summer when cultivated land is exposed (Healy and Sojka, 1985). The objective of this study was to determine the effects of LCD on soil erosion and nutrient runoff in sloping fields in comparison with other conventional fertilizer application methods, and to evaluate the applicability of the LCD method in sloping fields in order to improve nutrient use efficiency and reduce water contamination.

MATERIALS AND METHODS

Three fertilizer application treatments were used to determine the influence of fertilizer application method on soil erosion and nutrient runoff in a sloping field. The treatments consisted of conventional no-till broadcast (NTB) application, no-till coulter

(NTC) injection of liquid nitrogen (N) and phosphorous (P), and LCD injection of liquid N and P. Band application of nitrogen solutions and/or liquid nitrogen-phosphorus starter fertilizer using a coulter under no-till conditions is practiced on a small part of Tennessee. This practice is thought to reduce nutrient runoff potential under no-till conditions. The LCD is another fertilization method of zonal fertilization and soil incorporation of fertilizers.

The experiment was performed at the University of Tennessee Plant Science Farm in Knoxville, Tennessee. Twelve 6.1 m wide by 25.9 m long plots were isolated from the surrounding area using soil berms. A randomized block design was used such that the twelve plots were blocked into four groups of three based on slope, soil type, and slope aspect. Blocks 1 and 2 were mapped as Captina sandy loam (fine-silty, siliceous, active, mesic Typic Fragiudults) and had a west-facing aspect, with block 1 slopes ranging from 13.4% to 13.9%, and block 2 slopes ranging from 14.5% to 15.2%. Blocks 3 and 4 were mapped as Etowah clay loam (fine-loamy, siliceous, semiactive, thermic Typic Paleudults) and had an east-facing aspect. Block 3 slopes ranged from 8.7% to 8.9%, and block 4 slopes ranged from 9.8% to 11.6%. Selected chemical and physical properties of the soils are shown in Table 2.1. Normal annual precipitation at the Plant Science Farm in Knoxville is 1355 mm with the annual distribution shown in Fig. 2.1.

The study was conducted over two consecutive years: 2003 and 2004. The plots had been in grass for five years prior to the study. Approximately four weeks before planting in 2003 the area was sprayed with Roundup at a rate of 4.7 L ha^{-1}. A glyphosate-tolerant corn (*Zea mays* L.) sold by Monsanto as Roundup Ready corn (DK23007) was planted on April 15 with 76 cm row spacing, resulting in a population of 74,000 plants ha^{-1}. All plots were fertilized on May 27, when the corn was approximately 76 cm tall. Wet soil conditions and technical difficulties prevented earlier injection. The rainfall amount in May 2003 was 185 mm, 47% greater than the normal monthly precipitation. Liquid N and P (10-34-0 + 32-0-0) were used for the NTC and LCD plots, while solid fertilizers (18-46-0 + 34-0-0) were used for NTB plots. Fertilizers for both NTC and LCD were injected using a solid-stream spray nozzle, with constant pressure (31 psi) maintained by a CO_2 pressurized system. Solid K as potassium chloride was applied to all plots. Fertilizer application rates were 143 kg ha^{-1} N, 116 kg ha^{-1} P_2O_5, and 67 kg ha^{-1} K_2O. For the NTC method, a coulter made a narrow slot into which the fertilizer solution was sprayed, and the slot behind the coulter remained open. Only a knife and a covering disk were used for the LCD method in this study because preliminary tests showed that the cone disk guide wheel was not effective under no-till conditions due to the abundance of large clods and heavy grass/root residue. The fertilizers were applied at about 15 cm depth for LCD, while the fertilizers were broadcast on the soil surface for NTB and sprayed in a slot at a depth of less than 10 cm for NTC. Liming was not required because the soil pH for all plots ranged from 6.8 to 7.0.

In 2004, the same agronomic practices for plant stand and fertilization rates were used as in 2003. Corn was planted on May 14 and fertilizers (N, P_2O_5, K_2O) were applied on May 18 when plant emergence was observed. Bromide (Br) was also sprayed on all plots as a conservative tracer along with other fertilizers, at a rate of 114 kg ha^{-1}. Because Br imitates nitrate movement and natural occurrences are generally rare, it has been used as a tracer to simulate nitrate movement in soils (Bowman, 1984; Mulla and Annandale, 1990; Ressler et al., 1998b; Paramasivam et al., 1999; van den Bosch et al., 1999). Additionally, Br is not subject to microbial processes and gaseous losses. Since Br was applied as a form of potassium bromide solution, liquid K instead of solid K was used in 2004. Three soil cores in each plot were taken at depths of 0-15 cm, 15-30 cm, 30-45 cm, and 45-60 cm on June 17, 30 days after fertilization, to quantify movement of Br and NO_3-N in the soil profile. Soil profile samples for LCD and NTC were collected from the inter-row where fertilizers had been applied. Nitrate and Br were extracted with 0.01 M $CaCl_2$ at a rate of 1:5 soil/solution for 2 h (Houba et al., 1990) and then determined using an ion chromatograph (Dionex Corp., Sunnyvale, Cal.).

A tipping-bucket raingauge was used to measure rain depth and intensity of each rainfall event. The storm erosivity (EI_{30}) was determined by multiplying the total storm energy (E) by the maximum 30 min intensity (I_{30}). The total energy is sum of the unit energy obtained by following equation:

$$\text{Unit energy} = 0.29 \times [1 - 0.72 \times \exp(-50 \times i)] \tag{2.1}$$

where i is the intensity (m h^{-1}) for each storm period of relatively constant intensity.

Runoff collection systems (Pinson et al., 2004) were installed just after fertilizer application and removed before corn harvest. Soil erosion and nutrient losses in surface runoff were determined during this period only. Runoff was routed into the first 19 L bucket in a series of buckets fitted with a divider containing 24 22.5° V-notch weirs. Once this bucket was completely filled with runoff, overflowing water/sediment was evenly divided between the 24 weirs. Flow from one of the 24 overflowing notches was collected in a second bucket. Likewise, one twenty-fourth of the excess flow was channeled in to a third bucket. Runoff and sediment was calculated by adding the amount in the first bucket, the amount in the second bucket multiplied by 24, and the amount in the third bucket multiplied by $(24)^2$.

Runoff and sediment loss from LCD, NTB, and NTC plots were measured and compared each other. Water depth in the buckets was measured to calculate runoff volume. Duplicate grab water samples in each bucket were taken while the bucket was being thoroughly stirred, and filtered through a 0.45 μm membrane filter. After taking runoff samples and settling the sediment in buckets, the supernatant water was decanted and the remaining sediment and water was transferred into baking pans. The sediment was dried at 105°C and weighed to calculate sediment loss. Concentrations of dissolved Br and nitrate-nitrogen (NO_3-N) in the runoff were determined using an ion chromatograph. Concentrations of phosphate-phosphorus (PO_4-P) were measured using a Lachat spectrophotometer (Zellweger Analytics, Milwaukee, Wisc.). Levels of total Kjeldahl nitrogen (TKN) and total phosphorus (TP) in the runoff were determined using a Lachat spectrophotometer after digestion in a block-type digester. Total nitrogen (TN) was computed by adding TKN and NO_3-N, since TKN is the sum of organic nitrogen and ammonia. Total mass of Br, NO_3-N, PO_4-P, TN, and TP for each storm was calculated by multiplying the concentration in the runoff by the runoff volume.

RESULTS AND DISCUSSION

Rainfall amounts after fertilizer application in 2003 and 2004 are shown in Fig. 2.2. In 2003, there was no significant storm after fertilizer application until early July when the soil surface was fully covered by a corn canopy. Total precipitation in June

2003 amounted to 67 mm, 59% of normal. Conversely, in 2004, many significant storms occurred when the soil surface was exposed. A significant storm is defined as a depth greater than 13 mm unless 6.4 mm fell within 15 min, and the storm is divided into two events if there is less than 1.27 mm of rain for 6 h (Renard et al., 1997). It should be noted that significant runoff and sediment loss were not observed for every significant storm, possibly due to low rainfall intensity, temporal distribution, antecedent soil condition, and/or high infiltration rate. Burk et al. (2000) showed that antecedent soil moisture conditions should be considered for summer storm runoff.

Runoff and sediment loss for the LCD method were less than measured losses for NTC and NTB in 2003, but the differences were not statistically significant (Table 2.2). Loose soil structure from the action of the LCD applicator may have caused high infiltration rates and thus low runoff. Additionally, the increased surface roughness caused by the LCD applicator may act as a natural barrier to runoff and may trap sediment. Furthermore, Wilson et al. (2004) reported that sediment concentration from tilling historical no-till land was significantly lower than from conventional tillage land, but this effect was fully lost within one year. This residual effect may reduce tillage effects for soil erosion in the first year.

In 2004, runoff and sediment loss in all treatments were greater when compared to 2003 (Table 2.3). The primary reason for this difference is likely to be the timing, intensity, amount, and frequency of rainstorms, and duration between rainfall events. A significant rainstorm was not observed until corn canopy was fully developed in 2003. In addition to protecting the soil surface from raindrop impact, vegetation can decrease runoff volumes by reducing the average flow velocity and allowing significant post-storm infiltration (Dunne and Dietrich, 1980), and crop roots can be effective in decreasing soil erosion rates (Gyssels et al., 2002). Furthermore, the rainfall amounts in late May (89%) and June (47%) of 2004 were greater than normal. Another reason for the difference was greater infiltration in 2003 because the plots had been in grass for five years prior to the study. Grassland generally has more tubular macropores and greater infiltration rates than cultivated soils (Eynard et al., 2004). There was an extensive root system and soil aggregation in the first year. Roots increase soil aggregation by exuding binding agents and serving as a food source for microorganisms, thus increasing infiltration and decreasing runoff. Additionally, roots and incorporated residues physically bind soil particles together and act as mechanical barriers to soil erosion (Yoder et al., 1997). Loss of this root system in the second year diminishes that "sod effect," causing more runoff and sediment loss.

In 2004, there were significantly less runoff and soil erosion from LCD compared to other treatments for the first rainfall event, but the LCD produced greater sediment loss for later events (Table 2.3). Breaking up surface crust, increased surface roughness, large depression storage, and interception in LCD plots may have promoted infiltration and reduced runoff during the first two rainfall events. As surface roughness increases, transport capacity and runoff detachment decreases because of flow velocity reduction (Johnson et al., 1979a). Additionally, tillage has been reported to result in higher hydraulic conductivity and rapid drainage by decreasing bulk density, increasing porosity, and increasing proportion of larger pores compared with conservation tillage systems (Lindstrom and Onstad, 1984; Hill et al., 1985). But the reduction in runoff and soil erosion for LCD disappeared rapidly and there was soon more soil erosion. These results are consistent with those of Dabney et al. (2004). They reported that surface disturbance decreased runoff from the first storm following tillage, but increased total soil loss.

One of the major causes for the greater amount of erosion during later rain events is reduced infiltration rate, due to a combination of factors including physical soil settling by aggregate breakdown, clogging of macropores by fines, slaking, and surface sealing. The relative impacts of these processes depend greatly on soil type, intensity of the rainfall, and duration between storm events. Fox et al. (1998) showed a decrease in surface roughness due to filling of depressions and erosion of mounds during a simulated rainfall. In this study, surface random roughness was measured during 2004 using the chain method (Saleh, 1993). Surface random roughness in the LCD plots decreased from 10.4 (unitless) on May 26 to 5.6 on June 21. Total sediment loss for LCD was 1.6 Mg ha^{-1}, which was significantly greater than sediment loss for NTC (0.1 Mg ha^{-1}) and NTB (0.2 Mg ha^{-1}). The greater soil loss from LCD compared to NTC and NTB methods may be due to tillage effects, which may dominate once the initial surface roughness has diminished. There was very little residue cover in the LCD treatments by tillage. This allowed surface sealing by raindrop impact and detachment of soil particles. Dabney et al. (2004) suggested that erosion resistance in no-till systems can be due to both residue cover and improved soil quality factors. When the random roughness decreased and runoff increased in LCD, the greater detachment of soil by raindrops led to higher concentration of sediment and more total soil loss. Destruction of soil structure by tillage also left the soil more susceptible to detachment by runoff. Soileau et al. (1994) reported more sediment discharge from a watershed with conventional tillage than with conservation tillage, and Johnson et al. (1979b) showed that conservation tillage systems reduced soil loss from 60% to 90% compared with conventional tillage systems.

In 2003, runoff from the LCD plots had less PO_4-P but greater NO_3-N mass than the other fertilization methods (Table 2.4). For the no-till plots, mobile N could be leached, while P remained on the soil surface. Tyler and Thomas (1977) reported that surface-applied NO_3 under no-tillage conditions could be washed into natural soil cracks and channels. Furthermore, less intense rainfall events following fertilizer application may leach considerable N into the soil profile, thus reducing the possibility of runoff removal of soluble N during a subsequent severe storm (Römkens et al., 1973). For the LCD plots, N may have been retained in the application zone through reduced NO_3 leaching, and direct exposure of P to rainstorms was probably prevented because P was incorporated into the soil profile. Total nitrogen (TN) and total phosphorus (TP) showed similar trends to NO_3-N and PO_4-P (Table 2.4). Dissolved PO_4-P was about 70% of TP in runoff for NTB, while less than 10% for LCD, indicating that PO_4-P from fertilizer and decaying organic residues was incorporated into the soil profile and physically protected from being removed in runoff for LCD.

In 2004, total masses of Br, NO_3-N, and PO_4-P in runoff for LCD were significantly less than the masses for other treatments (Table 2.5). Soileau et al. (1994) reported that less P runoff occurred with conventional tillage than with conservation tillage, and suggested that subsurface fertilizer placement reduces surface runoff of N and P. As explained for the 2003 results, N loss reduction by subsurface placement may depend on climate and soil condition. Total masses of TN and TP showed similar trends in 2004 (Table 2.6). The NTC method did not significantly reduce nutrient runoff compared to NTB, which was not expected. Fertilizer injection has been recommended in no-till to reduce nutrient runoff. The reasons that coulter injection did not reduce nitrogen and phosphorus loss here may have been (1) the slot behind the coulter into which the fertilizer solution was sprayed was not closed, and/or (2) the rows were oriented parallel to the slope, which may have left the open coulter slot as a preferential surface flow path. In no-till production in the southeastern U.S., the injection slot is not actively closed when farmers inject liquid fertilizer. This study indicates that this may not be an effective strategy for reducing runoff loss, at least if the row orientation is not on the contour.

Concentrations of Br, NO_3-N, and PO_4-P in runoff for NTC and NTB decreased over time, while the concentrations for LCD had little change (Fig. 2.3). For the first four rain events, the concentrations of NO_3-N from NTB and NTC were greater than 10 mg L^{-1}. For the rain event on July 27, significantly greater concentrations of Br and NO_3-N were detected in runoff for LCD than other methods, implying that more Br and NO_3 were retained in the surface soil at that time. Note that LCD is designed to reduce anion leaching to deeper soil profile, enhancing nutrient availability during the late growing season. Greater concentrations of Br and NO_3-N in late runoff events from LCD may be due to the reduced leaching plus enhanced upward movement of anions by evaporation. The LCD causes more disturbance of soil compared to other methods, resulting in less plant residue along the fertilizer band. The disturbance of soil and less residue in the LCD plots may cause enhanced evaporation, which can result in greater concentrations of anions in the later runoff events.

Concentrations of Br and NO_3-N in the soil profile were greater for LCD than for NTB and NTC at 30 days after fertilizer application (Fig. 2.4). The fertilizers were evenly applied on the whole plot for NTB, while they were injected in a band for LCD and NTC. Bromide concentrations at the 15-30 cm depth for LCD were greater than the concentrations at the 0-15 cm depth, while NO_3-N was greatest in the 0-15 cm depth. This showed that Br distributions may not be representative of NO_3 movement in the soil because Br can be leached more easily than NO_3 (Kessavalow et al., 1996; Clay et al., 2004). Ressler et al. (1998a) suggested that zonal soil management can preserve macropores to aid infiltration in solute-free zones, while destroying macropores to limit preferential flow in solute placement zones. They showed that solutes restricted to soil management zones with disrupted macropores had slower transport through soil compared with broadcast application. The knife on the LCD applicator closes macropores that can be present in no-till plots. Furthermore, a surface dome can protect the fertilizer band by letting water move to either side of the band (Ressler et al., 1997). Ressler et al. (1998c) reported that the LCD method can limit NO_3 movement out of the injection zone in a cornfield when precipitation is abundant. In addition to nutrient losses in runoff, the soil concentration profile also implied less susceptibility to downward movement and greater accumulation of applied Br and nitrate for LCD compared with other methods.

In summary, the LCD method can reduce P loss in runoff compared with the other methods. However, it may cause more soil erosion from sloping fields than conventional methods, especially during years when the soil surface is directly exposed to frequent heavy rainfall. In addition, the NTC method did not significantly reduce N or P losses in runoff compared to NTB in this study.

CONCLUSIONS

Three fertilizer application methods were evaluated for sediment loss, runoff, and nutrient loss in a sloping field for two years. Many significant storms occurred when bare soil was directly exposed to rainfall in 2004, while there was no significant storm activity until the corn reached full canopy cover in 2003. Runoff and sediment losses for LCD were not significantly different from those for NTC and NTB in 2003. In 2004, there were significantly less runoff and erosion for LCD than for the other methods in early rainfall events, but there was more sediment loss for later events. Total sediment loss for LCD was significantly greater than for NTC and NTB. Masses of the applied nutrients in runoff for LCD were less than for the other methods, especially for P. In 2004, total masses of Br (applied as a tracer), NO_3-N, and PO_4-P in runoff for LCD were only 1.2%, 12.5%, and 1.5%, respectively, of their total masses in runoff for NTB. Additionally, soil concentration profile values measured 30 days after fertilizer application also showed less susceptibility to downward movement and greater retention of applied Br and NO_3-N in the upper soil layers for LCD than for the other methods. The NTC method did not significantly reduce nutrient runoff compared to NTB, possibly due to the open coulter slot.

REFERENCES

Bowman, R. S. 1984. Evaluation of some new tracers for soil water studies. Soil Sci. Soc. Am. J. 48: 987-993.

Burk, A. R., D. S. Chanasyk, and E. Mapfumo. 2000. Antecedent soil water for managed landscapes in central Alberta. Trans. ASAE 43: 1467-1475.

Clay, D. E., Z. Zheng, Z. Liu, S. A. Clay, and T. P. Trooien. 2004. Bromide and nitrate movement through undisturbed soil columns. J. Environ. Qual. 33: 338-342.

Dabney, S. M., G. V. Wilson, K. C. McGregor, and G. R. Foster. 2004. History, residue, and tillage effects on erosion of loessial soil. Trans. ASAE 47: 767-775.

Dunne, T., and W. E. Dietrich. 1980. Experimental study of Horton overland flow on tropical hillslopes: II. Sheetflow hydraulics and hillslope hydrographs. Z. Geomorphol. Suppl. 33: 40-80.

Eynard, A., T. E. Schumacher, M. J. Lindstrom, and D. D. Malo. 2004. Porosity and pore-size distribution in cultivated Ustolls and Usterts. Soil Sci. Soc. Am. J. 68: 1927-1934.

Fox, D. M., Y. L. Bissonnais, and P. Quetin. 1998. The implications of spatial variability in surface seal hydraulic resistance for infiltration in a mound and depression microtopography. Catena 32: 101-114.

Gyssels, G., J. Poesen, J. Nachtergaele, and G. Govers. 2002. The impact of sowing density of small grains on rill and ephemeral gully erosion in concentrated flow zones. Soil and Tillage Res. 64: 189-201.

Hargrove, W. L. 1985. Influence of tillage on nutrient uptake and yield of corn. Agron. J. 77: 763-768.

Healy, R. G., and R. E. Sojka. 1985. Agriculture in the South: Conservation's challenge. J. Soil and Water Conserv. 40: 189-194.

Hill, R. L., R. Horton, and R. M. Cruse. 1985. Tillage effects on soil water retention and pore size distribution of two Mollisols. Soil Sci. Soc. Am. J. 49: 1264-1270.

Houba, V. J. G., I. Novozamsky, T. M. Lexmond, and J. J. van der Lee. 1990. Applicability of 0.01 M $CaCl_2$ as a single extraction solution for the assessment of the nutrient status of soils and other diagnostic purposes. Comm. in Soil Sci. Plant Anal. 21: 2281-2290.

Howard, D. D., and D. D. Tyler. 1987. Comparison of surface applied rates of phosphorus and potassium and in-furrow fertilizer solution combinations for no-till corn production. J. Fert. Issues 4: 48-52.

Johnson, C. B., J. V. Mannering, and W. C. Moldenhauer. 1979a. Influence of surface roughness and clod size and stability on soil and water losses. Soil Sci. Soc. Am. J. 43: 772-777.

Johnson, H. P., J. L. Baker, W. D. Sharder, and J. M. Laflen. 1979b. Tillage system effects on sediment and nutrients in runoff from small watersheds. Trans. ASAE 22: 1110-1114.

Kessavalow, A., J. W. Doran, W. L. Powers, T. A. Kettler, and J. H. Qian. 1996. Bromide and nitrogen-15 tracers of nitrate leaching under irrigated corn in central Nebraska. J. Environ. Qual. 25: 1008-1014.

Lindstrom, M. J., and C. A. Onstad. 1984. Influence of tillage systems on soil physical parameters and infiltration after planting. J. Soil and Water Conserv. 39: 149-152.

McGregor, K. C., and C. K. Mutchler. 1992. Soil loss from conservation tillage for sorghum. Trans. ASAE 35: 1841-1845.

Mulla, D. J., and J. G. Annandale. 1990. Assessment of field-scale leaching patterns for management of nitrogen fertilizer application. In Field-Scale Water and Solute Flow in Soils, 55-63. K. Roth, H. Flühler, W. A. Jury, and J. C. Parker, eds. Boston, Mass.: Birkhäuser Verlag.

National Soil Erosion - Soil Productivity Research Planning Committee. 1981. Soil erosion effects on soil productivity: A research perspective. J. Soil and Water Conserv. 36: 82-90.

Paramasivam, S., A. K. Alva, and W. D. Graham. 1999. Transport of bromide in an Entisol and its dissipation in a surficial aquifer. J. Environ. Sci. Health, Part A A34: 585-604.

Parry, R. 1998. Agricultural phosphorus and water quality: A U.S. Environmental Protection Agency perspective. J. Environ. Qual. 27: 258-261.

Pinson, W. T., D. C. Yoder, J. R. Buchanan, W. C. Wright, and J. B. Wilkerson. 2004. Design and evaluation of an improved flow divider for sampling runoff plots. Applied Eng. in Agric. 20: 433-438.

Pote, D. H., T. C. Daniel, A. N. Sharpley, P. A. Moore, Jr., D. R. Edwards, and D. J. Nichols. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. Soil Sci. Soc. Am. J. 60: 855-859.

Renard, K. G., G. R. Foster, G. A. Weesies, D. K. McCool, and D. C. Yoder. 1997. Predicting Soil Erosion by Water: A Guide to Conservation Planning with the Revised Universal Soil Loss Equation (RUSLE). USDA Agriculture Handbook No. 703. Washington, D.C.: USDA.

Ressler, D. E., R. Horton, J. L. Baker, and T. C. Kaspar. 1997. Testing a nitrogen fertilizer applicator designed to reduce leaching losses. Applied Eng. in Agric. 13: 345-350.

Ressler, D. E., R. Horton, and G. J. Kluitenberg. 1998a. Laboratory study of zonal management effects on preferential solute movement in soil. Soil Sci. 163: 601-610.

Ressler, D. E., R. Horton, J. L. Baker, and T. C. Kaspar. 1998b. Evaluation of localized compaction and doming to reduce anion leaching losses using lysimeters. J. Environ. Qual. 27: 910-916.

Ressler, D. E., R. Horton, T. C. Kaspar, and J. L. Baker. 1998c. Localized soil management in fertilizer injection zone to reduce nitrate leaching. Agron. J. 90: 747-752.

Römkens, J. J. M., D. W. Nelson, and J. V. Mannering. 1973. Nitrogen and phosphorus composition of surface runoff as affected by tillage method. J. Environ. Qual. 2: 292-295.

Saleh, A. 1993. Soil roughness measurement: Chain method. J. Soil and Water Conserv. 48: 527-529.

Sharpley, A. N. 2003. Soil mixing to decrease surface stratification of phosphorus in manured soils. J. Environ. Qual. 32: 1375-1384.

Soileau, J. M., J. T. Touchton, B. F. Hajek, and K. H. Yoo. 1994. Sediment, nitrogen, and phosphorus runoff with conventional- and conservation-tillage cotton in a small watershed. J. Soil and Water Cons. 49: 82-89.

Stamm, C., H. Fluhler, R. Gachter, J. Leuenberger, and H. Wunderli. 1998. Preferential transport of phosphorus in drained grassland soils. J. Environ. Qual. 27: 515-522.

Torbert, H. A., T. C. Daniel, J. L. Lemunyon, and R. M. Jones. 2002. Relationship of soil test phosphorus and sampling depth to runoff phosphorus in calcareous and noncalcareous soils. J. Environ. Qual. 31: 1380-1387.

Tyler, D. D., and G. W. Thomas. 1977. Lysimeter measurements of nitrate and chloride losses from soil under conventional and no-tillage corn. J. Environ. Qual. 6: 63-66.

van den Bosch, H., C. J. Ritsema, J. J. T. I. Boesten, L. W. Dekker, and W. Hamminga. 1999. Simulation of water flow and bromide transport in a water-repellent sandy soil using a one-dimensional convection-dispersion model. J. Hydrol. 215: 172-187.

Vollenweider, R. A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. Rep. OAS/CS1/68.27. Paris, France: Organization for Economic Co-operation and Development.

Wilson, G. V., S. M. Dabney, K. C. McGregor, and B. D. Barkoll. 2004. Tillage and residue effects on runoff and erosion dynamics. Trans. ASAE 47: 119-128.

Yoder, D. C., J. P. Porter, J. M. Laflen, J. R. Simanton, K. G. Renard, D. K. McCool, and G. R. Foster. 1997. Cover-management factor (C). In Predicting Soil Erosion by Water: A Guide to Conservation Planning with the Revised Universal Soil Loss Equation (RUSLE), 143-181. K. G. Renard, G. R. Foster, G. A. Weesies, D. K. McCool, and D. C. Yoder, coordinators. USDA Agriculture Handbook No. 703. Washington, D.C.: USDA.

APPENDIX

Table 2.1. Chemical and physical properties of the soils located at the study site.

Series	Sand	Silt	Clay	pH (H_2O)	Total C	Total N	Phosphorus[†]
	%	%	%		%	%	kg ha^{-1}
Captina	56	26	18	6.8	1.5	0.14	7
Etowah	26	45	29	6.9	1.6	0.16	27

† Mehlich 1 method

Table 2.2. Runoff and sediment loss in 2003.

Date	Rainfall	Storm Erosivity	Runoff (mm)[†]			Sediment loss (kg ha^{-1})[†]		
	mm	MJ·mm· ha^{-1}·h^{-1}	LCD	NTC	NTB	LCD	NTC	NTB
July10	51.6	266.3	2.8±1.9 a	3.8±1.0 a	3.8±2.2 a	6±8 a	15±18 a	15±19 a
July11	25.9	116.1	0.3±0.3 a	1.7±1.5 a	0.8±0.7 a	1±2 a	6±8 a	5±8 a
July31	20.5	26.7	0.2±0.1 a	0.2±0.2 a	0.2±0.1 a	1±1 a	1±2 a	1±1 a
Aug. 4	18.8	53.8	0.1±0.1 a	0.6±0.5 a	0.5±0.4 a	1±1 a	1±0 a	3±2 a
Total	116.8	462.9	3.4±2.1 a	6.3±2.7 a	5.3±3.1 a	9±11 a	23±25 a	24±28 a

[†] Treatment values (with standard deviations) followed by the same letter in each row for the same rainfall event are not significantly different at the 0.05 probability level by t-test.

Table 2.3. Runoff and sediment loss in 2004.

Date	Rainfall	Storm Erosivity	Runoff (mm)†			Sediment loss (kg ha^{-1})†		
	mm	MJ·mm· ha^{-1}·h^{-1}	LCD	NTC	NTB	LCD	NTC	NTB
May 26	34.5	83.0	0.1±0.0 a	2.0±1.3 b	1.7±1.1 b	1±2 a	20±9 b	25±17 b
May 30	26.8	163.2	1.1±0.7 a	4.8±2.3 b	5.0±2.5 b	39±8 a	25±14 a	64±47 a
June 2	16.3	62.3	2.8±0.4 a	3.7±0.8 a	3.3±0.6 a	413±125 a	40±13 b	61±39 b
June 3	10.1	7.1	1.0±0.5 a	0.5±0.4ab	0.3±0.1 b	104±82 a	4±3 b	4±3 b
June 15	26.7	47.4	0.5±0.2 a	0.1±0.0 b	0.2±0.1ab	66±56 a	1±0 b	2±2 b
June 17	19.5	62.7	1.8±1.1 a	1.4±1.5 a	1.3±1.7 a	414±330 a	11±11 b	20±24 b
June 25	48.5	168.5	3.7±1.5 a	2.8±0.1 a	4.6±3.1 a	440±341 a	18±13 b	21±13 b
July 5	25.6	91.3	0.8±0.7 a	0.6±0.8 a	0.8±0.6 a	37±53 a	3±4 a	4±5 a
Total	208.0	685.5	11.7±3.0 a	15.9±5.4 a	17.1±7.0 a	1517±1006a	122±27 b	202±121 b

† Treatment values (with standard deviations) followed by the same letter in each row for the same rainfall event are not significantly different at the 0.05 probability level by t-test.

Table 2.4. Masses (g ha^{-1}) of NO_3-N, PO_4-P, TN, and TP in runoff in 2003.

		Treatment†		
Nutrient	Date	LCD	NTC	NTB
NO_3-N	July 10	347 a	126 ab	29 b
	July 11	6 a	15 a	5 a
	July 31	1 a	1 a	1 a
	Aug. 4	1 a	3 a	4 a
	Total	355 a	145 ab	39 b
PO_4-P	July 10	2 a	19 b	45 b
	July 11	0 a	13 b	12 b
	July 31	0 a	0 a	1 a
	Aug. 4	0 a	0 a	2 a
	Total	2 a	32 b	60 b
TN	July 10	458 a	268 a	107 b
	July 11	12 a	71 a	29 a
	Total	470 a	339 a	136 b
TP	July 10	27 a	45 a	62 a
	July 11	2 a	22 b	17 b
	Total	29 a	67 a	79 a

† Treatment values followed by the same letter in each row for the same rainfall event are not significantly different at the 0.05 probability level by t-test.

Table 2.5. Masses (g ha^{-1}) of Br, NO_3-N, and PO_4-P in runoff in 2004.

		Treatment[†]		
Nutrient	Date	LCD	NTC	NTB
Br	May 26	0 a	580 b	1216 b
	May 30	0 a	957 b	1092 b
	June 2	0 a	399 b	303 b
	June 3	0 a	91 b	38 b
	June 15	0 a	2 b	5 b
	June 17	0 a	104 b	64 b
	June 25	3 a	12 a	4 a
	July 5	29 a	15 a	30 a
	Total	32 a	2160 b	2752 b
NO_3-N	May 26	1 a	417 b	496 b
	May 30	28 a	650 b	1354 b
	June 2	80 a	340 b	365 b
	June 3	29 a	80 a	51 a
	June 15	4 a	2 a	4 a
	June 17	107 a	129 a	92 a
	June 25	46 a	36 a	33 a
	July 5	6 a	4 a	6 a
	Total	301 a	1658 b	2401 b
PO_4-P	May 26	0 a	78 b	78 b
	May 30	0 a	85 b	170 b
	June 2	1 a	50 b	53 b
	June 3	0 a	13 b	9 b
	June 15	0 a	0 ab	1 b
	June 17	0 a	26 b	28 b
	June 25	1 a	22 b	47 c
	July 5	3 a	3 a	4 a
	Total	6 a	277 b	390 b

[†] Treatment values followed by the same letter in each row for the same rainfall event are not significantly different at the 0.05 probability level by t-test.

Table 2.6. Masses (g ha^{-1}) of TN and TP in runoff in 2004.

		Treatment†		
Nutrient	Date	LCD	NTC	NTB
TN	May 26	3 a	602 b	595 b
	May 30	52 a	1004 b	1515 b
	June 2	156 a	493 b	445 b
	June 3	52 a	104 a	62 a
	June 15	12 a	6 a	12 a
	June 17	140 a	175 a	133 a
	June 25	95 a	79 a	98 a
	July 5	15 a	12 a	11 a
	Total	525 a	2475 b	2871 b
TP	May 26	0 a	80 b	84 b
	May 30	1 a	94 b	189 b
	June 2	2 a	69 b	66 b
	June 3	1 a	14 b	9 b
	June 15	0 a	1 a	1 a
	June 17	1 a	26 b	30 b
	June 25	2 a	22 b	47 b
	July 5	3 a	3 a	4 a
	Total	10 a	309 b	430 b

† Treatment values followed by the same letter in each row for the same rainfall event are not significantly different at the 0.05 probability level by t-test.

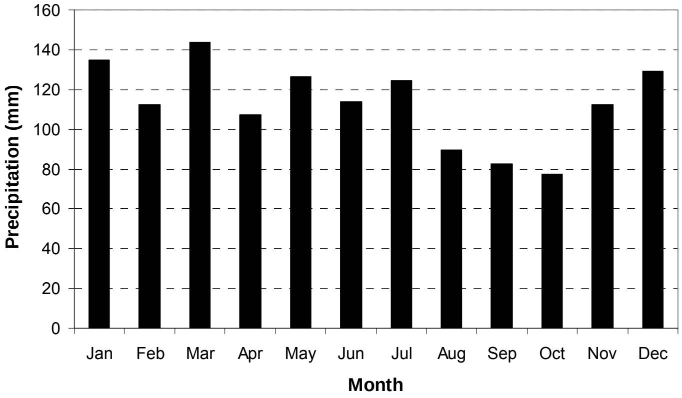

Figure 2.1. Normal precipitation (1971-2000) at the Plant Science Farm in Knoxville, Tennessee.

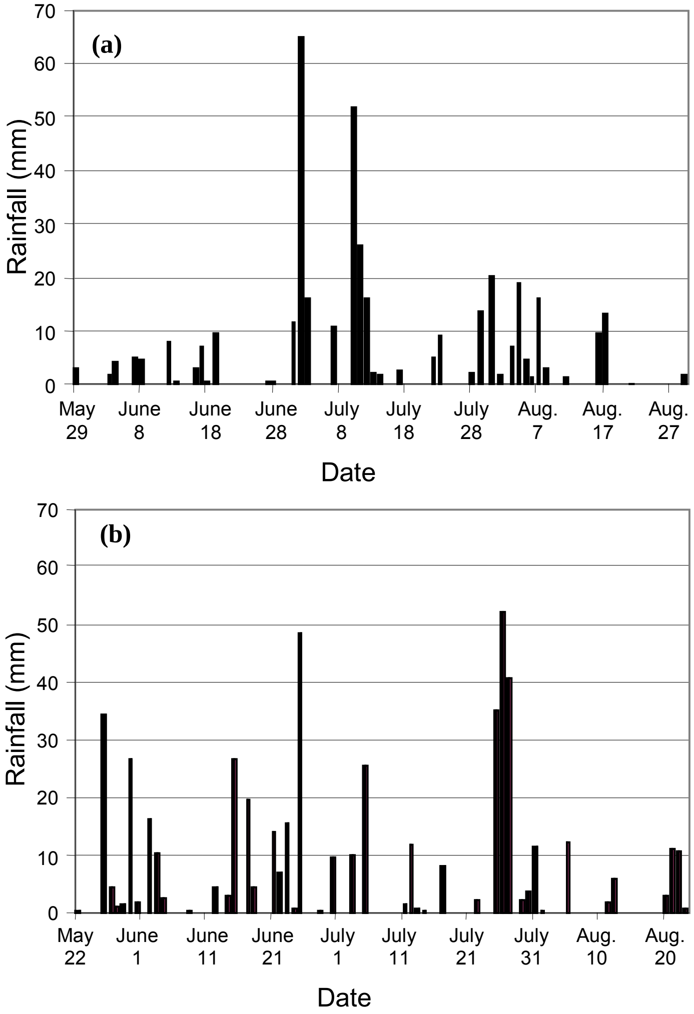

Figure 2.2. Rainfall data during growing season in (a) 2003 and (b) 2004.

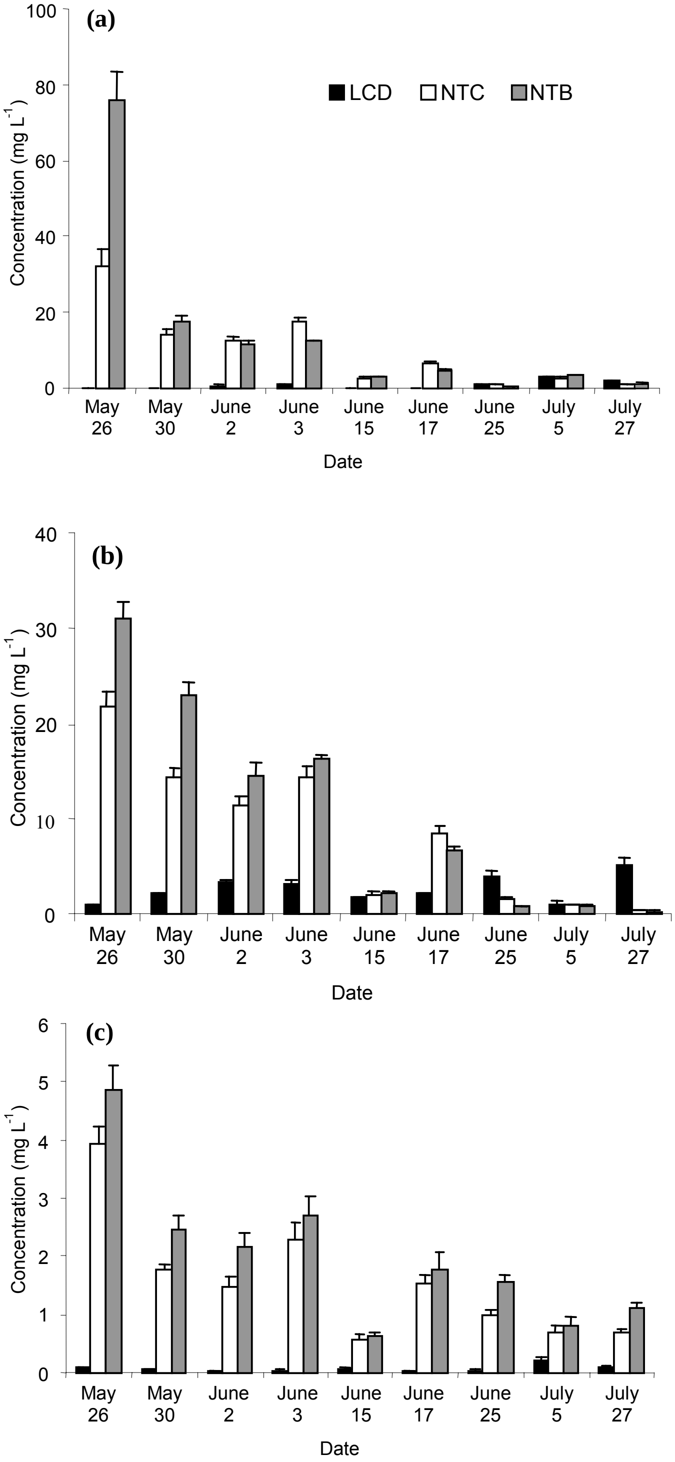

Figure 2.3. Concentrations of (a) Br, (b) NO_3-N, and (c) PO_4-P in runoff in 2004. Error bars indicate standard error.

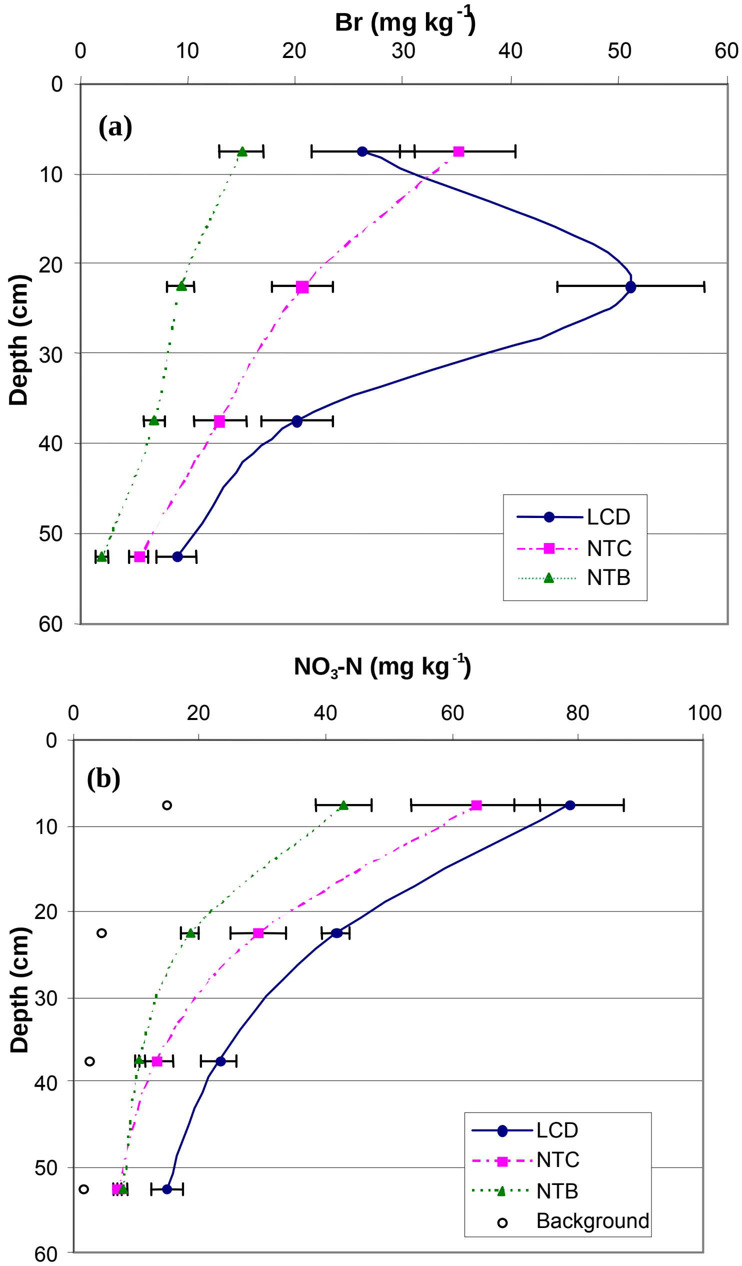

Figure 2.4. Residual concentration profiles for (a) Br and (b) NO_3-N in LCD, NTC, and NTB, 30 days after fertilizers were applied. Error bars indicate ±1 standard error. Background nitrate concentration before fertilization is shown by an open circle.

Part 3

Influence of Soil Chemical Properties on Sorption and Mobility of Antibiotics in Soil

ABSTRACT

One of the major routes of veterinary antibiotics entering soil and aquatic environments is via the application of antibiotic-laden animal manure to agricultural land as an organic fertilizer. Land application of animal manure can change the soil chemical properties, thus affecting sorption and mobility of agricultural antibiotics in soil. The effects of soil properties on the fate and transport of chlortetracycline (CTC), tylosin (TYL), and sulfamethazine (SMT) were examined by conducting batch and column experiments. Sorption of CTC and TYL to montmorillonite and kaolinite generally decreased with increasing pH and ionic strength, implying that cation exchange may be one of the major sorption processes for the antibiotics. Decreased retention of CTC and TYL to the clays and soils (surface and subsurface soil of Etowah clay loam and Captina sandy loam) was observed in the presence of Ca ion compared with Na. Weak SMT sorption to clays relative to CTC and TYL and inability of a surface complexation model to adequately predict SMT sorption in the pH range greater than 4 may imply hydrophobic interactions between neutral SMT species and clay surfaces. Additionally, the SMT retention by soils was strongly influenced by soil organic matter content. Sorption of CTC and TYL to clays and soils decreased by adding dissolved organic carbon (DOC) derived from dairy manure, while SMT sorption increased by DOC addition. Column miscible displacement experiments using surface and subsurface soil from a sandy loam showed increased CTC mass recovery in effluents and decreased retardation factors (*R*) in the presence of dairy manure DOC. Elevated levels of DOC also resulted in decreased *R* of TYL and increased SMT mass recovery in effluents for surface soil column. In summary, changes in pH, ionic strength, DOC level, and background electrolyte cation type in soil solution caused by concomitant addition of animal manure can influence fate and transport of agricultural antibiotics in soils. The results obtained in this study imply that failure to take the animal manure application effects into account can lead to conclusions that have little relevance to real situations.

INTRODUCTION

Antibiotics have been administered to livestock in order to treat disease when illness is present. In addition to these therapeutic uses, antibiotics are routinely given to healthy livestock by adding to feed or water to increase feed efficiency, to prevent disease, and to promote growth. Drugs administered orally are generally slowly absorbed to animals, and a mixture of the parent compound and metabolites can be excreted in the urine and feces (Halling-Sorensen et al., 1998; Montforts et al., 1999; Tolls, 2001; Winckler and Grafe, 2001; Boxall et al., 2002; Halling-Sorensen et al., 2002; Aga et al., 2003; Vaclavik et al., 2004). Therefore, one of the major routes of veterinary antibiotics entering soil and waster environment is via the application of animal manure to agricultural land as an organic fertilizer.

Land application of animal manure can change the soil chemical properties, thus affecting fate and mobility of agricultural antibiotics in soil. The major soil properties affected by manure amendment include pH, dissolved organic carbon (DOC), ionic strength, and background electrolyte type. Animal manure generally contains high concentration of ammonia that can increase soil pH when it is applied to the soil. The pH values of swine slurry samples range from 7.0 to 9.8 (De la Torre et al., 2000), and treatment of animal manures or slurries increases soil pH (Baskaran et al., 1996; Boxall et al., 2002; Kay et al., 2005b). The contents of DOC in swine manure and poultry manure were 995-1,965 mg L^{-1} at an extraction ratio of 1:3 with water, and addition of manure increased the DOC in the soil aqueous phase (Baskaran et al., 1996).

Antibiotics used in this study were chlortetracycline (CTC), tylosin (TYL), and sulfamethazine (SMT) because they are commonly used agricultural antibiotics in the United States. Their chemical structures are shown in Fig. 3.1. Tetracyclines, tylosin, and sulfonamides are antibiotics approved for growth promotion and feed efficiency enhancement during the growing and finishing periods of animal production (Bloom, 2004). The estimated use of CTC, TYL, and SMT in cattle, swine, and poultry production for nontherapeutic purposes is about 3,600 Mg per year (Mellon et al., 2000), and they have been detected in animal manure, soil, and surface water (Langhammer et al., 1988; Hirsch et al., 1999; Montforts et al., 1999; Hamscher et al., 2000; Linsey et al., 2001;

Campagnolo et al., 2002; Hamscher et al., 2002; Höper et al., 2002; Kolpin et al., 2002, Christian et al., 2003; Kumar et al., 2004; Vaclavik et al., 2004; Yang et al., 2004; Yang and Carlson, 2004; Kreuzig et al., 2005).

Chlortetracycline has a water solubility of 8,600 mg L^{-1} at 28 °C (Mitscher, 1978), and an octanol-water partition coefficient (K_{ow}, a measure of hydrophobicity) of 0.41 at pH 5.6 (Colaizzi and Klink, 1969). Chlortetracycline exhibits three acidity constants: pK_1 (3.27), pK_2 (7.43), and pK_3 (9.33) (Benet and Goyan, 1965). The first deprotonation occurs at the C-3 hydroxyl group, resulting in the zwitterionic form of the neutral compound. The second and third macroscopic acidity constants are assigned to the C-12 hydroxyl group and the C-4 dimethylamino group, respectively. Tylosin has a K_{ow} of 316, a water solubility of 5,000 mg L^{-1}, and pK_a of 7.1 (Tolls, 2001; Wollenberger et al., 2000). Sulfamethazine has a K_{ow} of 7.76 (Tolls, 2001), a water solubility of 1,500 mg L^{-1} at 29 °C (Merck, 2001). The water solubility of SMT depends on pH; 438 mg L^{-1} at pH 5.5 and 7,000 mg L^{-1} at pH 7.0 at 25 °C (Hekster and Vree, 1982). The nonionic species of SMT predominates at pH between 3 and 7 because pK_a values of SMT are 2.65 for the anilinic amine ($RNH_3^+ = RNH_2 + H^+$) and 7.65 for the sulfonamide group ($R_1SO_2NHR_2 = R_1SO_2NR_2^- + H^+$) (Papastephanou and Frantz, 1978; Lin et al, 1997; Tolls, 2001).

The sorption properties and mobility of antibiotics in soil is influenced by pH. The protonation or deprotonation reactions of antibiotics depend on the pH of media and the pK_a of antibiotics. As pH increases, cationic forms of antibiotics decrease and neutral/anionic species increase. The solution speciation diagrams of CTC, TYL, and SMT are shown in Fig. 3.2. Sorption affinity of agricultural antibiotics may decrease with increasing pH when cation exchange is the dominant sorption mechanism. At high pH, the repulsion between anionic antibiotic and negative soil surface may reduce the sorption. The adsorption coefficients of sulfachloropyridazine decreased with an increase in pH, indicating higher mobility of the antibiotic in alkaline soil (Boxall et al., 2002). The maximum adsorption capacity of montmorillonite for tetracycline decreased as pH increased from 1.5 to 11.0 (Porubcan et al., 1978). Sithole and Guy (1987a and 1987b) reported that tetracycline adsorption to bentonite and humic substances decreased as pH of the suspension increased from 4 to 7. Oxytetracycline showed less sorption to montmorillonite and kaolinite as pH increased from 4 to 9 (Figueroa et al., 2004). An increase in anionic charge on both antibiotics and the organic matter under high pH condition can increase electrostatic repulsions. Further, a decrease in the number of protonated sites on the organic matter may impact the hydrogen bonding between antibiotics and humic substances. On the other hand, Holten-Lützhoft et al. (2000) showed that distribution coefficients of flumequine and oxolinic acid for humic acid were greater at pH 7 and 8 than at pH 3 and 4 because of electrostatic interactions between the carboxylic and carbonyl groups of antibiotics and the positively charged amine groups in humic acid at pH 5-8.

The DOC in animal wastes may play an important role in the distribution of antibiotics between solids and the aqueous fraction in soil. Since distribution coefficients of antibiotics to DOC are greater than values based on octanol-water partition coefficients of neutral hydrophobic compounds, association of antibiotics to DOC may be much stronger than predicted from hydrophobic interactions possibly due to hydrogen bonding and cation bridging (Burkhard, 2000; Tolls, 2001). For example, less hydrophobic sarafloxacin showed a higher degree of interaction with DOC than did more hydrophobic flumequine (Holten-Lützhoft et al., 2000). The impact of DOC on transport and mobility of organic contaminants is complicated (Totsche and Kögel-Knabner, 2004). The presence of DOC can enhance the antibiotic mobility through the formation of a mobile DOC-antibiotic associate or through competition between DOC and antibiotics for sorption sites on soil solids. It has been reported that DOC can increase mobility of hydrophobic or moderately soluble organic contaminants (Barriuso et al., 1992; Johnson and Amy, 1995; Baskaran et al., 1996; Abu-zreig and Rudra, 1999; Suba and Essington, 1999; Williams et al., 2000; Huang and Lee, 2001; Prechtel et al., 2002). However, DOC, especially hydrophobic components, can be immobilized by sorption to mineral surfaces (Jardine et al., 1989; Dunnivant et al., 1992; Kaiser et al., 1996; Kaiser and Zech, 1997; Han and Thompson, 2003). Therefore, the mobility of antibiotics can be reduced by DOC through the formation of ternary complexes between the antibiotics, DOC, and soil solids and/or an increase in the organic carbon content of the bulk soil (Totsche et al., 1997; Totsche and Kögel-Knabner, 2004). The DOC effect can be determined by examining the interactions among DOC, antibiotic and soil solid as well as the chemical properties of DOC, antibiotic, and soil.

The objective of this study was to determine the influence of soil chemical properties on the fate and transport of antibiotics in soil by conducting batch equilibration adsorption experiments and column miscible displacement experiments. The soil chemical properties tested in the batch experiments were pH, ionic strength, background electrolyte cation type, and manure DOC concentration. The influence of manure DOC on the mobility of antibiotics was examined by column studies using a sandy loam soil.

LITERATURE REVIEW

Dewey et al. (1999) reported that 88% of 712 swine farms in the United States used antibiotics in feeds and most (92%) antibiotics were fed on a continuous basis, especially for young growing swine. Mellon et al. (2000) estimated that 11,200 Mg of antibiotics are used for nontherapeutic purposes for cattle, swine, and poultry in the absence of disease in the United States every year. The antibiotic treatment at nontherapeutic levels is considered to increase weight gain by suppression of intestinal bacteria (Mitscher, 1978), inhibition of subclinical infections, reduction in harmful microbial metabolites, and/or enhanced nutrient uptake by reducing microbial use (Gaskins et al., 2002). Net gain by feeding antibiotics to swine is estimated to be $45.5 million per year (Mathews Jr., 2001).

There are 95 million cattle, 8.5 billion chickens, and 60 million swine in the United States (National Agriculture Statistics Service, 2002), and about 1.4 billion Mg of animal waste were produced in 1997 (Horrigan et al., 2002). Drugs administered orally are generally slowly absorbed by animals, and a mixture of the parent compound and metabolites can be excreted in the urine and feces (Halling-Sorensen et al., 1998; Montforts et al., 1999; Tolls, 2001; Winckler and Grafe, 2001; Boxall et al., 2002; Halling-Sorensen et al., 2002; Aga et al., 2003; Vaclavik et al., 2004). Therefore, one of the major routes of veterinary antibiotics entering soil and waster environment is via the application of animal manure to agricultural land as an organic fertilizer. Antibiotics applied to soil have the potential to contaminate surface waters through overland flow (runoff) and via drainflow, and to groundwater by leaching (Halling-Sorensen et al., 1998; Boxall et al., 2004; Kay et al., 2004; Burkhardt et al., 2005; Kreuzig et al., 2005; Kay et al., 2005a; Kay et al., 2005c). Kay et al. (2004) reported that peak concentrations of sulfachloropyridazine and oxytetracycline in drainflow from a 1.55 ha field were 613 and 36 µg L^{-1}, respectively, although mass losses of the antibiotics were less than 0.5%. They suggested that preferential flow via desiccation cracks and worm channels to the tile drains was the most important route. In runoff from 5×2 m plots, sulfachloropyridazine and oxytetracycline were detected at 703 and 71 µg L^{-1}, and their mass losses were 0.42% and 0.07%, respectively (Kay et al., 2005c). One or more antibiotics were found in about 50% of 139 stream water samples obtained from across the United States (Kolpin et al., 2002). Ingerslev et al. (2001) reported that tylosin and oxytetracycline are considered moderately persistent in surface water systems, whereas olaquindox is more biodegradable. Ash et al. (2002) studied 16 rivers in the United States and found that more than 40% of bacteria were resistant to antibiotics.

Antibiotics can be persistent in animal manure and soil although they are gradually decomposed by physical, chemical, and biological reactions. The half-life of chlortetracycline in manure is reportedly more than 30 days (Gavalchin and Katz, 1994; Montforts et al., 1999). The decomposition rate of antibiotics may be affected by the antibiotic properties and environmental conditions. The major antibiotic properties include water solubility, photosensitivity, biodegradation, acid-base dissociation constant (pK_a), and sorption behavior. The environmental conditions include temperature, redox conditions, pH, and bacterial activity. The residual chlortetracycline in soil after 30 days was 44% at 30°C, 88% at 20°C, and nearly 100% at 4°C (Gavalchin and Katz, 1994). The half-life of chlortetracycline in field soils was 25-34 days (Halling-Sorensen et al., 2005) and 21-24 days (Carlson and Mabury, 2006). About 40% of the tylosin remained in soil after 30 days at 4°C (Gavalchin and Katz, 1994). The half-life of tylosin was less than 8 days under aerobic soil conditions (Ingerslev and Halling-Sorensen, 2001; Teeter and Meyerhoff, 2003), 49-67 days in field soils (Halling-Sorensen et al., 2005), and 5-6 days in a sandy loam soil (Carlson and Mabury, 2006). Antibiotics can accumulate in soil with the continuous application of animal manure to agricultural land. Such accumulations may adversely affect soil ecosystems. Soil microbes that are resistant to tylosin and tetracyclines have been reported in soil amended with animal manures (Halling-Sorensen et al., 2002; Onan and LaPara, 2003; Sengelov et al., 2003; Halling-Sorensen et al., 2005).

Chlortetracycline, the first tetracycline antibiotic, was discovered in 1948. The antibiotic has a broad spectrum of antimicrobial activity by preventing the binding of aminoacyl transfer to DNA and inhibiting protein synthesis, and has been used for diseases treatment and growth promotion. About 2,700 Mg of CTC is estimated to be used for cattle, swine, and poultry for nontherapeutic purposes every year (Mellon et al., 2000). Ingested tetracyclines were rapidly excreted via feces and urine, and significant amounts of the active ingredient are found in excrement within two days of ingestion (Winckler and Grafe, 2001). Halling-Sorensen et al. (2002) estimated that 50-80% of treated tetracyclines can be found in the urine as parent compound, and Montforts et al. (1999) reported that up to 75% of an oral dosage of CTC can be excreted as the parent compound by young bulls. Chlortetracycline was present at concentrations of up to 2.7 mg L^{-1} in liquid manure samples (Höper et al., 2002), 7.7 mg L^{-1} in swine manure (Kumar et al., 2004), and 0.03 mg kg^{-1} in soils applied with liquid manure (Hamscher et al., 2000). Campagnolo et al. (2002) reported that CTC was detected in all seven swine-waste storage lagoon samples at concentrations of 68-1,000 μg L^{-1}. Hamscher et al. (2002) concluded that tetracyclines accumulate in soil via repeated fertilizations with liquid manure. Sengelov et al. (2003) suggested that increased bacterial tetracycline resistance in soil may be caused by swine manure slurry amendment to the soil by showing that higher amounts of the slurry treatment resulted in greater levels of resistance. About 2% of the initial CTC concentration was detected at 25-35 cm depth in a sandy loam soil (Carlson and Mabury, 2006). Chlortetracycline was found in 2.4% of 84 stream water samples collected from the United States at concentrations of up to 0.69 μg L^{-1} (Kolpin et al., 2002), and it was measured in a concentration of 0.15 μg L^{-1} in water sample from Snake Creek, GA (Lindsey et al., 2001). Yang et al. (2004) analyzed water samples from five sites on the Poudre River in Colorado, and reported that CTC concentration increased with inputs from agricultural lands. When tested with aerobic sludge bacteria, the toxicity (EC_{50}) value of chlortetracycline was 0.03 mg L^{-1} (Halling-Sorensen et al., 2002). Kumar et al. (2005a) reported that CTC concentrations in three crops grown in manure-amended soil were 2-17 μg kg^{-1} fresh weight and these concentrations increased with increasing CTC amount present in the manure.

Chlortetracycline exhibits three acidity constants: pK_1, pK_2, and pK_3 (Table 3.1). The first deprotonation has been considered to occur at C-3 hydroxyl group, resulting in the zwitterionic form of the neutral compound (CTC^{-+0}). There has been a great deal of discussion about assignment of the second and third macroscopic acidity constant to the two relevant functional groups; C-4 dimethylamino group and C-12 hydroxyl group. Schneider (2001) estimated that about 80% occurs at C-12 (CTC^{-+-}) and 20% at C-4 (CTC^{-00}) based on Martin's (1985) microscopic acidity constants. Additionally, CTC molecules are not flat but have two conformations (Fig. 3.3); extended conformation (A conformation) and twisted conformation (B conformation) (Mitscher et al., 1972; Gulbis and Everett, Jr., 1976; Lambs et al., 1988; Wessels et al., 1998; Schneider, 2001). At neutral to acidic pH, the dimethylamino group lies above the ring system due to the steric crowding between the protonated nitrogen of the dimethylamino group, amino group at C-2, and hydroxyl group at C-12. As a result, the primary conformation is the twisted conformation. At basic pH, the extended conformation is favored because of strong hydrogen bonding between the deprotonated dimethylamino group at C-4 and hydroxyl group at C-12. Since a change in pH results in an alteration of conformations and a modification of the strength of intramolecular hydrogen bonding, pK_2 and pK_3 can differ by one unit depending on the detection technique (absorption, circular dichroism, and fluorescence) and the direction of titration (high to low pH or low to high pH) (Schneider, 2001).

Tetracyclines interact with various multivalent cations including Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, and Fe^{3+} (Albert, 1953; Albert and Rees, 1956; Doluisio and Martin, 1963; Martin, 1979; Sachan and Gupta, 1980; Lambs et al., 1985; Martin, 1985; Wessels et al., 1998; Schneider, 2001; Halling-Sorensen et al., 2002; Loke et al., 2002; Christian et al., 2003). Stability constants, as log K, for metal cation complex formation, $HL^- + M^{2+} = MHL^+$, are 9.4 for Fe^{3+}, 7.2 for Al^{3+}, 5.8 for Ni^{2+} (Albert and Rees, 1956), 7.6 for Cu^{2+}, 5.7 for Fe^{2+}, 4.8 for Co^{2+}, 4.5 for Zn^{2+}, 4.3 for Mn^{2+} (Albert, 1953), 3.6 for Pb^{2+}, and 3.1 for Cd^{2+} (Sachan and Gupta, 1980), 3.2 for Mg^{2+}, and 2.9 for Ca^{2+} (Martin, 1979). Metal ions bind to C-11-C-12 β-diketone system, while the dimethylamino group at C-4 is not involved in the binding (Martin, 1985). Calcium forms stable chelates with CTC, but no complexation occurs when the C-11-C-12 β-diketone system is destroyed (Doluisio and Martin, 1963). Lambs et al. (1985) reported that the major Ca-CTC complex was $Ca(H\text{-}CTC^-)_2$ with the formation constant of log K = 7.8 for $2\ H\text{-}CTC^- + Ca^{2+} = Ca(H\text{-}CTC^-)_2$. Wessels et al. (1998) suggested that chelation of Ca^{2+} at C-11-C-12 β-diketone system induces a deprotonation of the dimethylamino nitrogen at C-4 which occurs in the presence of a 164-fold excess of Ca^{2+} above pH 7.7. An approximately 100-fold excess of Ca^{2+} is needed at pH 7.0, whereas 2-fold is sufficient at pH 8.5 for half of the tetracyclines to be bound (Schneider, 2001).

Chlortetracycline adsorbed more strongly to montmorillonite than to illite or kaolinite, and the CTC-montmorillonite complex gave an expansion of the d-spacing to 1.79 nm (Pinck et al., 1961). Porubcan et al. (1978) suggested that tetracycline can adsorb to montmorillonite by a cation exchange mechanism at low pH values by showing an increase in interlayer spacing from 0.97 nm to 1.64 nm. Additionally, the IR spectrum for sorbed tetracycline to montmorillonite did not show significant shifts, suggesting no covalent interaction between tetracycline and montmorillonite. They also showed that the IR spectrum of calcium saturated montmorillonite interacted with tetracycline at pH 5.0 corresponded to the spectrum of tetracycline-calcium complex, indicating complexation between divalent exchangeable cation and tetracycline. Sithole and Guy (1987a) showed tetracycline sorption to montmorillonite decreased with increasing ionic strength and pH. They also suggested that tetracycline interacts with divalent cations adsorbed onto the clay surface and with Al ions exposed at the edges of the clay. Figueroa et al. (2004) suggested that tetracyclines sorbs to clays by cation exchange plus surface complexation of zwitterion forms that is accompanied by proton uptake. They also showed less oxytetracycline sorption with increasing salt concentration. Kulshrestha et al. (2004) proposed that cation exchange is the dominant sorption mechanism of oxytetracycline to montmorillonite at lower pH and hydrophobic interaction is predominant at pH 5. They reported that the addition of humic acid at a concentration of 10 mg L^{-1} decreased oxytetracycline sorption to Na-montmorillonite at pH 11. Jones et al. (2005) proposed that soil clay content, effective cation exchange capacity, and DCB-extractable iron oxide content are the most important soil properties for oxytetracycline sorption by 30 soil samples collected from Alfisols, Inceptisols, Spodosols, Ultisols, and Vertisols; while soil organic matter may influence OTC sorption only in soils with as high as 90 g kg^{-1} organic carbon. Sassman and Lee (2005) reported that sorption of three tetracyclines to eight soils decreased with increasing pH and suggested that cation exchange is the primary sorption process.

Tylosin is a widely used macrolide antibiotic that is primarily active against Gram-positive bacteria, and its action mechanism is the inhibition of the protein synthesis in the bacteria. Tylosin is one of the most extensively used feed additives in swine production. About 590 Mg of TYL are estimated to be used for cattle and swine each year (Mellon et al., 2000). About 78% of administered TYL may be excreted as the parent compound through the urine and feces (Vaclavik et al., 2004), and swine manure has been reported to contain as high as 4.0 mg L^{-1} (Kumar et al., 2004). Onan and LaPara (2003) reported that the proportion of tylosin-resistant bacteria in soils affected by antibiotic use was significantly higher than soils unaffected by antibiotic use. Tylosin was detected in 13.5% of 104 stream samples, with concentrations as high as 0.28 μg L^{-1} (Kolpin et al., 2002). The EC_{50} of tylosin was 0.034 mg L^{-1} for freshwater cyanobacteria (Halling-Sorensen, 2000) and 0.95 mg L^{-1} for alga (De Liguoro et al., 2003).

Much more TYL could be adsorbed by smectites than by illite and kaolinite (Bewick, 1979). Rabolle and Spliid (2000) suggested that TYL sorption might correlate with the soil clay content. Loke et al. (2002) reported that TYL sorption to manure is mainly caused by hydrophobic interaction, because the organic carbon normalized sorption coefficient (K_{oc}) is correlated with the octanol-water partition coefficient. The distribution coefficients (K_d) values of tylosin were 8-11 L kg^{-1} for sandy soils with pH in $CaCl_2$ of 5.6-6.1 and 62-128 L kg^{-1} for sandy loam soils with pH of 5.6-6.3 at an initial concentration of 5 mg L^{-1} (Rabolle and Spliid, 2000), and 240 L kg^{-1} for swine manure at an initial concentration of 200 mg L^{-1} (Loke et al., 2002). Clay et al. (2005) reported that Freundlich coefficients (K_F) were 1,260-1,510 for silty clay loam soils with pH of 6.1-7.1, and desorption over a four-day period was less than 0.2% of the added TYL. Kolz et al. (2005) suggested that tylosin mobility might be enhanced through complexation with colloidal manure materials.

Sulfamethazine, one of the most widely used sulfonamides, was introduced in 1942 and has been mainly administrated to swine to control atrophic rhinitis and other infections. Sulfonamides are generally active against both Gram-positive and Gram-negative bacteria by competing with para-aminobenzoic acid used in the synthesis of folic acid that is necessary for DNA synthesis. About 360 Mg of sulfamethazine are estimated to be used annually in swine and cattle production (Mellon et al., 2000). Sulfonamides including SMT are not readily biodegradable (Ingerslev and Halling-Sorensen, 2000). Campagnolo et al. (2002) reported that SMT was detected in all their test swine-waste storage lagoon samples at concentrations of 2.5-400 μg L^{-1}. Maximum concentration of SMT detected was 40 mg L^{-1} in liquid manure (Langhammer et al., 1988). Christian et al. (2003) reported that SMT was found at levels around 1 mg kg^{-1} in swine liquid manure, 15 μg kg^{-1} in soil fertilized with liquid manure 7 months after the application, and up to 7 ng L^{-1} in 6 water samples collected from creeks. Höper et al. (2002) reported that SMT was found at concentrations up to 0.011 mg kg^{-1} in soil fertilized with liquid manure. Ground water samples collected in an agricultural area had SMT at a level of 0.16 μg L^{-1} (Hirsch et al., 1999). About 27% of applied SMT can be released by runoff from grassland (Kreuzig et al., 2005). Burkhardt et al. (2005) found that SMT in runoff from manured plots was 6.3% of input SMT concentration after a 3-d contact time. Sulfamethazine was detected in 4.8% of 104 stream samples and its maximum concentration was 0.22 μg L^{-1} (Kolpin et al., 2002). Yang and Carlson (2004) reported that SMT was found at a level of 0.22 μg L^{-1} from Sheldon lake, CO, and Yang et al. (2004) reported that SMT was detected at sites where agricultural land use predominates among five sites along the Poudre River in Colorado.

Sakurai and Ishimitsu (1980) reported that pK_1 and pK_2 of SMT ranged from 2.49 to 2.85 and from 7.42 to 7.72, respectively, at 0.1 M ionic strength and 25°C, depending on the detection method. They also showed that the neutral form (SMT^0) dominated over the zwitterion form ($SMT^{\pm}$) by $10^{2.8}$. Distribution coefficients of SMT were 1.2-3.1 L kg^{-1} for loamy sands, 2.0 L kg^{-1} for a loam, 1.0 L kg^{-1} for a silt loam (Langhammer, 1989), and 0.6 L kg^{-1} for a clay loam (Thurman and Lindsey, 2000). Boxall et al. (2002) reported that linear sorption coefficients of sulfachlorophyridazine, a sulfonamide antibiotic, were 1.8 L kg^{-1} for a clay loam and 0.9 L kg^{-1} for a sandy loam, and the values decreased with the increase in the pH. Thiele-Bruhn et al. (2004) reported that K_d for silt loam from an unfertilized Chernozem with pH in $CaCl_2$ of 7.0 was 2.4 L kg^{-1} at the spiking concentration of 10 mg kg^{-1}. They suggested that sulfonamides bind to functional groups of soil organic matter, especially phenolic and carboxylic groups, N-heterocyclic compound, and lignin decomposition products through hydrogen bonds and van der Waals interaction. Gao and Pedersen (2005) found that SMT adsorption on montmorillonite and kaolinite exhibited pronounced pH dependence and adsorption of neutral SMT (SMT^0) to montmorillonite was insensitive to pH, ionic strength, and type of exchangeable cation. They suggested that neutral SMT (SMT^0) interacted primarily with external montmorillonite surfaces by showing no increase in interlayer spacing by the adsorption.

Sorption and mobility of an antibiotic are influenced by properties of the antibiotic and soil. Antibiotic properties include pK_a, water solubility, K_{ow}, molecular weight, volatility, chemical structure, and degradation rate. Whereas, soil properties include pH, organic matter content, type and quantity of clay, ionic strength, background electrolyte type, and soil texture and structure. The fate and transport of antibiotic in soil are also influenced by other factors including preferential flow, climate, moisture regime, and application method and timing. For instance, Kay et al. (2005a) suggested that soil tillage can significantly reduce antibiotic mobility in soil by decreasing connectivity of macropores.

Most of studies have focused on fate and transport of agricultural antibiotics themselves without considering the influences of concomitant animal manure application. Land application of animal manure can change the soil properties, thus affecting behavior and transport of antibiotics in soil. For example, little is known about the effect of DOC from animal manure on sorption and mobility of antibiotics although land application of animal waste can increase DOC level in soil solution. In order to further our ability to predict the fate and transport of veterinary antibiotics in soil and accurately assess risk of the antibiotic contamination in soil and sensitive aquatic environments, it is necessary to understand the influence of soil chemical properties on the fate and mobility of antibiotics in soil and manure-amended soil.

MATERIALS AND METHODS

1. Preparation of clays and soil samples

Montmorillonite and kaolinite were chosen as model clays because montmorillonite has a high exchange capacity and a high surface area, while kaolinite exhibits a low exchange capacity and a low surface area. Furthermore, surface charge characteristics of montmorillonite are not greatly influenced by pH due to permanent charge by isomorphic substitution, while surface characteristics of kaolinite are strongly influenced by pH due to the protonation and deprotonation of surface hydroxyl groups (pH-dependent charge). The montmorillonite was obtained as commercial bentonite available from American Colloidal Co. (Chicago, IL) and prepared for study following the procedure of Porubcan et al. (1978). About 60 g of the clay was placed in 1 L of distilled water and mixed for approximately 45 min. The < 2 μm size fraction was isolated by sedimentation, and then suspended in 1 M $NaNO_3$. The supernatant was decanted after centrifugation and 0.01 M $NaNO_3$ was added to the clay. The suspension was centrifuged after shaking. The 0.01 M $NaNO_3$ washing procedure was repeated several times. Kaolinite (KGa-1b) was obtained from Source Clays Repository of The Clay Minerals Society, and prepared for batch sorption studies following the procedure of Mattigod et al. (1985). A distilled water suspension of kaolinite (67 g L^{-1}) was dispersed in a blender for approximately 45 min. The suspension was then adjusted to pH 9.5 with 0.1 M NaOH, and the 0.2-2.0 μm size fraction was isolated by sedimentation. This separate was then suspended in 1 M $NaNO_3$ adjusted to pH 3 with HNO_3. The supernatant was decanted after centrifugation and 0.01 M $NaNO_3$ was added to the clay.

The suspension was rinsed with 0.01 M $NaNO_3$ several times, following the washing procedure used for montmorillonite, until the pH of the supernatant was approximately 5.5. Calcium saturated clays were prepared with 0.01 M $Ca(NO_3)_2$ as the exchanging solution. All clays were stored as concentrated suspensions.

Soil samples were collected from a no-till field located at the University of Tennessee Plant Science Farm in Knoxville, TN. The soils are classified as Captina sandy loam (fine-silty, siliceous, active, mesic Typic Fragiudults) and Etowah clay loam (fine-loamy, siliceous, semiactive, thermic Typic Paleudults). The clay fractions consist of hydroxyl-interlayered vermiculite, vermiculite, kaolinite, mica, and quartz for Etowah, and kaolinite, chlorite, and mica for Captina (Levy and Francis, 1976; Ketelle and Huff, 1984). Two depth samples (surface [0-to-15-cm] and subsurface [30-to-45-cm]) were obtained from each site. The soils were air-dried and passed through a 2-mm sieve prior to use in the batch and column experiments.

2. Characterization of clays and soils

Selected chemical and physical properties of clays and soils are shown in Table 3.2. Soil texture was determined using the pipette method (Gee and Or, 2002), and particle density was measured by the liquid displacement method (Flint and Flint, 2002). Surface area was determined by the ethylene glycol monoethyl ether method (Pennell, 2002). Soil pH was measured by mixing deionized water with soil at a ratio of 1:1 (Thomas, 1996). Total carbon (C) was analyzed by the dynamic flash combustion method using a soil CN analyzer (FlashEA 1112 Elemental Analyzer, Thermo Finnigan Italia S.p.A., Rodano, Italy). Dissolved organic carbon was determined by extraction with 0.01 M $Ca(NO_3)_2$ at a ratio of 1:10 for 24 h. Cation exchange capacity (CEC) was measured using a 1 M ammonium acetate procedure (Sumner and Miller, 1996).

3. Dissolved organic carbon

Dissolved organic carbon (DOC) was obtained from dairy manure following the procedure of Suba and Essington (1999). Dairy manure was obtained from the University of Tennessee Knoxville Experiment Station. The extraction of DOC was carried out by adding 0.01 M $Ca(NO_3)_2$ at a ratio of 1:20 solid:solution and shaking for 24 hours. The sample was centrifuged at 4800 × g for 1 hr and filtered sequentially through a 0.8 μm glass filter, a 0.45 μm membrane filter, and a 0.2 μm membrane filter to isolate the DOC and minimize microbial activity. The filtered extract was stabilized with 5 mg L^{-1} $HgCl_2$ and stored at 4°C in amber glass bottles. The total carbon content of the DOC extracts was analyzed by a total organic carbon analyzer (Shimadzu TOC-V_{CPH}, Shimadzu Scientific Instruments, Inc., Columbia, MD). To determine the relative size of the DOC molecules and the humic or fulvic nature of the DOC, the spectrometric absorbance ratio (E_4/E_6) was obtained by measuring the absorbance at 465 nm and 665 nm (Swift, 1996). Total acidity and carboxyl acidity (strong acidic groups) were determined by indirect titration method using barium hydroxide and calcium acetate, respectively (Swift, 1996). For total acidity, 20 ml of 0.1 M $Ba(OH)_2$ was mixed with 20 ml of DOC solution and shake for 24 h. The solution was filtered through 0.45 μm membrane filter and titrated with 0.02 M HCl to pH 8.4. For carboxyl acidity, 10 ml of 0.5 M $Ca(OAc)_2$ was mixed with 20 ml of DOC solution and shake for 24 h. The solution was filtered through 0.45 μm membrane filter and titrated with 0.1 M NaOH to pH 9.8.

4. Batch equilibration experiments

Preliminary evaluations indicated that sorption equilibrium is attained in 48 h for CTC, and 24 h for TYL and SMT. To investigate the pH effect on antibiotic sorption to clay, the pH of montmorillonite and kaolinite suspensions was adjusted as needed with the addition of small volumes of 0.1 M HNO_3 or 0.1 M NaOH. Since CTC readily and irreversibly degrades to isochlortetracycline in alkaline solutions (Kühne et al., 2000; Halling-Sorensen et al., 2002), the pH effect experiments for CTC were conducted between pH 4 and 7. Because TYL is stable at pH 4-9 and desmycosin is formed when pH is less than 4 (Merck Index, 2001), pH effect on TYL sorption was examined between pH 4-9. Clay loadings for the CTC batch study were 0.45 g montmorillonite L^{-1} and 3.6 g kaolinite L^{-1}, 0.3 g montmorillonite L^{-1} and 6.0 g kaolinite L^{-1} for TYL, and 6.5 g montmorillonite L^{-1} and 20 g kaolinite L^{-1} for SMT. The initial antibiotic concentrations were 0.072 mM for CTC, 0.038 mM for TYL, and 0.005 mM for SMT. The antibiotic solution was freshly prepared every day. The duplicated samples were wrapped in foil to eliminate photodegradation and equilibrated by shaking at ambient temperature (20°C to 22°C). After sorption equilibrium was attained, antibiotic in solution was separated from the solid phase by centrifugation at 4800 × g for 10 min. A 2 mL aliquot of the equilibrium solution was filtered through a 0.45 μm membrane filter. The equilibrium concentration of antibiotics in solution was analyzed using a high performance liquid chromatography (HPLC) system coupled with UV detection (Hewlett-Packard series 1100, Hewlett-Packard, Palo Alto, CA). The HPLC analysis conditions are shown in Table 3.3. The amount of antibiotic sorbed was calculated from the difference between the applied amount and the amount in solution at equilibrium.

To determine ionic strength effects, adsorption isotherms were employed. Montmorillonite or kaolinite was added to antibiotic solution containing five initial concentrations ranging from 0.003 to 0.087 mM for CTC, from 0.0008 to 0.059 mM for TYL, and from 0.0006 to 0.016 mM for SMT. These concentration ranges are consistent with previous sorption isotherm experiments which were conducted at initial concentrations of 0.008-0.23 mM (Figueroa et al., 2004) and 0.43-4.3 mM (Kulshrestha et al., 2004) for oxytetracycline, 0.0003-0.0055 mM (Rabolle and Spliid, 2000), 0.094-1.876 mM (Loke et al., 2002), and 0.025-0.23 mM (Clay et al., 2005) for TYL, and 0.0014-0.14 mM (Thiele-Bruhn et al., 2004) and 0.000036-0.36 mM (Gao and Pedersen, 2005) for SMT. The ionic strength was adjusted to 0.005, 0.01, and 0.05 M using $NaNO_3$. The average ionic strength of soils in the temperate region is about 0.011 (Harter and Naidu, 2001), and the ionic strength of soil solution can be increased by application of animal manure. At the end of equilibration, antibiotic concentration in solution was determined by the same procedure as described above for the pH effect experiments. Solution pH values were measured at the end of equilibration and the values were 4.4 (montmorillonite) and 5.3 (kaolinite) for CTC, 5.6 (montmorillonite) and 5.7 (kaolinite) for TYL, and 4.9 (montmorillonite) and 5.7 (kaolinite) for SMT.

Calcium saturated clays and 0.01 M $Ca(NO_3)_2$ were used to study the effect of background electrolyte cation type. In addition to the two clays, antibiotic adsorption by four soil samples was conducted using a soil loading of 17 g soil L^{-1} for CTC, 50 g soil L^{-1} for TYL, and 500 g soil L^{-1} for SMT. Sorption isotherms of SMT for soils were developed at initial concentrations of 0.001 to 0.018 mM, corresponding to 0.6 to 10 µg g^{-1} soil. Thiele-Bruhn et al. (2004) conducted sorption isotherm experiments of sulfonamides for soils at initial concentrations of 1-100 µg g^{-1} soil based on calculation of the predicted environmental concentrations of sulfonamides. Mercuric chloride was added to the soil sorption systems to minimize microbial degradation at a concentration of 500 mg kg^{-1} soil (Wolf et al., 1989). Solution pH values were measured at the end of equilibration and the values were 4.3 (montmorillonite), 5.1 (kaolinite), 5.2 (CL-S), 5.2 (CL-SS), 5.2 (SL-S), and 5.4 (SL-SS) for CTC, 5.0 (montmorillonite), 5.2 (kaolinite), 5.3 (CL-S), 5.4 (CL-SS), 5.4 (SL-S), and 5.6 (SL-SS) for TYL, and 4.2 (montmorillonite), 5.2 (kaolinite), 5.2 (CL-S), 5.3 (CL-SS), 5.4 (SL-S), and 5.5 (SL-SS) for SMT. For sodium nitrate system of soils, pH values were 5.7 (CL-S), 5.8 (CL-SS), 5.8 (SL-SS), and 5.8 (SL-SS) for CTC, 5.8 (CL-S), 5.9 (CL-SS), 6.0 (SL-S), and 6.0 (SL-SS) for TYL, and 5.5 (CL-S), 5.6 (CL-SS), 5.7 (SL-S), and 5.8 (SL-SS) for SMT.

The effect of DOC on antibiotic sorption was examined by adding DOC solution extracted from dairy manure to the antibiotic solutions and adding the mixture to soils or calcium saturated clays. The DOC concentrations in each system were 21 and 63 mg L^{-1}, which is relatively low level compared with previous studies for DOC effect on sorption and mobility of organic contaminants: 383-983 mg L^{-1} (Baskaran et al., 1996), 100-920 mg L^{-1} (Suba and Essington, 1999), 60-150 mg L^{-1} (Seol and Lee, 2000), and 70 mg L^{-1} (Huang and Lee, 2001). The DOC concentrations of soils used in this study were 7.1-9.7 mg L^{-1} for surface soil and 2.9-4.2 mg L^{-1} for subsurface soil at an extraction ratio of 1:10 with 0.01 M calcium nitrate (Table 3.2). Dalva and Moore (1991) reported that DOC concentrations of soil leachates collected in zero tension lysimeters installed at forest plots were from 15 to 69 mg L^{-1} for surface soil and from 3 to 10 mg L^{-1} for subsurface soil. To minimize both the pH effect on the antibiotic sorption and CTC degradation with alkali, pH of DOC solution was adjusted to 5.5 with the addition of 0.1 M HNO_3 and the solution was filtered through a 0.2 μm membrane filter. Solution pH values were measured at the end of equilibration and the values were 4.7 (montmorillonite), 5.6 (kaolinite), 5.3 (CL-S), 5.4 (CL-SS), 5.3 (SL-S), and 5.4 (SL-SS) for CTC, 5.6 (montmorillonite), 5.3 (kaolinite), 5.3 (CL-S), 5.5 (CL-SS), 5.5 (SL-S), and 5.6 (SL-SS) for TYL, and 4.2 (montmorillonite), 5.2 (CL-S), 5.3 (CL-SS), 5.4 (SL-S), and 5.5 (SL-SS) for SMT. The DOC-free 0.01 M $Ca(NO_3)_2$ was used as a reference.

5. Surface complexation model and sorption isotherm model

A surface complexation model was used to predict antibiotic sorption to clay, based on batch sorption data under various pH conditions. Clay minerals contain permanent charge surface functional groups (X) arising from isomorphic substitution of lattice cations by lower valence cations and variable charge surface functional groups (≡ SOH) on the edge surface due to ionization of surface hydroxyl groups as a function of the solution pH. Antibiotic interactions with clay minerals may occur through electrostatic ion exchange and ligand complexation interactions. An excess of aqueous cations are held in close proximity to the clay surface by electrostatic attraction to maintain charge neutrality, and cation exchange reaction can explain antibiotic sorption to permanently charged surface sites.

$$\text{NaX} + \text{Antibiotic}^{+} = \text{Antibiotic-X} + \text{Na}^{+} \qquad [3.1]$$

The properties of the edge surface of clay minerals are similar to those on oxide surfaces which can undergo protonation ($\equiv SOH_2^{+}$) and deprotonation ($\equiv SO^{-}$) reactions (Sposito, 1984). Surface complexation reaction can occur between antibiotics and the amphoteric ≡ SOH sites.

$$\equiv \text{SOH} + \text{Antibiotic}^{+} = \equiv \text{SO-Antibiotic} + \text{H}^{+} \qquad [3.2]$$

A number of surface complexation models have been proposed to explain and predict the binding of protons, cations, and anions to mineral surfaces. The diffuse double layer model (DDLM) proposed by Stumm et al. (1970) was used to describe antibiotic sorption by montmorillonite and kaolinite in this study because this model requires fewer adjustable parameters than other comparable models. Dzombak and Morel (1990) reviewed the DDLM, in which all ions are sorbed as coordination complexes within the surface layer and the nonspecifically sorbed ions present in the diffuse layer. The Gouy-Chapman theory is assumed to describe the distribution of counter ions in the diffuse layer. The surface charge density (σ) is related to the potential at the surface (Ψ) by

$$\sigma = 0.1174 \times C^{1/2} \times \sinh(Z \times \Psi \times 19.46) \qquad [3.3]$$

at 25°C, where C is the molar electrolyte concentration and Z is the valence of a symmetrical electrolyte. Fitting of conditional intrinsic equilibrium constants for cation exchange and surface complexation reactions was performed with FITEQL 4.0 (Herbelin and Westall, 1999). The model parameters were optimized for the experimental data obtained at an ionic strength of 0.01 M $NaNO_3$.

All variable charge sites on montmorillonite surfaces are collectively referred to as $\equiv$ SOH, and the intrinsic equilibrium constants of the surface protolysis reactions are listed in Table 3.4. The surface charge of kaolinite edge sites was assumed to be controlled by $\equiv$ SiOH and $\equiv$ AlOH sites and the edges was assumed to be composed of roughly equal proportions of $\equiv$ SiOH and $\equiv$ AlOH sites (Ward and Brady, 1998; Sarkar et al., 2000). The intrinsic acidity constants of the surface protolysis reactions (as log K^{int}) are listed in Table 3.4.

Sorption isotherms were obtained from batch equilibration studies to examine effect of ionic strength, background electrolyte cation type, and manure DOC concentration on antibiotic sorption to clays and soils. In our study, the shape of sorption isotherms of CTC and TYL was an L-curve. The sorption of SMT to clays showed an S-curve isotherm, but an L-curve for soils. The L-type sorption data in our study were fit to Freundlich or Langmuir isotherms through a nonlinear curve-fitting procedure of SAS (ver. 9.1, SAS, Cary, NC) program with Gauss-Newton iteration method. The Freundlich isotherm is given by

$$q = K_F \times Ceq^N \qquad [3.4]$$

where q is equilibrium mass of sorbed antibiotic per unit mass of adsorbent, K_F is the Freundlich coefficient, Ceq is antibiotic mass in the aqueous phase at equilibrium per unit volume, and N is a linearity parameter which is constrained to lie between 0 and 1. The

Freundlich coefficient is equal to q when Ceq is unity, and N is a measure of the heterogeneity of surface sorption sites.

The Langmuir isotherm is given by

$$q = K_L \times b \times Ceq / (1 + K_L \times Ceq) \tag{3.5}$$

where K_L is the Langmuir coefficient, which is a measure of the intensity of the adsorption isotherm, and b is an adjustable parameter representing the adsorption maxima as Ceq becomes infinitely large.

The S-type isotherms, as for sulfamethazine retention on clays, occur less frequently than the other types of isotherms. None of the isotherm equations tested (Freundlich, Langmuir, Two-site Langmuir, Modified Langmuir, Linear, or combination of two models) could adequately fit the SMT sorption data on clays. Several researchers have used a Freundlich model with N greater than one to describe S-class isotherms (Hinz, 2001; Pusino et al., 2003). However, the heterogeneity coefficient, N, should be less than unity.

A model based on cooperative adsorption proposed by Homenauth and McBride (1994) was used to describe S-type isotherms of SMT on clays. They developed the model to describe S-type adsorption isotherms of aniline on layer silicate clays and an organic soil. Two simultaneous adsorption reactions were considered; adsorption of monomers and "clusters" on sorbents.

$$\mathrm{S} + \mathrm{A} = \mathrm{S\text{-}A} \tag{3.6}$$

$$\mathrm{S} + n\mathrm{A} = \mathrm{S\text{-}A}_n \tag{3.7}$$

where S is surface sites, A is adsorbate, and n is average number of molecules in adsorbing clusters and reflects the degree of cooperativity. The equilibrium constants, K_1 and K_n, for these reactions are

$$K_1 = (\mathrm{S\text{-}A})/((\mathrm{S}) \times (\mathrm{A})) \tag{3.8}$$

$$K_n = (\mathrm{S\text{-}A}_n)/((\mathrm{S}) \times (\mathrm{A})^n) \tag{3.9}$$

where (A) is the activity of free, unbound adsorbate at equilibrium. For dilute solutions, (A) corresponds to Ceq for other sorption isotherm models. It is assumed that the activities of surface species, (S), (S-A), and (S-A_n), are proportional to mole fractions. Thus activity ratios of surface species in Eq. 3.8 and Eq. 3.9 are given by

$$(\mathrm{S\text{-}A})/(\mathrm{S}) = \varphi_{\mathrm{A}}/(1-\varphi_{\mathrm{T}}) = K_1 \times (\mathrm{A}) \qquad [3.10]$$

$$(\mathrm{S\text{-}A}_n)/(\mathrm{S}) = \varphi_{\mathrm{A}n}/(1-\varphi_{\mathrm{T}}) = K_n \times (\mathrm{A})^n \qquad [3.11]$$

where φ_{A} and $\varphi_{\mathrm{A}n}$ are the mole fraction of total adsorption sites for monomers and clusters, respectively, and φ_{T} is the sum of φ_{A} and $\varphi_{\mathrm{A}n}$. From Eq. 3.10 and Eq. 3.11, φ_{T} is give by

$$\varphi_{\mathrm{T}} = \varphi_{\mathrm{A}} + \varphi_{\mathrm{A}n} = K_1 \times (\mathrm{A}) \times (1-\varphi_{\mathrm{T}}) + K_n \times (\mathrm{A})^n \times (1-\varphi_{\mathrm{T}}) \qquad [3.12]$$

$$\varphi_{\mathrm{T}} = (K_1 \times (\mathrm{A}) + K_n \times (\mathrm{A})^n) / (1 + K_1 \times (\mathrm{A}) + K_n \times (\mathrm{A})^n) \qquad [3.13]$$

Adsorption isotherms are expressed in terms of how much adsorbate is adsorbed to the sorbent, q. In this model, n adsorbate molecules are adsorbed to the sorbent for each adsorbed cluster. For a given total adsorption sites, m, the adsorbed quantity, Q_{A}, is given by

$$\begin{aligned} Q_{\mathrm{A}} &= m \times (\varphi_{\mathrm{A}} + n \times \varphi_{\mathrm{A}n}) \\ &= m \times (K_1 \times (\mathrm{A}) \times (1-\varphi_{\mathrm{T}}) + n \times K_n \times (\mathrm{A})^n \times (1-\varphi_{\mathrm{T}})) \\ &= m \times (K_1 \times (\mathrm{A}) + n \times K_n \times (\mathrm{A})^n) \times (1-\varphi_{\mathrm{T}}) \\ &= m \times (K_1 \times (\mathrm{A}) + n \times K_n \times (\mathrm{A})^n) / (1 + K_1 \times (\mathrm{A}) + K_n \times (\mathrm{A})^n) \qquad [3.14] \end{aligned}$$

The estimated parameters m, K_1, K_n, and n were obtained by fitting SMT sorption data to Eq. 3.14 through a nonlinear curve-fitting procedure of SAS program with Gauss-Newton iteration method.

6. Column transport study (DOC effect on antibiotics mobility)

Column miscible displacement experiments were conducted on columns packed with Captina sandy loam soil (surface and subsurface soil). The soil passed through 2 mm sieve was packed in stainless steel columns (44 mm diameter) to a length of 0.05 m for CTC and 0.10 m for TYL and SMT. Column conditions of miscible displacement experiment for each antibiotic are listed in Table 3.5. The columns were saturated from the bottom with a background solution of 0.01 M $\mathrm{Ca(NO_3)_2}$. More than 10 pore volumes of background solution were leached before applying antibiotic solution to establish a constant water head of 1 cm on top of the soil column. The application of background solution was then stopped, letting the ponding solution infiltrate. A pulse of antibiotic solution in 0.01 M $CaCl_2$ was applied to the top of the column. The background solution was then applied again to the soil column shortly after the input solution infiltrated the soil surface. Effluent samples were collected at intervals of about 0.03 pore volume using a fraction collector at the bottom of the column. Breakthrough curves (BTCs) for antibiotic were obtained by determining the concentration of antibiotics in the effluents using an HPLC. Chloride (Cl^-) breakthrough was also obtained at the same time using a digital chloridometer (Labconco Corporation, Kansas, MO). To determine the DOC effect on fate and mobility of antibiotics, the input solution applied to the soil columns contained the antibiotic and additionally DOC from dairy manure at a concentration of 21 or 63 mg L^{-1}. To minimize both pH effect and CTC degradation at high pH, the pH of DOC solution was adjusted to 5.5 with the addition of 0.1 M HNO_3 and the solution was filtered through a 0.2 μm membrane filter prior to mixing with antibiotics.

7. Column transport parameter estimation

In this study, antibiotics showed asymmetric BTCs, indicating nonequilibrium transport. Solute tailing of the BTCs of antibiotics can be attributed to physical and/or chemical nonequilibrium processes. Physical nonequilibrium is caused by diffusion between mobile (flowing) water regions (e.g. inter-aggregate pores) and immobile (stagnant) water regions (e.g. intra-aggregate pores), while chemical nonequilibrium by sorption-desorption kinetics for rapid initial sorption on instantaneous equilibrium sites followed by slow sorption on time-dependent (rate-limited) sites (van Genuchten and Wierenga, 1976; Selim et al., 1977; van Genuchten and Wagenet, 1989; Gaber et al., 1995). Although these two nonequilibrium models have physically distinct hypotheses, they have similar mathematical structure and can be put in the same dimensionless form (Nielsen et al., 1986). Therefore, measured BTC alone cannot be used to differentiate between the physical and chemical nonequilibrium. However, only reactive solutes are subject to chemical nonequilibrium, while both reactive and conservative chemicals are related to physical nonequilibrium (Rao et al., 1979). Conservative solutes have been used to distinguish physical and chemical processes by determining if immobile water is significant in the system.

To examine physical nonequilibrium processes in the soil column systems, the Cl^- BTCs were fitted with a two-region model using a conventional inverse curve fitting method (CXTFIT, Toride et al., 1999) with an assumption of no Cl^- sorption. In the two-region mobile-immobile model, volumetric water content is divided into a mobile region where solute transport is by convection and dispersion, and an immobile region where solute moves by diffusion only. The one-dimensional two-region model for steady flow of non-sorbing solutes can be expressed as:

$$\theta = \theta_m + \theta_{im} \qquad [3.15]$$

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \qquad [3.16]$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = a(C_m - C_{im}) \qquad [3.17]$$

where θ is volumetric water content, θ_m and θ_{im} are mobile and immobile water contents, respectively, C_m and C_{im} are concentrations in mobile and immobile domains, respectively, t is time, D_m is dispersion coefficient, q is water flux, x is distance, and α is a first-order mass transfer coefficient between mobile and immobile domains (van Genuchten and Wierenga, 1976). In the CXTFIT program, definitions of partitioning coefficient (β) and mass transfer coefficient (ω) are as given below (Toride et al., 1999):

$$\beta = \theta_m \div \theta \qquad [3.18]$$

$$\omega = \alpha \times L \div (\theta \times v) \qquad [3.19]$$

where L is soil column length and v is the mean pore water velocity.

The fitted β and ω were close to 1 and 0, respectively, for most Cl^- BTCs (Table 3.6), indicating all the water in the column systems was mobile and physical nonequilibrium was not significant except in columns 5 and 6.

When the Cl^- BTCs were fitted with the deterministic equilibrium convection-dispersion equation (CDE) model, the fitted retardation factors (R), a measure of solute sorption, ranged from 0.997 to 1.003. Column dispersivity (λ) and Column Peclet number (P) of the soil columns were computed:

$$\lambda = D \div v \tag{3.20}$$

$$P = v \times L \div D \tag{3.21}$$

where D is the dispersion coefficient. The P numbers smaller than 1 may imply the dispersion-dominated flow while the values greater than 10 imply convection-dominated flow.

The BTCs of antibiotics were fitted with a two-site equilibrium-kinetic model without degradation or transformation. The two-site model assumes that the sorption sites can be divided to two fractions: sites for instantaneous (equilibrium) sorption and sites for time-dependent (rate-limited) sorption. The one-dimensional two-site sorption/desorption transport model can be expressed as:

$$(1+\frac{f\rho_b K_d}{\theta})\frac{\partial C}{\partial t}+\frac{\rho_b}{\theta}\frac{\partial s_2}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x} \tag{3.22}$$

$$\frac{\partial s_2}{\partial t}=a[(1-f)K_d C-s_2] \tag{3.23}$$

where f is the fraction of exchange sites that are always at equilibrium, ρ_b is soil bulk density, K_d is the distribution coefficient, s_2 is sorbed concentration on kinetic sorption sites, and α is a first-order kinetic rate coefficient (van Genuchten and Wagenet, 1989). Two parameters, v and D, were obtained from Cl^- BTCs. The parameters f and α can be calculated as (Toride et al., 1999):

$$f = (\beta \times R - 1) \div (R - 1) \tag{3.24}$$

$$\alpha = \omega \times v \div [(1 - \beta) \times R \times L] \tag{3.25}$$

In order to quantify the DOC effect on the antibiotic mobility, R values were compared and K_d values were calculated from the R values:

$$K_d = (R - 1) \times \theta \div \rho_b \tag{3.26}$$

RESULTS AND DISSCUSION

1. Dissolved organic carbon characteristics

The pH of DOC extracts obtained from dairy manure was 8.7. The E_4/E_6 value for DOC solution from dairy manure was 6.3. Since this ratio is greater than 5, the dairy manure DOC may primarily consist of small fulvic acid-type molecules that have high oxygen and carboxyl group content and high total acidity (Chen et al., 1977; Swift, 1996). Total acidity and carboxyl acidity of the DOC measured by indirect titration method were 41.6 and 38.8 mmol g^{-1}, respectively. Suba and Essington (1999) reported that the E_4/E_6 ratio for DOC extracts from dairy manure was 6.1, and Seol and Lee (2000) reported that total acidity of DOC solution derived from swine wastes was 7.5 mmol g^{-1}. Huang and Lee (2001) suggested that DOC extracted from dairy waste-derived lagoon effluents has greater polarity than commercial humic acid by showing that the ratio of elemental carbon to sum of oxygen and nitrogen, C/(O+N), for dairy waste was 0.49 compared with 1.75 for humic acid. The low C/(O+N) ratio of dairy waste DOC may be related to the greater concentrations of oxygen or nitrogen containing functional groups including carboxyl group and amino group, and thus to the greater fulvic acid character of the DOC.

2. Batch equilibration experiments

Effect of pH and ionic strength on antibiotic sorption to clays: Sorption of CTC by montmorillonite and kaolinite decreased as pH increased (Fig. 3.4), which can be explained by a greater cationic character of tetracyclines as a function of decreasing pH (Porubcan et al., 1978; Figueroa et al., 2004), the repulsion of the anionic species by the clay surfaces at high pH (Porubcan et al., 1978; Sithole and Guy, 1987a), and the changes in the charges of the exposed Al edge groups (Sithole and Guy, 1987a).

It has been reported that tetracyclines are sorbed to clays mainly through cation exchange (Porubcan et al., 1978; Sithole and Guy, 1987a; Figueroa et al., 2004; Kulshrestha et al., 2004). Even though the zero charge form of CTC predominates at pH between 3.3 and 7.4, the zwitterion species (CTC^{-+0}) is favored over the species with all neutral groups (CTC^{000}) by 10^3 in water (Martin, 1985). Additionally, about 80% of anionic CTC (CTC^{-}) has positive charge at C-4; 80% CTC^{-+-} and 20% CTC^{-00} (Schneider, 2001). Therefore, positive charge on the dimethylamino group at C-4 may bind to negative charge surface sites of the clay minerals. Porubcan et al. (1978) and Kulshrestha et al. (2004) showed through spectroscopic studies that some degree of cation exchange can occur on Na-montmorillonite at pH 5.0. MacKay and Canterbury (2005) reported that cation exchange accounted for oxytetracycline sorption to resin beads even at pH 7.6. In addition to cation exchange, Figueroa et al. (2004) suggested that a surface complexation mechanism is important for oxytetracycline sorption of zwitterions forms to clays. The application of cation exchange and surface complexation mechanisms to predict the CTC sorption by clays resulted in a predicted sorption that describes CTC sorption behavior well (Fig. 3.4). For montmorillonite, the equilibrium constants (as log K^{int}) obtained from FITEQL program were 10.5 for the cation exchange (Eq. 3.1) and 8.5 for the surface complexation (Eq. 3.2). For kaolinite, log K^{int} values were 9.9 for the Na/CTC exchange (Eq. 3.1), 7.1 for the surface complexation with ≡ SiOH sites, and 6.9 for ≡ AlOH sites (Eq. 3.2). Sorption of CTC to clays decreased with increasing ionic strength (Fig. 3.5), which indicates that CTC competes for negative charge surface sites on the clay minerals with Na^+. The Freundlich isotherm model parameters for CTC are listed in Table 3.7.

In addition to cation exchange and surface complexation, CTC may sorb to montmorillonite via the combined influence of cation bridging through divalent cations adsorbed on clay surface (Porubcan et al., 1978; Sithole and Guy, 1987a; Kulshrestha et al., 2004), bonding with Al ions at the edges of clay surface (Sithole and Guy, 1987a), hydrogen bonding between the functional groups of CTC and the silanol groups of clay (Sithole and Guy, 1987a; Kulshrestha et al., 2004), and hydrophobic interaction between hydrophobic regions of clay and neutral CTC structures (Kulshrestha et al., 2004).

Decreased TYL sorption to montmorillonite with increasing pH was observed at pH greater than the pK_a (7.1), and TYL sorption to kaolinite decreased with increasing pH (Fig. 3.6). The protonated positively charged tertiary amine is the predominant TYL species under pK_a, but the proportion of cationic species decreases as pH increases (Fig. 3.2). Predicted TYL sorption by the DDLM tends to support the conclusion that cation exchange is a large contributor to overall TYL sorption when solution pH is less than 6.5 (Fig. 3.6). For montmorillonite, log K^{int} values were 9.3 for the cation exchange (Eq. 3.1) and 5.0 for the surface complexation (Eq. 3.2). For kaolinite, log K^{int} values were 6.6 for the Na/CTC exchange (Eq. 3.1), 5.3 for the surface complexation with ≡ SiOH sites, and 4.8 for ≡ AlOH sites (Eq. 3.2). Relatively poor prediction of TYL sorption to kaolinite by the DDLM may imply that sorption behavior of TYL by kaolinite is more complex than is addressed by chemical reactions and the DDLM in this study. Increasing ionic strength decreased the TYL sorption at pH 5.6-5.7, where cation exchange dominates (Fig. 3.7). The Freundlich isotherm model parameters for TYL are listed in Table 3.8. These results imply that cation exchange is the primary process for TYL sorption to clays at pH less than 6.5 and cations in the background electrolyte compete with TYL for negative charge sites on clays.

Sorption of SMT to clays decreased as pH increased to around 4 (Fig. 3.8) possibly due to the decreasing proportion of positively charged SMT species (Fig. 3.2), implying that cation exchange is the main sorption mechanism at pH less than 4. Little pH effect on SMT sorption to the clays at pH greater than 4 is consistent with the result obtained by Gao and Pedersen (2005), who showed slight pH-dependence for SMT adsorption to Na^+-saturated montmorillonite (Na-SAz-1) and kaolinite (Na-KGa-1b) between pH 4.3 and 8. They also found that surface charge density reduction by heat treatment significantly enhanced SMT adsorption to the Na-SAz-1. Additionally, weak SMT sorption to clays compared with CTC and TYL and inability of the DDLM to adequately predict SMT sorption in the range of pH greater than 4 may imply hydrophobic interactions between neutral SMT species and clay surfaces. For montmorillonite, log K^{int} values were 1.2 for the cation exchange (Eq. 3.1) and 0.5 for the surface complexation (Eq. 3.2). For kaolinite, log K^{int} values were 6.0 for the Na/CTC exchange (Eq. 3.1), 0.3 for the surface complexation with ≡ SiOH sites, and 0.5 for ≡ AlOH sites (Eq. 3.2).

Additionally, SMT sorption followed S-type sorption isotherms (Fig. 3.9) as compared to L-type isotherms for CTC and TYL (Fig. 3.5 and 3.7). The L-curve isotherms indicate that CTC and TYL have a high affinity for sorption sites at low surface coverage but a decreasing affinity with increasing surface coverage (Essington, 2004). Giles et al. (1974b) showed that S-type curves occur when the activation energy for removal of solute from adsorbent is concentration-dependent by strong lateral interaction among the adsorbed species relative to forces between solute and adsorbent ("cooperative adsorption"), and/or is markedly reduced by large negative contributions of water or a second solute. In the SMT sorption systems, there is no second solute such as chelating agent and DOC. The S-curve isotherms of SMT on the clays may imply that the affinity of the sorbents for SMT is weak when SMT concentration is low, presumably due to relatively strong SMT-SMT interactions compared to SMT-clay interactions and/or greater interaction of SMT with water than with the clays. Giles et al. (1974a) suggested an orientation of sorbed solute in which the molecules are stacked edge-on to the adsorbent surface, but with their main planes inclined at a low angle for S-curve isotherms. As SMT concentration in solution increases and greater amounts of SMT are forced to the clay surface, the hydrophilic part of SMT may sorb to the clay surface and the hydrophobic group outward, resulting the clay surfaces become more hydrophobic with increase in SMT sorption (Essington, 2004). In addition to the development of hydrophobic character of the clay surface, lateral interaction among sorbed SMT by hydrophobic effect may tend to pack more SMT to the clay surface. The parameter n was less than 2 (Table 3.9). Homenauth and McBride (1994) showed that n for aniline adsorption on montmorillonite, vermiculite, and kaolinite ranged from 2.28 to 4.52 with larger n for more pronounced cooperative adsorption. Gu and Zhu (1990) reported that n for nonionic surfactants ranged from 3.9 to 11.8 with higher value for longer hydrocarbon chain length. The cooperativity for SMT may be low compared with aniline and nonionic surfactants probably due to relatively weak solute-solute interactions and/or relatively less hydrophobic character of SMT.

Retention of SMT by the clays was little influenced by ionic strength at pH 4.9 for montmorillonite and 5.7 for kaolinite (Fig. 3.9 and Table 3.9), suggesting a lack of competition with Na^+ for the sorption sites and minor cation exchange at the pH. Gao and Pedersen (2005) found little change in SMT adsorption to Wyoming montmorillonite (Na-SWy-2) at ionic strength between 0.01 and 0.31 M when solution pH was between 5 and 7.

These results may imply that increase in soil pH and ionic strength caused by animal waste amendment may affect sorption behavior and mobility of some antibiotics including CTC and TYL in soil. When the antibiotics are applied to agricultural land, cationic species (e.g. CTC^+ and TYL^+) of antibiotics may decrease due to increase in pH by concomitant animal manure addition. Additionally, cations contained in animal manure may compete for sorption sites with antibiotics. Therefore, it should be taken into account that antibiotics are applied to agricultural land along with animal manure in order to accurately predict the potential of antibiotics to contaminate water environment by leaching or drainflow.

Effect of background electrolyte cation type on antibiotic sorption: Greater sorption of CTC and TYL was exhibited in the Na system than in the Ca system for clays and soils (Fig. 3.10 and 3.11, and Tables 3.7 and 3.8). Although ionic strength in the Ca system was 0.03 M, the greater sorption in the Na system was observed even in the 0.05 M ionic strength. Divalent cations such as Ca^{2+} have greater attraction force to charged surfaces and compete more effectively for cation exchange sites compared with monovalent cations such as Na^+. Additionally, the geometry of the interlayer region of montmorillonite might favor Ca^{2+} compared with Na^+ due to electrostatic repulsion between closely spaced Na^+ ions (McBride, 1994). Therefore, exchangeable Ca^{2+} ions are more difficult to replace compared with Na^+ ions. Additionally, background cation can influence diffuse double-layer chemistry, and increasing valence of cation can make the electrostatic potential less negative (Harter and Naidu, 2001). It was unlikely that formation of aqueous Ca-CTC complexation occurred at pH less than 5.4 as in this study. Tongaree et al. (1999) reported that no Ca-oxytetracycline complexation occurred at pH 5.6, while the complexation was observed at pH 7.5.

On the other hand, Figueroa et al. (2004) showed greater oxytetracycline sorption to Ca-saturated montmorillonite compared with Na-saturated under alkaline conditions through cation bridging of Ca to anionic oxytetracycline. Anionic tetracyclines can bind more strongly with an adsorbed metal ion compared with cationic/neutral species (Martin, 1985; Lambs et al., 1988; Schneider, 2001), and formation of ternary complexes between tetracyclines, metal cations, and sorbents favored at high pH (MacKay and Canterbury, 2005).

Greater sorption of CTC and TYL was observed for subsurface soils compared with surface soils (Fig. 3.10 and 3.11, Tables 3.7 and 3.8). Since subsurface soils have greater clay content and less sand fraction relative to surface soils (Table 3.2), soil clay content may be one of the major factors affecting the sorption of CTC and TYL (Rabolle and Spliid, 2000; Jones et al., 2005; Kumar et al., 2005b). Additionally, organic coatings on clay surfaces in surface soils may contribute to less retention of the antibiotics (Jones et al., 2005). Conversely, surface soils with high soil organic matter had greater sorbed SMT than corresponding subsurface soils (Fig. 3.12 and Table 3.8). A clay loam subsurface soil with high soil organic matter content relative to a sandy loam subsurface soil showed greater SMT sorption compared with a sandy loam subsurface soil (Fig. 3.12 and Table 3.9). These results imply that soil organic matter content is one of the more important soil properties for SMT retention by soils, which is consistent with partitioning of hydrophobic organic compounds into soil organic matter as the dominant mechanism of soil uptake.

Isotherms of SMT sorption to soils yielded nonlinear isotherms with N ranged from 0.72 to 0.86 (Table 3.9). This may imply that the associated sites for SMT on organic phase are heterogeneous and that the strongest binding sites are first occupied. Thiele-Bruhn et al. (2004) reported that sulfonamides bind to phenolic and carboxylic groups, N-heterocyclic compound, and lignin decomposition products in soil organic matter by hydrogen bonds and van der Waals interaction. In contrast, SMT may sorb to clay minerals through weak nonionic hydrophobic interaction at pH greater than 4 as previously explained in pH effect section (Fig. 3.8).

The type of background electrolyte cation exerted little influence on SMT retention on montmorillonite (Fig. 3.12). Gao and Pedersen (2005) also showed that SMT adsorption to Wyoming montmorillonite (SWy-2) was independent of cation type at pH 5.2. For soils, slightly greater SMT sorption was observed in the Na system compared with the Ca system (Fig. 3.12). In Ca system, relative size of soil organic matter may decrease by greater coiling (Murphy and Zachara, 1995). In addition to Ca electrolyte effect, higher ionic strength (0.03 M for the Ca system compared with 0.01 M for the Na system) and relatively low pH (5.3-5.6 for the Ca system compared with 5.8-6.0 for the Na system) can collapse the flexible, random coils into globular aggregate or ring-like structures (Essington, 2004). A greater coiling or relatively smaller size of soil organic matter may result in sorption domain size reduction and decreased SMT retention.

Effect of DOC on antibiotic sorption: The CTC sorption to clays and soils decreased by adding DOC solution extracted from dairy manure to the sorption system (Fig. 3.13 and Table 3.7). Reduced CTC sorption may be explained by competition between DOC and CTC for sorption sites and/or aqueous association of CTC with DOC. The mechanistic information for the reduced sorption by adding DOC cannot be derived from the sorption isotherms. The mineral surface covered by DOC may exhibit physicochemical properties of organic matter. Jones et al. (2005) showed a negative correlation between organic carbon content and oxytetracycline sorption to soils and suggested that greater organic carbon content resulted in less oxytetracycline sorption due to coverage of active sorption sites on soil minerals by organic matter. Furthermore, Kulshrestha et al. (2004) suggested that high concentration of free humic acids in solution can induce desorption of oxytetracycline. The hydrophilic character of the DOC may lead to formation of aqueous DOC-CTC complexes because the DOC used in this study is mainly composed of fulvic acid-type molecules. Sithole and Guy (1987b) and MacKay and Canterbury (2005) reported that tetracyclines sorbed to humic acid in solution phase through hydrogen bonding between acidic groups in the humic acid and the polar groups of tetracycline or via ionic binding to polyvalent cations present on the humic acid.

The Langmuir model proves the better fit for the isotherms of kaolinite and sandy loam surface soil in the presence of dairy manure DOC. The surface area of kaolinite and sandy loam surface soil is less than montmorillonite and other soils (Table 3.2), so applied DOC may interact with relatively high proportion of the sorption sites for CTC. At high initial concentrations of CTC the data seem to reach sorption maxima, implying that kaolinite and sandy loam surface soil may have a maximum capacity for CTC in the presence of dairy manure DOC.

Indigenous soil organic matter can influence the DOC effects on CTC sorption. Surface soils may bind less DOC compared with subsurface soils, possibly due to higher indigenous soil organic matter than subsurface soils and greater DOC sorption to subsurface soils (Jardine et al., 1989; Dalva and Moore, 1991; Jardine et al., 1992; Kaiser et al., 1996). However, there was little difference between the DOC effects for surface soils and subsurface soils in this study. This may be attributed to difference in type of soil organic matter and/or impact of clay on sorption of DOC and CTC.

Sorption of TYL to clay decreased in the presence of increased DOC (Fig. 3.14 and Table 3.8). For any given sorbent, the smaller DOC impact on TYL sorption at low DOC concentration may be explained by limited competition with the antibiotic for sorption sites and/or limited capacity to bind TYL in solution. It has been reported that the DOC effect on sorption and mobility of organic contaminants is a function of DOC concentration (Suba and Essington, 1999; Huang and Lee, 2001; Kulshrestha et al., 2004). Loke et al. (2002) suggested that tylosin sorption by manure is mainly caused by hydrophobic interactions and not by ionic binding between the aliphatic amine cation of TYL and organic matter.

These results imply that an increase in DOC concentration caused by animal manure treatment may result in reduced sorption of CTC and TYL to soils. Therefore, the potential for the antibiotics to contaminate aquatic environment by leaching or drainflow can be underestimated if the DOC effect is not considered.

Addition of dissolved organic carbon increased SMT sorption to clays and soils (Fig. 3.15 and Table 3.10). Totsche et al. (1997) suggested that enhanced retention of polycyclic aromatic hydrocarbons by DOC addition can be attributed to co-sorption of DOC-contaminant associate to solid phase and/or cumulative sorption by increased sorption capacity of the bulk phase. The DOC sorption to the solid phase may increase the organic matter character of the solid phase and provide new sorption sites for SMT, thus resulting in enhanced SMT partition (Murphy and Zachara, 1995). There was little difference in the DOC retention-enhancing effect between surface soils and subsurface soils although greater DOC may sorb to subsurface soils than to surface soils (Dalva and Moore, 1991; Jardine et al., 1992). This may be attributed to clay impact and/or soil organic matter characteristics.

Increasing DOC level caused increased SMT sorption in soils while decreasing sorption of CTC and TYL. This inconsistency can be explained by differences in the ionic and nonionic characteristics and sorption mechanisms for the antibiotics. Sulfamethazine has relatively low water solubility (438 mg L^{-1}) compared with CTC and TYL (5,000-8,600 mg L^{-1}), although K_{ow} of SMT is low (7.76). Additionally, nonionic SMT species (SMT^0) predominates at pH 3.5-7.0, while zwitterionic CTC form ($CTC^{\pm}$) and cationic TYL species (TYL^+) dominate in the pH range (Fig. 3.2). Sorption of an ionogenic compound in its neutral form can be similar to that of hydrophobic compounds (Brusseau et al., 1991). As previously mentioned, SMT may mainly partition to soil organic matter, while CTC and TYL may interact with the exchange complex of the solid phase. Binding of DOC with the solid phase can increase sorption sites for SMT, while competing for sorption sites with CTC and TYL. Additionally, the intensity of soluble SMT-DOC association may be small compared with CTC and TYL because of the hydrophilic character of dairy manure DOC used in this study. Note that E_4/E_6 ratio of the dairy manure DOC was 6.3, indicating a fulvic acid character of the DOC.

3. Column transport study (DOC effect on antibiotic mobility)

The *R* values of CTC and TYL for subsurface soil were greater than surface soil (Table 3.11 and Table 3.12). Conversely, the *R* value of SMT for surface soil was greater than subsurface soil (Table 3.13). The result indicates that SMT is mainly retained by soil organic matter, which is consistent with the result obtained from batch study.

Based on modeling results shown in Table 3.6, physical nonequilibrium is not considered to be significant in these soil column systems. Note that the probability of physical nonequilibrium processes for disturbed packed soil columns is low compared with undisturbed columns or columns packed with soil aggregates. Therefore, chemical nonequilibrium was a dominant process for asymmetric BTCs of antibiotics with tailing, and a two-site equilibrium-kinetic model was used to analyze our BTCs data using inverse curve fitting method (CXTFIT). The obtained parameter estimates are listed in Table 3.11 for CTC, Table 3.12 for TYL, and Table 3.13 for SMT. The goodness-of-fit of the model to the measured BTCs is given by the r^2 values. Note that the two-site model is mainly based on macroscopic data, while sorption/desorption processes are microscopic phenomena. Therefore, several models may provide similar predicted BTCs, and a good model match to the experimental data does not guarantee that the model provides an accurate explanation of antibiotic behavior in the soil column system.

DOC effect on CTC mobility: Elevated levels of DOC enhanced CTC mobility for both surface and subsurface soil of Captina sandy loam, while little effect of DOC was observed for conservative chloride (Fig. 3.16). The peak time of CTC in effluents moved from 11.4 pore volumes (PV) to 7.8 PV for surface soil and from 8.4 PV to 6.3 PV for subsurface soil in the presence of dairy manure DOC. The R values of CTC obtained using CXTFIT program decreased from 760 to 351 for surface soil and from 1,020 to 391 for subsurface soil, and thus the K_d values also decreased from 370 to 159 L kg^{-1} for surface soil and from 413 to 158 L kg^{-1} for subsurface soil by increasing DOC concentration (Table 3.11). Based on two methods suggested by van Genuchten (1981) to linearize the nonlinear isotherm, K_d can be obtained from K_F and N determined in batch studies. For surface soils, K_d values were 464 and 383 L kg^{-1} in the absence of DOC and 128 and 94 L kg^{-1} in the presence of dairy DOC. For subsurface soils, K_d values were 90 and 62 L kg^{-1} in the absence of DOC and 47 and 32 L kg^{-1} in the presence of DOC. Note that K_d values obtained from column study can be different from sorption parameters from batch experiments. Continuous addition of antibiotic drives the equilibrium towards further antibiotic sorption for column displacement experiments, while equilibrium is established for batch sorption experiments.

When mobility of organic chemicals is enhanced by DOC through co-transport of DOC and the chemicals, the DOC-induced transport may be more pronounced for hydrophilic organic pollutants than for hydrophobic chemicals (Kaiser and Zech, 1997) because of preferential adsorption of the hydrophobic organic components in DOC to soils (Jardine et al., 1989; Kaiser et al., 1996; Totsche et al., 1997; Han and Thompson, 2003) and rapid transport of hydrophilic components in DOC (Dunnivant et al., 1992). In the presence of dairy manure DOC, CTC mass recovery in effluents increased from 1.8 to 3.6% for surface soil and from 2.3 to 4.9% for subsurface soil, implying that greater amounts of CTC may reach groundwater in the presence of animal manure DOC.

Increased DOC level may result in desorption of CTC from soil solids. Kulshrestha et al. (2004) suggested that soil-bound tetracyclines can be mobilized by high concentrations of DOC in soil solution.

The degree of chemical nonequilibrium is reflected in β and ω. The β decreased from 0.12 to 0.056 for surface soil and from 0.080 to 0.021 for subsurface soil by DOC addition. The ω also decreased from 29 to 14 for surface soil and from 38 to 6 for subsurface soil. A small β value may indicate that a relatively large amount of solute resides in the nonequilibrium phase, and decreased ω may show an increased degree of nonequilibrium (Toride et al., 1999). However, relatively poor fitting CTC BTCs in the presence of DOC with transport parameter estimates may imply that CTC transport along with DOC is more complex than is addressed by the two-site model assuming no transformation or degradation. For example, the two-site model in this model assumes a linear isotherm (Eq. 3.23) while CTC sorption to soils is nonlinear, as shown in batch equilibrium experiments (Fig. 3.13).

DOC effect on TYL mobility: The maximum relative concentration of TYL in effluents ranged from 0.53-0.54 for surface soil and from 0.25-0.26 for subsurface soil. The TYL mass recovery in effluents ranged from 63 to 68% for surface soil and from 34 to 40% for subsurface soil. This is consistent with greater TYL sorption of subsurface soil than surface soil as shown in batch study section. Addition of DOC enhanced TYL mobility in the highly-sorbing subsurface soil (Fig. 3.17 b). In the presence of dairy manure DOC, R and K_d values of TYL for subsurface soil decreased from 24 to 21 and from 8.4 to 8.2 L kg^{-1}, respectively (Table 3.12). For surface soils, K_d values obtained by two methods of van Genuchten (1981) were 6.6 and 5.8 L kg^{-1} in the absence of DOC and 6.1 and 5.6 L kg^{-1} in the presence of dairy DOC. For subsurface soils, K_d values were 7.0 and 4.9 L kg^{-1} in the absence of DOC and 7.3 and 5.3 L kg^{-1} in the presence of DOC. The DOC effect on mobility of antibiotics may depend on sorption of DOC and antibiotics to soil solid. Greater DOC sorption to subsurface soil than to surface soil (Jardine et al., 1989; Dalva and Moore, 1991; Jardine et al., 1992; Kaiser et al., 1996) may cause greater competition for sorption sites with TYL. Sorption of carboxyl groups in DOC to metals at the clay mineral surfaces, probably by ligand exchange, may result in a preferential removal of carboxyl carbon fractions in DOC (Kaiser et al., 1997). As previously mentioned in DOC characteristics section, the dairy manure-derived DOC used in this study had a high content of carboxyl groups. In contrast, there was little DOC effect for surface soil. This result may be attributed to less sorption of added DOC to surface soil than to subsurface soil by indigenous soil organic matter.

It should be noted that physical and chemical nonequilibrium processes may occur simultaneously for surface soil columns because estimated mobile water fractions (β) were 0.65-0.66 using the two-region model with Cl^- BTCs (Table 3.6). Although the probability of physical nonequilibrium for packed soil columns is low and the CDE model fits well the Cl^- BTCs (Table 3.12 and Fig. 3.17), the possibility of nonequilibrium transport by physical processes cannot be completely excluded. It is difficult to identify the reaction mechanism or the controlling process based on BTCs alone (Srivastava and Brusseau, 1996; Selim and Amacher, 1997). To verify the physical and chemical nonequilibrium, independent parameter estimates are needed (Nielsen et al., 1986; Brusseau and Zachara, 1993; Ma and Selim, 1997). However, transport parameters may not be derived independently from batch equilibrium studies. For example, the parameters f, α, and R in the two-site model have been found to be functions of the pore water velocity (Nielsen et al., 1986; Hu and Brusseau, 1996; Chen and Wagenet, 1997; Pang et al., 2002). The velocity dependency indicates a wide range of heterogeneous sorption sites and/or different sorption processes under different velocities, so that the two-site model may be insufficient to describe the nonequilibrium transport (Chen and Wagenet, 1997). Young and Ball (1995) reported that α in the mobile-immobile model depends on flow velocity, column length, pulse duration, and solute adsorption. Additionally, column displacement experiments may be more sensitive to isotherm nonlinearity than are the batch equilibrium studies (Gamerdinger et al., 1990). It has been reported that some techniques including flow interruption during column transport experiments, manipulation of pore-water velocity, and/or application of multiple tracers with different diffusion coefficients and sizes can be used to provide more information for reaction mechanisms and/or physical nonequilibrium (Brusseau et al., 1997; Ma and Selim, 1997; Brusseau, 1998; Jardine et al., 1998).

DOC effect on SMT mobility: Mass recovery and the maximum relative concentration of SMT in effluents for subsurface soil ranged from 94-97% and 0.89-0.91, respectively, versus from 82-92% and 0.52-0.60 for surface soil, which is consistent with batch study results that surface soil has greater sorption affinity to SMT than subsurface soil due to high soil organic matter content. Increasing DOC level in input solution resulted in greater SMT concentration in effluents for surface soil (Fig. 3.18), and consequently increased SMT mass recovery in effluents from 82% to 92%. Greater amounts of SMT-DOC association may be leached from the column packed with surface soil than subsurface soil because indigenous soil organic matter reduces the sorption of added DOC in the mineral soil (Jardine et al., 1989; Kaiser et al., 1996) and higher organic matter content can increase leaching of DOC from soil column (Laegdsmand et al., 2005). The SMT mass recovery for subsurface soil was 97% in the presence of DOC and 94% in the absence of DOC. Adding DOC resulted in decreased R and K_d of SMT for surface soil while increased R and K_d for subsurface soil (Table 3.13). Relatively high v for surface soil column in the presence of DOC may partly contribute to decreased R. Pang et al. (2002) reported that R was inversely correlated with v under chemical nonequilibrium condition. The difference in DOC effect on SMT sorption between batch study and column study may be due to different reaction conditions in two techniques as previously mentioned. Kay et al. (2005a) reported that swine slurry incorporation had little influence on mobility of sulfachloropyridazine in undisturbed soil cores with 25 cm diameter and 60 cm depth. Additionally, chemical nonequilibrium by sorption-desorption kinetics may also yield different results for column studies.

These results imply that increased DOC concentration by animal manure amendment may enhance mobility of some antibiotics in soils and/or increase mass recovery in effluents, especially for CTC. In this case, the potential for antibiotics to contaminate aquatic environments can be underestimated if the DOC effect on antibiotics transport is not considered. It should be noted that the source of DOC influences the DOC effect on sorption and mobility of organic contaminants. Huang and Lee (2001) reported that distribution coefficient of DOC to soils were 1.5-5.6 L kg^{-1} for DOC from dairy waste-derived lagoon effluents and 5.1-20 L kg^{-1} for commercial humic acid, and Tipping (1981) showed that larger molecular-weight humic substances exhibited a greater sorption potential to soils. In addition to the DOC source, the extent of DOC effect on the transport of organic compounds in soil columns may depend on numerous factors including DOC concentration, degree of saturation, the pore water velocity, ionic strength, and the type and abundance of polyvalent cations.

The results obtained in this study show that the input of veterinary antibiotics to agricultural land in a manure matrix should be taken into account for proper risk assessment of antibiotic contamination in soil and aquatic environment because the influence of animal waste application on soil properties can be substantial for sorption, transport, and fate of the antibiotics in soil.

CONCLUSIONS

Batch and column study using montmorillonite, kaolinite, and surface and subsurface soil of Etowah clay loam and Captina sandy loam were conducted to determine the influence of soil chemical properties on the fate and transport of antibiotics in soil. Sorption of CTC and TYL generally decreased with increasing pH and ionic strength, suggesting that cation exchange may be one of the major sorption mechanisms of the antibiotics and antibiotics may compete for sorption sites with surrounding cations. Therefore, increased pH and ionic strength in soil solution caused by concomitant addition of animal manure may influence the sorption and behavior of CTC and TYL to soils. Weak SMT sorption to clays relative to CTC and TYL and the inability of a surface complexation model to describe SMT sorption in the pH range greater than 4 may imply weak hydrophobic interactions between neutral SMT species and clay surfaces. Greater sorption of CTC and TYL was observed in the Na system compared with Ca system. Surface soils having high soil organic matter showed greater SMT sorption than corresponding subsurface soils, but greater sorption of CTC and TYL to subsurface soils than surface soils. Therefore, SMT may mainly partition to organic components in soil, while CTC and TYL may interact with the exchange complex. Sorption of CTC and TYL to clays and soils decreased in the presence of dairy manure DOC, while SMT sorption increased with DOC addition. Mobility of CTC in a sandy loam was greatly enhanced in the presence of dairy manure DOC. The *R* values of CTC decreased from 760 to 351 for surface soil and from 1,020 to 391 for subsurface soil. Additionally, adding DOC to input solution increased CTC mass recoveries from 1.8 to 3.6% for surface soil, and from 2.3 to 4.9% for subsurface soil. Earlier breakthrough of TYL was shown in the presence of DOC for subsurface soil. The *R* values of TYL decreased from 14 to 10 for surface soil and from 24 to 21 for subsurface soil. Mass recovery of SMT for surface soil increased from 82 to 92% in the presence of DOC. The results obtained in this study showed that the effects of pH, ionic strength, DOC level, and background electrolyte cation type in soil solution are important factors for fate and transport of agricultural antibiotics in soils. Therefore, the input of veterinary antibiotics to agricultural land in a manure matrix should be taken into account for proper risk evaluation of antibiotic contamination in soil and aquatic environments.

REFERENCES

Abu-Zreig, M. and R.P. Rudra. 1999. The influence of manure on movement of atrazine through soil. Toxicol. Environ. Chem. 73: 153-162.

Aga, D.S., R. Goldfish, and R. Kulshrestha. 2003. Application of ELISA in determining the fate of tetracyclines in land-applied livestock wastes. Analyst. 128: 658-662.

Albert, A. 1953. Avidity of terramycin and aureomycin for metallic cations. Nature. 172: 201.

Albert, A. and C.W. Rees. 1956. Avidity of the tetracyclines for the cations of metals. Nature. 177: 433-434.

Ash, R., B. Mauck, and M. Morgan. 2002. Antibiotic resistance of gram-negative bacteria in rivers, United States. Emer. Infect. Dis. 8: 713-716.

Barriuso, E., U. Baer, and R. Calvet. 1992. Dissolved organic matter and adsorption-desorption of dimefuron, atrazine, and carbetamide by soils. J. Environ. Qual. 21: 359-367.

Baskaran, S., N.S. Bolan, A. Rahman, and R.W. Tillman. 1996. Effect of exogenous carbon on the sorption and movement of atrazine and 2,4-D by soils. Aust. J. Soil Res. 34: 609-622.

Benet, L.Z. and J.E. Goyan. 1965. Determination of the stability constants of tetracycline complexes. J. Pharm. Sci. 54: 983-987.

Bewick, M.W. 1979. The adsorption and release of tylosin by clays and soils. Plant and Soil. 51: 363-372.

Bloom, R.A. 2004. Use of veterinary pharmaceuticals in the United States. In Pharmaceuticals in the Environment. 2nd ed. Ed. K. Kümmerer. Springer. New York.

Boxall, A.B.A., P.A. Blackwell, R. Cavallo, P. Kay, and J. Tolls. 2002. The sorption and transport of a sulphonamide antibiotic in soil systems. Toxicology Letters 131: 19-28.

Boxall, A.B.A., P. Kay, P.A. Blackwell, and L.A. Fogg. 2004. Fate of veterinary medicines applied to soils. In Pharmaceuticals in the Environment. 2nd ed. Ed. K. Kümmerer. Springer. New York.

Brusseau, M.L. 1998. Multiprocess nonequilibrium and nonideal transport of solutes in porous media. In Physical Nonequilibrium in Soils. Modeling and Application. Ed. H.M. Selim and L. Ma. Ann Arbor Press. Chelsea, Michigan.

Brusseau, M.L., Q. Hu, and R. Srivastava. 1997. Using flow interruption to identify factors causing nonideal contaminant transport. J. Contam. Hydrol. 24: 205-219.

Brusseau, M.L., R.E. Jessup, and P.S.C. Rao. 1991. Nonequilibrium sorption of organic chemicals: elucidation of rate-limiting processes. Environ. Sci. Technol. 25: 134-142.

Brusseau, M.L. and J.M. Zachara. 1993. Transport of Co^{2+} in a physically and chemically heterogeneous porous medium. Environ. Sci. Technol. 27: 1937-1939.

Burkhard, L.P. 2000. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. Environ. Sci. Technol. 34: 4663-4668.

Burkhardt, M., C. Stamm, C. Waul, H. Singer, and S. Müller. 2005. Surface runoff and transport of sulfonamide antibiotics and tracers on manured grassland. J. Environ. Qual. 34: 1363-1371.

Campagnolo, E.R., K.R. Johnson, A. Karpati, C.S. Rubin, D.W. Kolpin, M.T. Meyer, J.E. Esteban, R.W. Currier, K. Smith, K.M. Thu, and M. McGeehin. 2002. Antimicrobial residues in animal waste and water resources proximal to large-scale swine and poultry feeding operations. Sci. Total Environ. 299: 89-95.

Carlson, J.C. and S.A. Mabury. 2006. Dissipation kinetics and mobility of chlortetracycline, tylosin, and monensin in an agricultural soil in Northumberland county, Ontario, Canada. Environ. Toxicol. Chem. 25: 1-10.

Chen, W. and R.J. Wagenet. 1997. Description of atrazine transport in soil with heterogeneous nonequilibrium sorption. Soil Sci. Soc. Am. J. 61: 360-371.

Christian, T., R.J. Schneider, H.A. Farber, D. Skutlarek, M.T. Meyer, and H.E. Goldbach. 2003. Determination of antibiotic residues in manure, soil, and surface waters. Acta Hydrochim. Hydrobiol. 31: 36-44.

Clay, S.A., Z. Liu, R. Thaler, and H. Kennouche. 2005. Tylosin sorption to silty clay loam soils, swine manure, and sand. J. Environ. Sci. Health Part B. 40: 841-850.

Colaizzi, J.L. and P.R. Klink. 1969. pH-partition behavior of tetracyclines. J. Pharm. Sci. 58: 1184-1189.

Dalva, M. and T.R. Moore. 1991. Sources and sinks of dissolved organic carbon in a forested swamp catchment. Biogeochemistry. 15: 1-19.

De la Torre, A.I., J.A. Jimenez, M. Carballo, C. Fernandez, J. Roset, and M.J. Munoz. 2000. Ecotoxicological evaluation of pig slurry. Chemosphere 41: 1629-1635.

De Liguoro, M., V. Cibin, F. Capolongo, B. Halling-Sorensen, and C. Montesissa. 2003. Use of oxytetracycline and tylosin in intensive calf farming: evaluation of transfer to manure and soil. Chemosphere 52: 203-212.

Dewey, C.E., B.D. Cox, B.E. Straw, E.J. Bush, and S. Hurd. 1999. Use of antimicrobials in swine feeds in the United States. Swine Health Prod. 7: 19-25.

Doluisio, J.T. and A.N. Martin. 1963. Metal complexation of the tetracycline hydrochlorides. J. Med. Chem. 6: 16-20.

Dunnivant, F.M., P.M. Jardine, D.L. Taylor, and J.F. McCarthy. 1992. Transport of naturally occurring dissolved organic carbon in laboratory columns containing aquifer material. Soil Sci. Soc. Am. J. 56: 437-444.

Dzombak, D.A. and F.M.M. Morel. 1990. Surface complexation modeling: Hydrous ferric oxides. John Wiley. New York.

Essington, M.E. 2004. Soil and water chemistry: An integrative approach. CRC Press. Boca Raton, FL.

Figueroa, R.A., A. Leonard, and A.A. MacKay. 2004. Modeling tetracycline antibiotic sorption to clays. Environ. Sci. Technol. 38: 476-483.

Figueroa, R.A. and A.A. MacKay. 2005. Sorption of oxytetracycline to iron oxides and iron oxide-rich soils. Environ. Sci. Technol. 39: 6664-6671.

Flint, A.L. and L.E. Flint. 2002. Particle density. In Methods of Soil Analysis, Part 4. Physical Methods. Ed. J.H. Dane and G.C. Topp. American Society of Agronomy-Soil Science Society of America. Madison, WI. pp 229-240.

Gaber, H.M., W.P. Inskeep, S.D. Comfort, and J.M. Wraith. 1995. Nonequilibrium transport of atrazine through large intact soil cores. Soil Sci. Soc. Am. J. 59: 60-67.

Gamerdinger, A.P., R.J. Wagenet, and M.Th. van Genuchten. 1990. Application of two-site/two-region models for studying simultaneous nonequilibrium transport and degradation of pesticides. Soil Sci. Soc. Am. J. 54: 957-963.

Gao, J. and J.A. Pedersen. 2005. Adsorption of sulfonamide antimicrobial agents to clay minerals. Environ. Sci. Technol. 39: 9509-9516.

Gaskins, H.R., C.C. Collier, and D.B. Anderson. 2002. Antibiotics as growth promotants: Mode of action. *In* Pork Quality and Safety Summit. Natl. Pork Board. Des Moines, IA.

Gavalchin, J. and S.E. Katz. 1994. The persistence of fecal-borne antibiotics in soil. J. AOAC Internat. 77: 481-485.

Gee, G.W. and D. Or. 2002. Particle-size analysis. In Methods of Soil Analysis, Part 4. Physical Methods. Ed. J.H. Dane and G.C. Topp. American Society of Agronomy-Soil Science Society of America. Madison, WI. pp 255-293.

Giles, C.H., A.P. D'Silva, and I.A. Easton. 1974a. A general treatment and classification of the solute adsorption isotherm. part II. experimental interpretation. Theoretical. J. Colloid Interface Sci. Technol. 47: 766-778.

Giles, C.H., D. Smith, and A. Huitson. 1974b. A general treatment and classification of the solute adsorption isotherm. I. theoretical. J. Colloid Interface Sci. Technol. 47: 755-765.

Gu, T. and B-Y. Zhu. 1990. The S-type isotherm equation for adsorption of nonionic surfactants at the silica gel-water interface. Colloids Surfaces. 44: 81-87.

Gulbis, J. and G.W. Everett, Jr. 1976. Metal binding characteristics of tetracycline derivatives in DMSO solution. Tetrahedron. 32: 913-917.

Halling-Sorensen, B. 2000. Algal toxicity of antibacterial agents used in intensive farming. Chemosphere 40: 731-739.

Halling-Sorensen, B., A.M. 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.

Halling-Sorensen, B., G. Sengelov, and J. Tjornelund. 2002. Toxicity of tetracyclines and tetracycline degradation products to environmentally relevant bacteria, including selected tetracycline-resistant bacteria. Arch. Environ. Contam. Toxicol. 42: 263-271.

Halling-Sorensen, B., S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten-Lützhoft, and S.E. Jorgensen. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment -A review. Chemosphere 36: 357-393.

Hamscher, G., S. Sczesny, A. Abu-Qare, H. Höper, and H. Nau. 2000. Substances with pharmacological effects including hormonally active substances in the environment: dentification of tetracyclines in soil fertilized with animal slurry. Deut. Tierarztl. Woch. 107: 334-334.

Hamscher, G., S. Sczesny, H. Höper, and H. Nau. 2002. Determination of persistent tetracycline residues in soil fertilized with liquid manure by high-performance liquid chromatography with electrospray ionization tandem mass spectrometry. Anal. Chem. 74: 1509-1518.

Han, N. and M.L. Thompson. 2003. Impact of dissolved organic matter on copper mobility in aquifer material. J. Environ. Qual. 32: 1829-1836.

Harter, R.D. and R. Naidu. 2001. An assessment of environmental and solution parameter impact on trace-metal sorption by soils. Soil Sci. Soc. Am. J. 65: 597-612.

Hekster, Y.A. and T.B. Vree. 1982. Clinical pharmacokinetics of sulphonamides and their N_4-acetyl derivatives. Antibiotics Chemother. 31: 22-118.

Herbelin, A.L. and J.C. Westall. 1999. FITEQL: a computer program for determination of chemical equilibrium constants from experimental data. Report 99-01, Department of Chemistry, Oregon State University, Corvallis, OR.

Hinz, C. 2001. Description of sorption data with isotherm equations. Geoderma. 99: 225-243.

Hirsch, R., T. Ternes, K. Haberer, and K. Kratz. 1999. Occurrence of antibiotics in the aquatic environment. Sci. Total Environ. 225: 109-118.

Holten-Lützhoft, H.C., W.H.J. Vaes, A.P. Freidig, B. Halling-Sorensen, and J.L.M. Hermens. 2000. Influence of pH and other modifying factors on the distribution behavior of 4-quinolones to solid phases and humic acids studied by negligible-depletion SPME-HPLC. Environ. Sci. Technol. 34: 4989-4994.

Homenauth, O.P. and M.B. McBride. 1994. Adsorption of aniline on layer silicate clays and an organic soil. Soil Sci. Soc. Am. J. 58: 347-354.

Höper, H., J. Kues, H. Nau, and G. Hamscher. 2002. Eintrag und Verbleib von Tierarzneimittelwirkstoffen in Böden. Bodenschutz. 7: 141-148.

Horrigan, L., R.S. Lawrence, and P. Walker. 2002. How sustainable agriculture can address the environmental and human health harms of industrial agriculture. Research Review. Environ. Health Persp. 110: 445-456.

Hu, Q. and M.L. Brusseau. 1996. Transport of rate-limited sorbing solutes in an aggregated porous medium: A Multiprocess non-ideality approach. J. Contam. Hydrol. 24: 53-73.

Huang, X. and L.S. Lee. 2001. Effects of dissolved organic matter from animal waste effluent on chlorphyrifos sorption by soils. J. Environ. Qual. 30: 1258-1265.

Ingerslev, F. and B. Halling-Sorensen. 2000. Biodegradability properties of sulfonamides in activated sludge. Environ. Toxicol. Chem. 19: 2467-2473.

Ingerslev, F. and B. Halling-Sorensen. 2001. Biodegradability of metronidazole, olaquindox, and tylosin and formation of tylosin degradation products in aerobic soil-manure slurries. Ecotoxicol. Environ. Safety. 48: 311-320.

Ingerslev, F., L. Torang, M. Loke, B. Halling-Sorensen, and N. Nyholm. 2001. Primary biodegradation of veterinary antibiotics in aerobic and anaerobic surface water simulation systems. Chemosphere 44: 865-872.

Jardine, P.M., N.L. Weber, and J.F. McCarthy. 1989. Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci. Soc. Am. J. 53: 1378-1385.

Jardine, P.M., R. O'Brien, G.V. Wilson, and J.P. Gwo. 1998. Experimental techniques for confirming and quantifying physical nonequilibrium processes in soils. In Physical Nonequilibrium in Soils. Modeling and Application. Ed. H.M. Selim and L. Ma. Ann Arbor Press. Chelsea, Michigan.

Johnson, W.P. and G.L. Amy. 1995. Facilitated transport and enhanced desorption of polycyclic aromatic hydrocarbons by natural organic matter in aquifer sediments. Environ. Sci. Technol. 29: 807-817.

Jones, A.D., G.L. Bruland, S.G. Agrawal, and D. Vasudevan. 2005. Factors influencing the sorption of oxytetracycline to soils. Environ. Toxicol. Chem. 24: 761-770.

Kaiser, K., G. Guggenberger, L. Haumaier, and W. Zech. 1997. Dissolved organic matter sorption on subsoils and minerals studied by ^{13}C-NMR and DRIFT spectroscopy. European J. Soil Sci. 48: 301-310.

Kaiser, K., G. Guggenberger, and W. Zech. 1996. Sorption of DOM and DOM fractions to forest soils. Geoderma 74: 281-303.

Kaiser, K. and W. Zech. 1997. Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. Soil Sci. Soc. Am. J. 61: 64-69.

Kay, P., P.A. Blackwell, and A.B.A. Boxall. 2004. Fate of veterinary antibiotics in a macroporous tile drained clay soil. Environ. Toxicol. Chem. 23: 1136-1144.

Kay, P., P.A. Blackwell, and A.B.A. Boxall. 2005a. A lysimeter experiment to investigate the leaching of veterinary antibiotics through a clay soil and comparison with field data. Environ. Pollution. 134: 333-341.

Kay, P., P.A. Blackwell, and A.B.A. Boxall. 2005b. Column studies to investigate the fate of veterinary antibiotics in clay soils following slurry application to agricultural land. Chemosphere 60: 497-507.

Kay, P., P.A. Blackwell, and A.B.A. Boxall. 2005c. Transport of veterinary antibiotics in overland flow following the application of slurry to arable land. Chemosphere 59: 951-959.

Ketelle, R.H. and Huff, D.D. 1984. Site characterization of the west chestnut ridge site. Oak Ridge National Laboratory. Oak Ridge, TN.

Kolpin, D.W., E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, and H.T. Buxton. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environ. Sci. Technol. 36: 1202-1211.

Kolz, A.C., S.K. Ong, and T.B. Moorman. 2005. Sorption of tylosin onto swine manure. Chemosphere. 60: 284-289.

Kreuzig, R., S. Höltge, J. Brunotte, N. Berenzen, J. Wogram, and R. Schulz. 2005. Test-plot studies on runoff of sulfonamides from manured soils after sprinkler irrigation. Environ. Toxicol. Chem. 24: 777-781.

Kühne, M., D. Ihnen, G. Möller, and O. Agthe. 2000. Stability of tetracycline in water and liquid manure. J. Vet. Med. A 47: 379-384.

Kulshrestha, P., R.F. Giese,Jr., and D.S. Aga. 2004. Investigating the molecular interactions of oxytetracycline in clay and organic matter: insights on factors affecting its mobility in soil. Environ. Sci. Technol. 38: 4097-4105.

Kumar, K., A. Thompson, A.K. Singh, Y. Chander, and S.C. Gupta. 2004. Enzyme-linked immunosorbent assay for ultratrace determination of antibiotics in aqueous samples. J. Environ. Qual. 33: 250-256.

Kumar, K., S.C. Gupta, S.K. Baidoo, Y. Chander, and C.J. Rosen. 2005a. Antibiotic uptake by plants from soil fertilized with animal manure. J. Environ. Qual. 34: 2082-2085.

Kumar, K., S.C. Gupta, Y. Chander, and A.K. Singh. 2005b. Antibiotic use in agriculture and its impact on the terrestrial environment. In Advances in Agronomy. Vol. 87. Ed. D.L. Sparks. Academic Press. New York.

Laegdsmand, M., L.W. de Jonge, and P. Moldrup. 2005. Leaching of colloids and dissolved organic matter from columns packed with natural soil aggregates. Soil Sci. 170: 13-27.

Lambs, L., M. Brion, and G. Berthon. 1985. Metal ion-tetracycline interactions in biological fluids. Part 4. Potential influence of Ca^{2+} and Mg^{2+} ions on the bioavailability of chlortetracycline and demethylchlortetracycline, as expected from their computer-simulated distributions in blood plasma. Inorg. Chim. Acta. 106: 151-158.

Lambs, L., B.D. Reverend, H. Kozlowski, and G. Berthon. 1988. Metal ion-tetracycline interactions in biological fluids. 9. Circular dichroism spectra of calcium and magnesium complexes with tetracycline, oxytetracycline, doxycycline, and chlortetracycline and discussion of their binding modes. Inorg. Chem. 27: 3001-3012.

Langhammer, J.P. 1989. Rheinische Friedrich-Wilhelms Universität Bonn, Bonn. Germany. Ph.D. Thesis.

Langhammer, J.P., H. Büning-Pfaue, J. Winkelmann, and E. Körner. 1988. Chemotherapeutika-Rückstände und Resistenzverhalten bei der Bestandsbehandlung von Sauen post partum. Tierärztl. Umschau. 43: 375-382.

Leeson, J.J., J.E. Krueger, and R.A. Nash. 1963. Concerning the structural assignment of the second and third acidity constants of the tetracycline antibiotics. Tetrahedron Letters. 18: 1155-1160.

Levy, R. and C.W. Francis. 1976. Adsorption and desorption of cadmium by synthetic and natural organo-clay complexes. Geoderma. 15: 361-370.

Lin, C., W. Lin, Y. Chen, and S. Wang. 1997. Migration behavior and selectivity of sulfonamides in capillary electrophoresis. J. Chromatogr. A. 792: 37-47.

Lindsey, M.E., M. Meyer, and E.M. Thurman. 2001. Analysis of trace levels of sulfonamide and tetracycline antimicrobials in groundwater and surface water using solid-phase extraction and liquid chromatography/mass spectrometry. Anal. Chem. 73: 4640-4646.

Loke, M., J. Tjornelund, and B. Halling-Sorensen 2002. Determination of the distribution coefficient (log Kd) of oxytetracycline, tylosin A, olaquindox and metronidazole in manure. Chemosphere 48: 351-361.

Ma, L. and H.M. Selim. 1997. Evaluation of nonequilibrium models for predicting atrazine transport in soils. Soil Sci. Soc. Am. J. 61: 1299-1307.

MacKay, A.A. and B. Canterbury. 2005. Oxytetracycline sorption to organic matter by metal-bridging. J. Environ. Qual. 34: 1964-1971.

Martin S.R. 1979. Equilibrium and kinetic studies on the interaction of tetracyclines with calcium and magnesium. Biophys. Chem. 10: 319-326.

Martin B.R. 1985. Tetracyclines and daunorubicin. In Antibiotics and their complexes. Ed. Sigel, H. Marcel Dekker, New York. Vol. 19: 19-52.

Mathews Jr., K.H. 2001. Antimicrobial drug use and veterinary costs in U.S. livestock production. USDA Agriculture Information Bulletin 766.

Mattigod, S.V., Frampton, J.A., and C.H. Lim. 1985. Effect of ion-pair formation on boron adsorption by kaolinite. Clays and Clay Minerals 33: 433-437.

Mellon, M., C. Benbrook, and K.L. Benbrook. 2000. Hogging it. Estimates of antimicrobial abuse in livestock. UCS Publications. Cambridge, MA.

Merck. 2001. The Merck Index. 13th ed. Merck & Co., Inc. Whitehouse Station, NJ.

Mitscher, L.A. 1978. The chemistry of the tetracycline antibiotics. Marcel Dekker, Inc. New York.

Mitscher, L.A., B. Slater-Eng, and T.D. Sokoloski. 1972. Circular dichroism measurements of the tetracyclines. IV. 5-hydroxylated derivatives. Antimicrob. Agents Chemother. 2: 66-72.

Montforts, M.H.M.M, D.F. Kalf, P.L.A. van Vlaardingen, and J.B.H.J. Linders. 1999. The exposure assessment for veterinary medicinal products. Sci. Total Environ. 225: 119-133.

Murphy, E.M. and J.M. Zachara. 1995. The role of sorbed humic substances on the distribution of organic and inorganic contaminants in groundwater. Geoderma. 67: 103-124.

National Agriculture Statistics Service. 2002. 2002 Census of agriculture. Available at http://www.nass.usda.gov/census/census02/volume1/us/index1.htm. (verified 3 April 2006). USDA-NASS. Washington, DC.

Nielsen, D.R., M.Th. van Genuchten, and J.W. Biggar. 1986. Water flow and solute transport processes in the unsaturated zone. Water Resour. Res. 22: 89S-108S.

Onan, L.J. and T.M. LaPara. 2003. Tylosin-resistant bacteria cultivated from agricultural soil. FEMS Microbiol. Lett. 220:15-20.

Pang, L., M. Close, D. Schneider, and G. Stanton. 2002. Effect of pore-water velocity on chemical nonequilibrium transport of Cd, Zn, and Pb in alluvial gravel columns. J. Contam. Hydrol. 57: 241-258.

Papastephanou, C. and M. Frantz. 1978. Sulfamethazine. In Analytical Profiles of Drug Substances. Vol. 7. Ed. K. Florey. Academic Press. New York.

Parke, T.V. and W.W. Davis. 1954. Use of apparent dissociation constants in qualitative organic analysis. Anal. Chem. 26: 642-645.

Pennell, K.D. 2002. Specific surface area. In Methods of Soil Analysis, Part 4. Physical Methods. Ed. J.H. Dane and G.C. Topp. American Society of Agronomy-Soil Science Society of America. Madison, WI. pp 295-315.

Pinck, L.A., W.F. Holton, and F.E. Allison. 1961. Antibiotics in soils: 1. physico-chemical studies of antibiotic-clay complexes. Soil Sci. 91: 22-28.

Porubcan, L.S., C.J. Serna, J.L. White, and S.L. Hem. 1978. Mechanism of adsorption of clindamycin and tetracycline by montmorillonite. J. Pharm. Sci. 67: 1081-1087.

Prechtel, A., P. Knabner, E. Schneid, and K.U. Totsche. 2002. Simulation of carrier-facilitated transport of phenanthrene in a layered soil profile. J. Contam. Hydrol. 56: 209-225.

Pusino, A., A. Gelsomino, M.G. Fiori, and C. Gessa. 2003. Adsorption of two quinolinecarboxylic acid herbicides on homoionic montmorillonites. Clays Clay Miner. 51: 143-149.

Rabolle, M. and N.H. Spliid. 2000. Sorption and mobility of metronidazole, olaquindox, oxytetracycline and tylosin in soil. Chemosphere 40: 715-722.

Rao, P.S.C., J.M. Davidson, R.E. Jessup, and H.M. Selim. 1979. Evaluation of conceptual models for describing nonequilibrium adsorption-desorption of pesticides during steady-flow in soils. Soil Sci. Soc. Am. J. 43: 22-28.

Sachan, N.P. and C.M. Gupta. 1980. Electroanalytical studies of complexes of tetracyclines with Cd(II), Pb(II) and Cu(II) in aqueous medium. Talanta. 27: 457-459.

Sakurai, H. and T. Ishimitsu. 1980. Microionization constants of sulphonamides. Talanta. 27: 293-298.

Sarkar, D., M.E. Essington, and K.C. Misra. 2000. Adsorption of mercury(II) by kaolinite. Soil Sci. Soc. Am. J. 64: 1968-1975.

Sassman, S.A. and L.S. Lee. 2005. Sorption of three tetracyclines by several soils: assessing the role of pH and cation exchange. Environ. Sci. Technol. 39: 7452-7459.

Schneider, S. 2001. Proton and metal ion binding of tetracyclines. In Tetracyclines in Biology, Chemistry and Medicine. Ed. Nelson, M., W. Hillen, and R.A. Greenwald. Birkhäuser Verlag. Switzerland.

Selim, H.M. and M.C. Amacher. 1997. Reactivity and Transport of Heavy Metals in Soils. CRC/Lewis, Boca Raton, Florida.

Selim, H.M., J.M. Davidson, and P.S.C. Rao. 1977. Transport of reactive solutes through multilayered soils. Soil Sci. Soc. Am. J. 41: 3-10.

Sengelov, G. Y. Agerso, B. Halling-Sorensen, S.B., Baloda, J.S. Anderen, and L.B. Jensen. 2003. Bacterial antibiotic resistance levels in Danish farmland as a result of treatment with pig manure slurry. Environ. International. 28: 587-595.

Seol, Y. and L.S. Lee. 2000. Effect of dissolved organic matter in treated effluents on sorption of atrazine and prometryn by soils. Soil Sci. Soc. Am. J. 64: 1976-1983.

Sithole, B.B. and R.D. Guy. 1987a. Models for tetracycline in aquatic environments. I. Interactions with bentonite clay systems. Water Air Soil Pollut. 32: 303-314.

Sithole, B.B. and R.D. Guy. 1987b. Models for tetracycline in aquatic environments. II. Interactions with humic substances. Water Air Soil Pollut. 32: 315-321.

Sposito, G. 1984. The surface chemistry of soils. Oxford University Press. New York.

Srivastava, R. and M.L. Brusseau. 1996. Nonideal transport of reactive solutes in heterogeneous porous media: 1. Numerical model development and moments analysis. J. Contam. Hydrol. 24: 117-143.

Stephens, C.R., L.H. Conover, F.A. Hochstein, P.P. Regna, F.J. Pilgrim, K.J. Brunings and R.B. Woodward. 1952. Terramycin. VIII. Structure of aureomycin and terramycin. J. Am. Chem. Soc. 74: 4976-4977.

Stephens, C.R., L.H. Conover, R. Pasternack, F.A. Hochstein, W.T. Moreland, P.P. Regna, F.J. Pilgrim, K.J. Brunings and R.B. Woodward. 1954. The structure of aureomycin. J. Am. Chem. Soc. 76: 3568-3575.

Stephens, C.R., K. Murai, K.J. Brunings, and R.B. Woodward. 1956. Acidity constants of the tetracycline antibiotics. The structure of aureomycin. J. Am. Chem. Soc. 78: 4155-4158.

Stumm, W., C.P. Huang, and S.R. Jenkins. 1970. Specific chemical interactions affecting the stability of dispersed systems. Croat. Chim. Acta. 42: 223-244.

Suba, J.D. and M.E. Essington. 1999. Adsorption of fluometuron and norflurazon: effect of tillage and dissolved organic carbon. Soil Sci. 164: 145-155.

Sumner, M.E. and W.P. Miller. 1996. Cation exchange capacity and exchange coefficients. In Methods of Soil Analysis, Part 3. Chemical Methods. Ed. Sparks, D.L. American Society of Agronomy-Soil Science Society of America. Madison, WI. pp 1201-1229.

Swift, R.S. 1996. Organic matter characterization. In Methods of Soil Analysis, Part 3. Chemical Methods. Ed. Sparks, D.L. American Society of Agronomy-Soil Science Society of America. Madison, WI. pp 1011-1070.

Teeter, J.S. and R.D. Meyerhoff. 2003. Aerobic degradation of tylosin in cattle, chicken, and swine excreta. Environ. Res. 93: 45-51.

Thiele-Bruhn, S., T. Seibicke, H.R. Schulten, and P. Leinweber. 2004. Sorption of sulfonamide pharmaceutical antibiotics on whole soils and particle-size fractions. J. Environ. Qual. 33: 1331-1342.

Thomas, G.W. 1996. Soil pH and soil acidity. In Methods of Soil Analysis, Part 3. Chemical Methods. Ed. Sparks, D.L. American Society of Agronomy-Soil Science Society of America. Madison, WI. pp 475-490.

Thurman, E.M. and M.E. Lindsey. 2000. Transport of antibiotics in soil and their potential for groundwater contamination. 3rd SETAC World Congress, Brighton, UK.

Tipping, E. 1981. The adsorption of aquatic humic substances to iron oxides. Geochim. Cosmochim. Acta 45: 463-466.

Tolls, J. 2001. Sorption of veterinary pharmaceuticals in soils: A review. Environ. Sci. Tech. 35: 3397-3406.

Tongaree, S., D.R. Flanagan, and R.I. Poust. 1999. The interaction between oxytetracycline and divalent metal ions in aqueous and mixed solvent systems. Pharm. Dev. Technol. 4: 581-591.

Toride, N., F.J. Leij, and M. Th. Van Genuchten. 1999. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.1. Res. Rep. No. 137. U.S. Salinity Laboratory. ARS-USDA, Riverside, CA.

Totsche, K.U. and I. Kögel-Knabner. 2004. Mobile organic sorbent affected contaminant transport in soil: Numerical case studies for enhanced and reduced mobility. Vadose Zone J. 3: 352-367.

Totsche, K.U., J. Danzer, and I. Kögel-Knabner. 1997. Dissolved organic matter-enhanced retention of polycyclic aromatic hydrocarbons in soil miscible displacement experiments. J. Environ. Qual. 26: 1090-1100.

Vaclavik, E., B. Halling-Sorensen, and F. Ingerslev. 2004. Evaluation of manometric respiration tests to assess the effects of veterinary antibiotics in soil. Chemosphere 56: 667-676.

van Genuchten, M.Th. 1981. Non-equilibrium transport parameters from miscible displacement experiments. Research Report No. 119. U.S. Salinity Laboratory. U.S. Department of Agriculture. Riverside, CA.

van Genuchten, M.Th. and P.J. Wierenga. 1976. Mass transfer studies in sorbing porous media. I. Analytical solutions. Soil Sci. Soc. Am. J. 40: 473-481.

van Genuchten, M.Th. and R.J. Wagenet. 1989. Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. Soil Sci. Soc. Am. J. 53: 1303-1310.

Wanner, H., Y. Albinsson, O. Karnland, E. Wieland, P. Wersin, and L. Charlet. 1994. The acid/base chemistry of montmorillonite. Radiochimica Acta. 66/67: 157-162.

Ward, D.B. and P.V. Brady. 1998. Effect of Al and organic acids on the surface chemistry of kaolinite. Clays and Clay Minerals. 46: 453-465.

Wessels, J.M., W.E. Ford, W. Szymczak, and S. Schneider. 1998. The complexation of tetracycline and anhydrotetracycline with Mg^{2+} and Ca^{2+}: a spectroscopic study. J. Phys. Chem. B. 102: 9323-9331.

Williams, C.F., M. Agassi, J. Letey, W.J. Farmer, S.D. Nelson, and M. Ben-Hur. 2000. Facilitated transport of napropamide by dissolved organic matter through soil columns. Soil Sci. Soc. Am. J. 64: 590-594.

Winckler, C. and A. Grafe. 2001. Use of veterinary drugs in intensive animal production evidence for persistence of tetracycline in pig slurry. J. Soils and Sediments. 1: 66-70.

Wolf, D.C., T.H. Dao, H.D. Scott, and T.L. Lavy. 1989. Influence of sterilization methods on selected soil microbiological, physical, and chemical properties. J. Environ. Qual. 18: 39-44.

Wollenberger, L., B. Halling-Sorensen, and K.O. Kusk. 2000. Acute and chronic toxicity of veterinary antibiotics to *Daphnia magna*. Chemosphere 40: 723-730.

Yang, S., J. Cha, and K. Carlson. 2004. Quantitative determination of trace concentrations of tetracycline and sulfonamide antibiotics in surface water using solid-phase extraction and liquid chromatography/ion trap tandem mass spectrometry. Rapid Commun. Mass Spectrom. 18: 2131-2145.

Yang, S. and K. Carlson. 2004. Routine monitoring of antibiotics in water and wastewater with a radioimmunoassay technique. Water Res. 38: 3155-3166.

Young, D.F. and W.P. Ball. 1995. Effects of column conditions on the first-order rate modeling of nonequilibrium solute breakthrough. Water Resour. Res. 31: 2181-2192.

APPENDIX

Table 3.1. Macroscopic acidity constant (pK_a) for CTC.

pK_1	pK_2	pK_3	Temperature, Ionic strength	Reference
3.30	7.44	9.27	20°C, 0.005	Albert (1953)
-	7.35	8.89	23.5°C, 0.15	Martin (1979)
3.30	7.44	9.27	25°C, 0.00†	Stephens et al. (1956)
3.27	7.36	9.22	25°C, 0.01	Leeson et al. (1963)
3.27	7.43	9.33	25°C, 0.01	Benet and Goyan (1965)
3.66	7.40	9.06	30°C, 0.01	Doluisio and Martin (1963)
3.40	7.08	8.44	30°C, 0.10	Sachan and Gupta (1980)
3.08	7.02	8.70	37°C, 0.15	Lambs et al. (1985)
3.14	7.33	9.24	nd‡	Parke and Davis (1954)
3.4	7.4	9.2	nd	Stephens et al. (1952, 1954)

† extrapolation to zero ionic strength

‡ nd: not described

Table 3.2. Chemical and physical properties of the clay and soils used in this study.

Sample	Sand/silt/clay fractions %	Particle density g cm^{-3}	Surface area M^2 g^{-1}	pH 1:1 H_2O	Total C g kg^{-1}	DOC[†] mg L^{-1}	CEC[‡] cmol kg^{-1}
Kaolinite	-	-	22(±2)[§]	-	-	-	2.2(±0.1)
Montmorillonite	-	-	523(±53)	-	-	-	104 (±1)
CL-S[¶]	26/45/29	2.62(±0.01)	60(±1)	5.6(±0.1)	16(±1)	7.1(±0.2)	11.7(±0.1)
CL-SS	19/37/44	2.66(±0.01)	78(±1)	5.8(±0.1)	6(±0)	2.9(±0.1)	11.9(±0.7)
SL-S	56/26/18	2.61(±0.02)	26(±1)	5.9(±0.0)	15(±0)	9.7(±0.3)	10.6(±0.1)
SL-SS	45/35/20	2.65(±0.01)	42(±2)	5.7(±0.0)	2(±0)	4.2(±0.0)	6.0(±0.0)

[†] DOC= Dissolved organic carbon.

[‡] CEC= Cation exchange capacity.

[§] Values in parentheses are standard deviation (sample number = 3).

[¶] CL= Etowah clay loam; SL= Captina sandy loam;
S= surface (0-15 cm); SS= subsurface (30-45 cm).

Table 3.3. HPLC conditions for the analysis of antibiotics.

Antibiotic[†]	Column	Mobile phase	Input µl	Flow rate ml min^{-1}	Detection nm	Rt[‡] min	MDL[§] mgL^{-1}
CTC	Phenomenex® Luna C18(2) 25 cm×4.6 mm 5 µm	Acetonitrile-water, pH 2.1 (H_2SO_4) gradient (15:85 to 60:40 over 12 min)	80	0.7	380	10.1	0.02
TYL	Ascentis® C18 15 cm×4.6 mm 5 µm	Acetonitrile-0.01M KH_2PO_4 gradient (20:80 to 60:40 over 10min)	100	1.0	280	7.8	0.02
SMT	Phenomenex® Luna C18(2) 25 cm×4.6 mm 5 µm	Acetonitrile-water gradient (15:85 to 60:40 over 12 min)	80	1.0	254	8.7	0.05

[†] CTC= Chlortetracycline; TYL= Tylosin; SMT= Sulfamethazine

[‡] Rt= Retention time

[§] MDL= Method detection limit

Table 3.4. Intrinsic acidity constants of the surface protolysis reactions.

Clay	Surface protolysis reaction	log K^{int}	Reference
Montmorillonite	$\equiv SOH_2^+ \leftrightarrow \equiv SOH + H^+$	5.4	Wanner et al., 1994
	$\equiv SOH \leftrightarrow \equiv SO^- + H^+$	-6.7	
Kaolinite	$\equiv SiOH_2^+ \leftrightarrow \equiv SiOH + H^+$	2.77	Sarkar et al., 2000
	$\equiv SiOH \leftrightarrow \equiv SiO^- + H^+$	-6.77	
	$\equiv AlOH_2^+ \leftrightarrow \equiv AlOH + H^+$	4.7	
	$\equiv AlOH \leftrightarrow \equiv AlO^- + H^+$	-8.7	

Table 3.5. Experimental conditions of the soil column studies for DOC effect on mobility of antibiotics.

Antibiotic[†]	Soil[‡]	Column number	Column length m	Bulk density g cm^{-3}	Water content $m^3 m^{-3}$	Pore water velocity m h^{-1}	Pulse input PV[§]	Input concentration	
								Antibiotic $\times 10^{-3}$ M	DOC[¶] mgL^{-1}
CTC	SL-S	1	0.05	1.15	0.56	0.14	6	0.19	0
	SL-S	2	0.05	1.19	0.54	0.10	6	0.19	63
	SL-SS	3	0.05	1.31	0.51	0.08	6	0.58	0
	SL-SS	4	0.05	1.28	0.52	0.09	6	0.58	21
TYL	SL-S	5	0.10	1.19	0.54	0.12	5	0.09	0
	SL-S	6	0.10	1.19	0.54	0.13	5	0.09	63
	SL-SS	7	0.10	1.35	0.49	0.04	5	0.38	0
	SL-SS	8	0.10	1.27	0.52	0.09	5	0.38	63
SMT	SL-S	9	0.10	1.25	0.52	0.04	2	0.07	0
	SL-S	10	0.10	1.25	0.52	0.06	2	0.07	63
	SL-SS	11	0.10	1.36	0.49	0.04	2	0.07	0
	SL-SS	12	0.10	1.36	0.49	0.05	2	0.07	63

[†] CTC= Chlortetracycline; TYL= Tylosin; SMT= Sulfamethazine.

[‡] SL= Captina sandy loam; S= surface (0-15 cm); SS= subsurface (30-45 cm).

[§] PV= Pore volume.

[¶] DOC= Dissolved organic carbon.

Table 3.6. Estimated partitioning coefficient (β) and mass transfer coefficient (ω).

Column number	Soil	DOC[†] (mgL^{-1})	β[‡]	ω[‡]
1	Surface	0	0.998 (±0.023)	1.9×10^{-4} (±0.018)
2	Surface	63	0.972 (±0.136)	4.8×10^{-3} (±0.086)
3	Subsurface	0	1.000 (±0.017)	1.0×10^{-7} (±0.000)
4	Subsurface	21	0.962 (±0.075)	5.3×10^{-3} (±0.058)
5	Surface	0	0.650 (±0.022)	0.371 (±0.037)
6	Surface	63	0.661 (±0.026)	0.330 (±0.041)
7	Subsurface	0	0.997 (±0.012)	1.0×10^{-7} (±0.000)
8	subsurface	63	1.000 (±0.013)	1.0×10^{-7} (±0.000)
9	Surface	0	1.000 (±0.031)	1.0×10^{-7} (±0.000)
10	Surface	63	1.000 (±0.033)	1.0×10^{-7} (±0.000)
11	Subsurface	0	1.000 (±0.039)	8.6×10^{-5} (±0.081)
12	Subsurface	63	0.998 (±0.023)	1.8×10^{-2} (±0.113)

[†] DOC= dissolved organic carbon added to input solution.

[‡] Values in parentheses are standard error.

Table 3.7. Freundlich coefficient (K_F) and exponent (N) of chlortetracycline (CTC).

Clay/Soil	Ionic strength	Background cation	DOC[†] (mgL^{-1})	K_F[‡]	N[‡]	r^2[§]	adjusted r^2[¶]
Montmorillonite	0.005	Na	0	$1.38(\pm0.03)\times10^{5}$	0.22(±0.02)	0.993	0.991
	0.01	Na	0	$1.28(\pm0.01)\times10^{5}$	0.21(±0.01)	0.988	0.985
	0.05	Na	0	$1.09(\pm0.01)\times10^{5}$	0.18(±0.01)	0.985	0.981
	0.03	Ca	0	$9.90(\pm0.07)\times10^{4}$	0.17(±0.01)	0.989	0.986
	0.03	Ca	21	$8.08(\pm0.07)\times10^{4}$	0.30(±0.01)	0.995	0.994
Kaolinite	0.005	Na	0	$3.31(\pm0.12)\times10^{3}$	0.31(±0.03)	0.961	0.951
	0.01	Na	0	$3.03(\pm0.11)\times10^{3}$	0.29(±0.03)	0.956	0.945
	0.05	Na	0	$2.26(\pm0.05)\times10^{3}$	0.33(±0.01)	0.985	0.981
	0.03	Ca	0	$1.36(\pm0.04)\times10^{3}$	0.34(±0.02)	0.976	0.970
	0.03	Ca	21	-[#]	-		
CL-S[††]	0.01	Na	0	$5.51(\pm0.10)\times10^{3}$	0.51(±0.02)	0.990	0.988
	0.03	Ca	0	$4.84(\pm0.04)\times10^{3}$	0.69(±0.01)	0.998	0.998
	0.03	Ca	21	$2.75(\pm0.18)\times10^{3}$	0.88(±0.08)	0.978	0.973
CL-SS	0.01	Na	0	$7.64(\pm0.16)\times10^{3}$	0.44(±0.03)	0.964	0.955
	0.03	Ca	0	$6.23(\pm0.15)\times10^{3}$	0.45(±0.04)	0.971	0.964
	0.03	Ca	21	$2.86(\pm0.17)\times10^{3}$	0.66(±0.06)	0.976	0.970
SL-S	0.01	Na	0	$4.72(\pm0.09)\times10^{3}$	0.55(±0.04)	0.982	0.978
	0.03	Ca	0	$2.40(\pm0.05)\times10^{3}$	0.65(±0.04)	0.977	0.971
	0.03	Ca	21	-[#]	-		
SL-SS	0.01	Na	0	$4.69(\pm0.09)\times10^{3}$	0.28(±0.02)	0.981	0.976
	0.03	Ca	0	$3.61(\pm0.09)\times10^{3}$	0.36(±0.04)	0.937	0.921
	0.03	Ca	21	$2.00(\pm0.05)\times10^{3}$	0.35(±0.02)	0.985	0.981

[†] DOC= Dissolved organic carbon added to the sorption systems.

[‡] Values in parentheses are standard error.

[§] r^2 = coefficient of determination for the regression of observed versus fitted data.

[¶] adjusted $r^2 = 1-a\times(1-r^2)/(a-p)$ where a is the number of observations used to fit the model and p is the number of parameters in the model.

[#] Better fits were obtained with Langmuir isotherm model. Langmuir coefficient and b for kaolinite were 0.54(±0.08) L kg^{-1} and 0.89(±0.05) mmol kg^{-1}, respectively, and 0.43(±0.09) L kg^{-1} and 4.72(±0.43) mmol kg^{-1} for sandy loam surface soil. Their r^2 were 0.982 and 0.949, respectively. Their adjusted r^2 were 0.978 and 0.936, respectively.

[††] CL= Etowah clay loam; SL= Captina sandy loam;

S= surface (0-15 cm); SS= subsurface (30-45 cm).

Table 3.8. Freundlich coefficient (K_F) and exponent (N) of tylosin (TYL).

Clay/Soil	Ionic strength	Background cation	DOC[†] (mgL^{-1})	K_F[‡]	N[‡]	r^2[§]	Adjusted r^2[¶]
Montmo-rillonite	0.005	Na	0	$1.33(\pm0.01)\times10^{5}$	0.24(±0.01)	0.998	0.998
	0.01	Na	0	$1.18(\pm0.01)\times10^{5}$	0.24(±0.00)	0.998	0.998
	0.05	Na	0	$7.31(\pm0.20)\times10^{4}$	0.35(±0.02)	0.992	0.990
	0.03	Ca	0	$6.65(\pm0.19)\times10^{4}$	0.24(±0.02)	0.972	0.965
	0.03	Ca	21	$5.02(\pm0.09)\times10^{4}$	0.34(±0.01)	0.996	0.995
	0.03	Ca	63	$4.93(\pm0.08)\times10^{4}$	0.30(±0.01)	0.996	0.995
Kaolinite	0.005	Na	0	273(±9)	0.26(±0.02)	0.973	0.966
	0.01	Na	0	190(±5)	0.39(±0.02)	0.988	0.985
	0.05	Na	0	157(±8)	0.34(±0.03)	0.948	0.935
	0.03	Ca	0	98(±3)	0.48(±0.02)	0.991	0.989
	0.03	Ca	21	27(±4)	0.91(±0.06)	0.982	0.978
	0.03	Ca	63	15(±4)	0.67(±0.14)	0.820	0.775
CL-S[#]	0.01	Na	0	82(±1)	1.00(±0.03)	0.997	0.996
	0.03	Ca	0	24(±2)	0.77(±0.04)	0.993	0.991
	0.03	Ca	21	22(±2)	0.80(±0.04)	0.990	0.988
	0.03	Ca	63	16(±1)	0.97(±0.03)	0.998	0.998
CL-SS	0.01	Na	0	341(±11)	0.63(±0.02)	0.997	0.996
	0.03	Ca	0	161(±8)	0.53(±0.03)	0.986	0.983
	0.03	Ca	21	166(±4)	0.52(±0.01)	0.997	0.996
	0.03	Ca	63	142(±6)	0.56(±0.02)	0.990	0.988
SL-S	0.01	Na	0	67(±4)	0.68(±0.04)	0.989	0.986
	0.03	Ca	0	17(±2)	0.76(±0.06)	0.983	0.979
	0.03	Ca	21	15(±2)	0.79(±0.07)	0.974	0.968
	0.03	Ca	63	12(±1)	0.83(±0.04)	0.990	0.988
SL-SS	0.01	Na	0	325(±17)	0.56(±0.03)	0.993	0.991
	0.03	Ca	0	173(±8)	0.40(±0.02)	0.985	0.981
	0.03	Ca	21	152(±6)	0.48(±0.02)	0.992	0.990
	0.03	Ca	63	132(±5)	0.46(±0.02)	0.990	0.988

[†] DOC= Dissolved organic carbon added to the sorption systems.

[‡] Values in parentheses are standard error.

[§] r^2 = coefficient of determination for the regression of observed versus fitted data.

[¶] adjusted $r^2 = 1-a\times(1-r^2)/(a-p)$ where a is the number of observations used to fit the model and p is the number of parameters in the model.

[#] CL= Etowah clay loam; SL= Captina sandy loam;

S= surface (0-15 cm); SS= subsurface (30-45 cm).

Table 3.9. Cooperative sorption model parameters for sulfamethazine (SMT).

Clay	Ionic strength	Background cation	m[†] (μmol kg^{-1})	K_1[‡]	K_n[‡]	n[§]	r^2[¶]	adjusted r^2[#]
Montmo-rillonite	0.005	Na	310(±400)[††]	10^{-8}	82(±196)	1.32(±0.23)	0.993	0.988
	0.01	Na	84(±16)	10^{-8}	897(±274)	1.56(±0.09)	0.982	0.970
	0.05	Na	215(±134)	10^{-8}	149(±214)	1.37(±0.17)	0.996	0.993
	0.03	Ca	654(±4065)	10^{-8}	15(±126)	1.17(±0.39)	0.986	0.977
Kaolinite	0.005	Na	27.8(±2.6)	10^{-8}	$1.4(\pm0.3)\times10^3$	1.37(±0.06)	0.984	0.973
	0.01	Na	27.2(±7.2)	10^{-8}	$1.4(\pm1.9)\times10^3$	1.39(±0.22)	0.979	0.965
	0.05	Na	30.6(±3.5)	10^{-8}	$8.8(\pm2.0)\times10^2$	1.32(±0.06)	0.980	0.967

[†] m = total sorption sites per unit mass of sorbent.

[‡] K_1, K_n = equilibrium constants for sorption of monomers and clusters, respectively.

[§] n = average number of molecules that sorb together.

[¶] r^2 = coefficient of determination for the regression of observed versus fitted data.

[#] adjusted $r^2 = 1 - a\times(1-r^2)/(a-p)$ where a is the number of observations used to fit the model and p is the number of parameters in the model.

[††] Values in parentheses are standard error.

Table 3.10. Freundlich coefficient (K_F) and exponent (N) for sulfamethazine (SMT).

Clay/Soil	Ionic strength	Background cation	DOC[†] (mgL^{-1})	K_F[‡]	N[‡]	r^2[§]	adjusted r^2[¶]
Montmorillonite	0.03	Ca	21	14.4(±2.3)	0.80(±0.08)	0.966	0.958
Kaolinite	0.03	Ca	21	-[#]	-		
CL-S[††]	0.01	Na	0	3.7(±0.1)	0.79(±0.02)	0.998	0.998
	0.03	Ca	0	3.1(±0.1)	0.80(±0.01)	0.999	0.999
	0.03	Ca	21	3.9(±0.1)	0.84(±0.02)	0.998	0.998
CL-SS	0.01	Na	0	0.85(±0.03)	0.84(±0.02)	0.990	0.988
	0.03	Ca	0	0.78(±0.02)	0.82(±0.01)	0.999	0.999
	0.03	Ca	21	1.3(±0.0)	0.77(±0.02)	0.998	0.998
SL-S	0.01	Na	0	3.7(±0.1)	0.80(±0.02)	0.998	0.998
	0.03	Ca	0	3.2(±0.1)	0.82(±0.02)	0.999	0.999
	0.03	Ca	21	3.7(±0.2)	0.86(±0.03)	0.994	0.993
SL-SS	0.01	Na	0	0.40(±0.02)	0.85(±0.02)	0.997	0.996
	0.03	Ca	0	0.37(±0.02)	0.77(±0.02)	0.997	0.996
	0.03	Ca	21	0.70(±0.04)	0.72(±0.03)	0.993	0.991

[†] DOC= Dissolved organic carbon added to the sorption systems.

[‡] Values in parentheses are standard error.

[§] r^2 = coefficient of determination for the regression of observed versus fitted data.

[¶] adjusted $r^2 = 1-a\times(1-r^2)/(a-p)$ where a is the number of observations used to fit the model and p is the number of parameters in the model.

[#] Better fits were obtained with Langmuir isotherm model. Langmuir coefficient and b were 2.21(±0.52) L kg^{-1} and 2.98(±0.14) μmol kg^{-1}, respectively. The r^2 and adjusted r^2 were 0.826 and 0.783, respectively.

[††] CL= Etowah clay loam; SL= Captina sandy loam;

S= surface (0-15 cm); SS= subsurface (30-45 cm).

Table 3.11. Column transport parameter estimates obtained from CXTFIT program for chlortetracycline (CTC).

Parameter[†]	Surface soil[‡]		Subsurface soil[‡]	
	DOC[§] absent	DOC present	DOC absent	DOC present
D (cm^2 h^{-1})	78.2(±0.9)	26.3(±5.2)	6.41(±0.54)	9.14(±1.86)
R (Cl^-)	0.999(±0.019)	1.001(±0.065)	0.999(±0.016)	1.000(±0.042)
λ (cm)	5.79	2.69	0.84	1.04
r^2 (Cl^-)	0.99	0.97	1.00	0.97
R (CTC)	760(±30)	351(±10)	1,020(±30)	391(±27)
K_d (L kg^{-1})	370	159	413	158
f	0.11(±0.00)	0.053(±0.002)	0.079(±0.002)	0.018(±0.001)
α (h^{-1})	0.12(±0.01)	0.085(±0.003)	0.064(±0.003)	0.027(±0.002)
r^2 (CTC)	0.99	0.91	0.95	0.92

[†] D = dispersion coefficient; R = retardation factor; λ = dispersivity; K_d = sorption coefficient; f = fraction of exchange sites that are always at equilibrium; α = first-order kinetic rate coefficient; r^2 = coefficient of determination for the regression of observed versus fitted data. The D, R (Cl^-), and λ parameters were estimated from chloride (Cl^-) breakthrough curves (BTCs) while R (CTC), K_d, f, and α parameters from CTC BTCs.

[‡] Values in parentheses are standard error.

[§] DOC= dissolved organic carbon added to input solution.

Table 3.12. Column transport parameter estimates obtained from CXTFIT program for tylosin (TYL).

Parameter[†]	Surface soil[‡]		Subsurface soil[‡]	
	DOC[§] absent	DOC present	DOC absent	DOC present
D (cm^2 h^{-1})	57.3(±2.0)	69.7(±2.9)	2.67(±0.25)	7.76(±0.67)
R (Cl$^-$)	1.002(±0.011)	1.003(±0.014)	0.997(±0.012)	1.000(±0.012)
λ (cm)	4.90	5.20	0.68	0.91
r^2 (Cl$^-$)	1.00	1.00	0.99	0.99
R (TYL)	14.1(±0.9)	9.91(±1.52)	24.0(±1.0)	21.0(±0.6)
K_d (L kg^{-1})	5.94	4.04	8.35	8.19
f	0.23(±0.02)	0.32(±0.06)	0.19(±0.01)	0.14(±0.01)
α (h^{-1})	0.093(±0.011)	0.29(±0.11)	0.038(±0.003)	0.10(±0.01)
r^2 (TYL)	0.99	0.91	0.87	0.89

[†] D = dispersion coefficient; R = retardation factor; λ = dispersivity; K_d = sorption coefficient; f = fraction of exchange sites that are always at equilibrium; α = first-order kinetic rate coefficient; r^2 = coefficient of determination for the regression of observed versus fitted data. The D, R (Cl$^-$), and λ parameters were estimated from chloride (Cl$^-$) breakthrough curves (BTCs) while R (TYL), K_d, f, and α parameters from TYL BTCs.

[‡] Values in parentheses are standard error.

[§] DOC= dissolved organic carbon added to input solution.

Table 3.13. Column transport parameter estimates obtained from CXTFIT program for sulfamethazine (SMT).

Parameter[†]	Surface soil[‡]		Subsurface soil[‡]	
	DOC[§] absent	DOC present	DOC absent	DOC present
D ($\mathrm{cm^2\ h^{-1}}$)	10.8(±0.8)	30.4(±1.8)	4.03(±0.24)	5.19(±0.48)
R ($\mathrm{Cl^-}$)	0.999(±0.026)	1.000(±0.025)	1.001(±0.010)	1.001(±0.016)
λ (cm)	2.99	5.0	1.02	1.05
r^2 ($\mathrm{Cl^-}$)	0.97	0.99	0.99	0.98
R (SMT)	2.92(±0.07)	2.08(±0.02)	1.48(±0.17)	1.84(±0.41)
K_d ($\mathrm{L\ kg^{-1}}$)	0.80	0.45	0.17	0.30
f	0.057(±0.026)	0.56(±0.02)	0.38(±0.32)	0.21(±0.11)
α ($\mathrm{h^{-1}}$)	0.24(±0.02)	0.68(±0.12)	0.11(±0.06)	0.071(±0.035)
r^2 (SMT)	0.99	1.00	0.99	0.99

[†] D = dispersion coefficient; R = retardation factor; λ = dispersivity; K_d = sorption coefficient; f = fraction of exchange sites that are always at equilibrium; α = first-order kinetic rate coefficient; r^2 = coefficient of determination for the regression of observed versus fitted data. The D, R ($\mathrm{Cl^-}$), and λ parameters were estimated from chloride ($\mathrm{Cl^-}$) breakthrough curves (BTCs) while R (SMT), K_d, f, and α parameters from SMT BTCs.

[‡] Values in parentheses are standard error.

[§] DOC= dissolved organic carbon added to input solution.

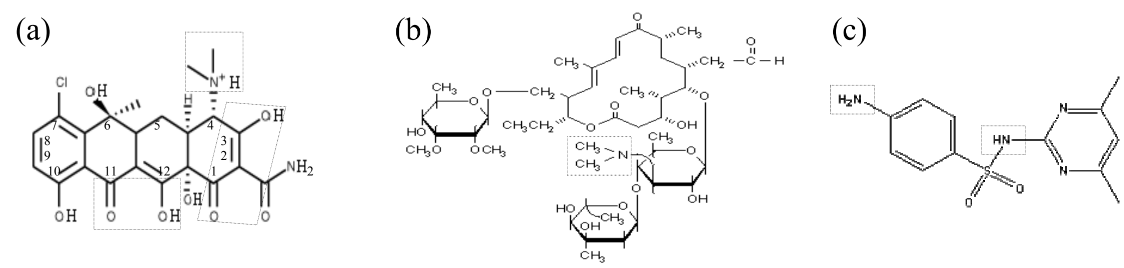

Figure 3.1. Chemical structure of (a) chlortetracycline (CTC), (b) tylosin (TYL), and (c) sulfamethazine (SMT).

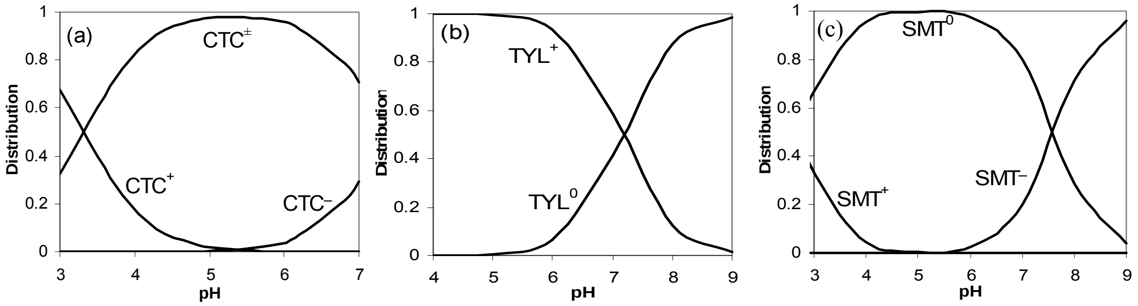

Figure 3.2. Solution speciation of (a) chlortetracycline (CTC), (b) tylosin (TYL), and (c) sulfamethazine (SMT).

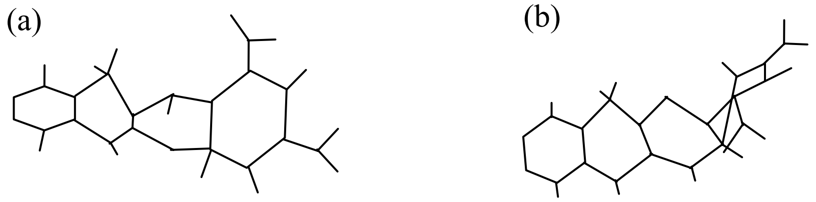

Figure 3.3. Two conformations of chlortetracycline (CTC). (a) extended conformation. (b) twisted conformation.

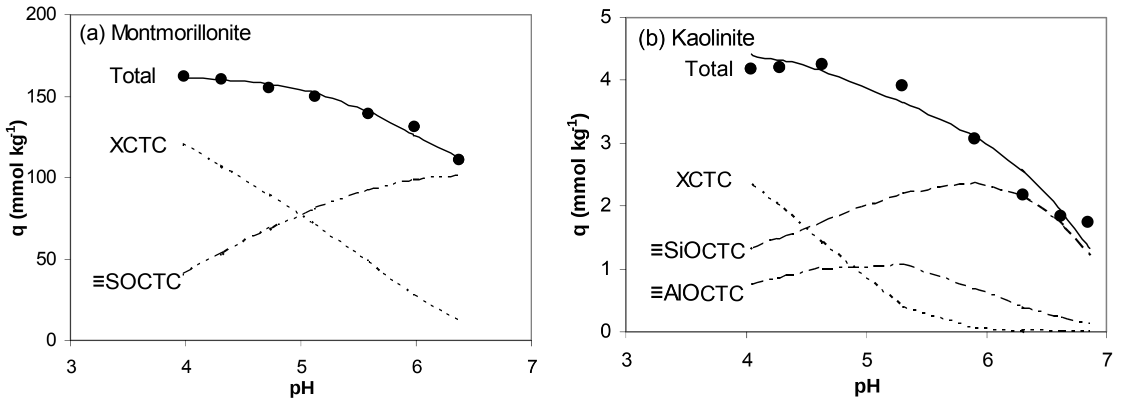

Figure 3.4. Effect of pH on chlortetracycline (CTC) sorption. Closed circles represent experimental data and lines represent modeled complexes. The sorption data were obtained by equilibrating 0.45 g L^{-1} of Na^+-saturated montmorillonite or 3.6 g L^{-1} of Na^+-saturated kaolinite in 0.01 M $NaNO_3$ containing 0.072 mM CTC. The suspensions were equilibrated for 48 h at 20 to 22°C.

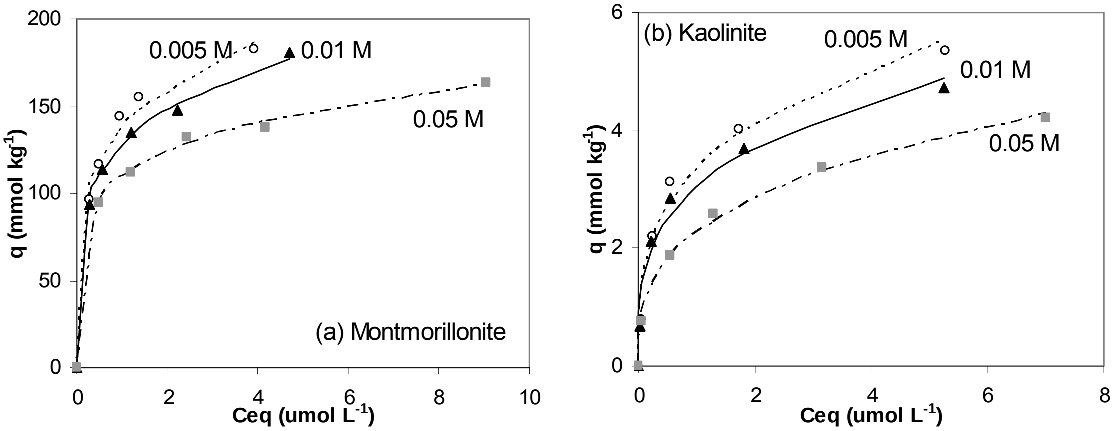

Figure 3.5. Ionic strength effect on chlortetracycline (CTC) sorption. Symbols represent experimental data and lines represent Freundlich isotherm models for which the parameters are listed in Table 3.7. The sorption data were obtained by equilibrating 0.45 g L^{-1} of Na^+-saturated montmorillonite or 3.6 g L^{-1} of Na^+-saturated kaolinite in 0.005-0.05 M $NaNO_3$ containing 0.003-0.087 mM CTC. Solution pH values were 4.4 (montmorillonite) and 5.3 (kaolinite). The suspensions were equilibrated for 48 h at 20 to 22°C.

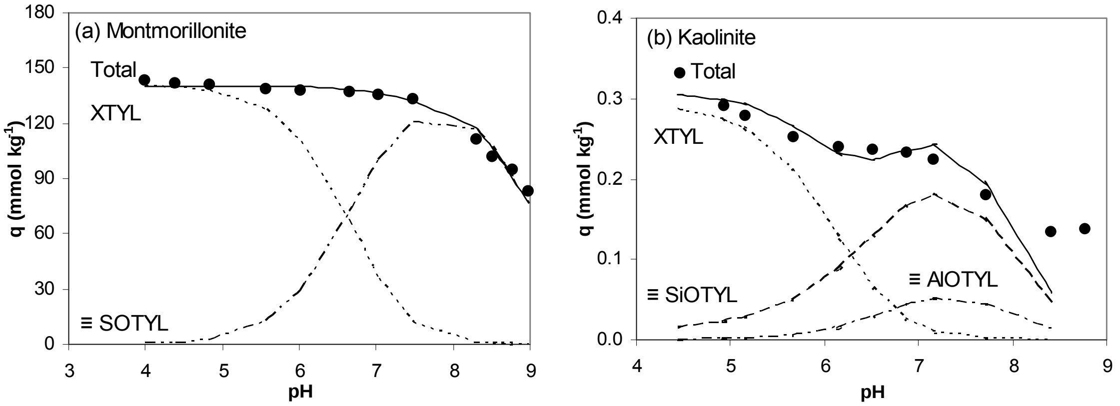

Figure 3.6. Effect of pH on tylosin (TYL) sorption. Closed circles represent experimental data and lines represent modeled complexes. The sorption data were obtained by equilibrating 0.30 g L^{-1} of Na$^+$-saturated montmorillonite or 6.0 g L^{-1} of Na$^+$-saturated kaolinite in 0.01 M NaNO$_3$ containing 0.038 mM TYL. The suspensions were equilibrated for 24 h at 20 to 22°C.

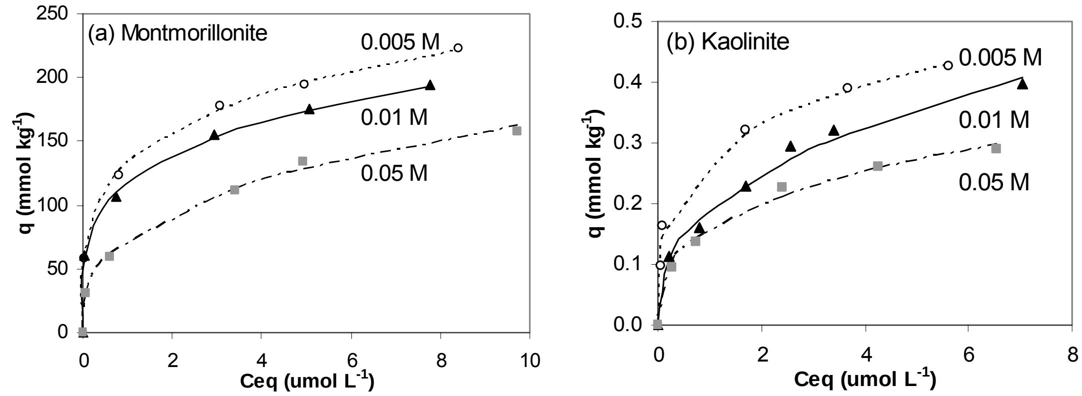

Figure 3.7. Ionic strength effect on tylosin (TYL) sorption. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.8. The sorption data were obtained by equilibrating 0.30 g L^{-1} of Na$^+$-saturated montmorillonite or 6.0 g L^{-1} of Na$^+$-saturated kaolinite in 0.005-0.05 M NaNO$_3$ containing 0.0008-0.059 mM TYL. Solution pH values were 5.6 (montmorillonite) and 5.7 (kaolinite). The suspensions were equilibrated for 24 h at 20 to 22°C.

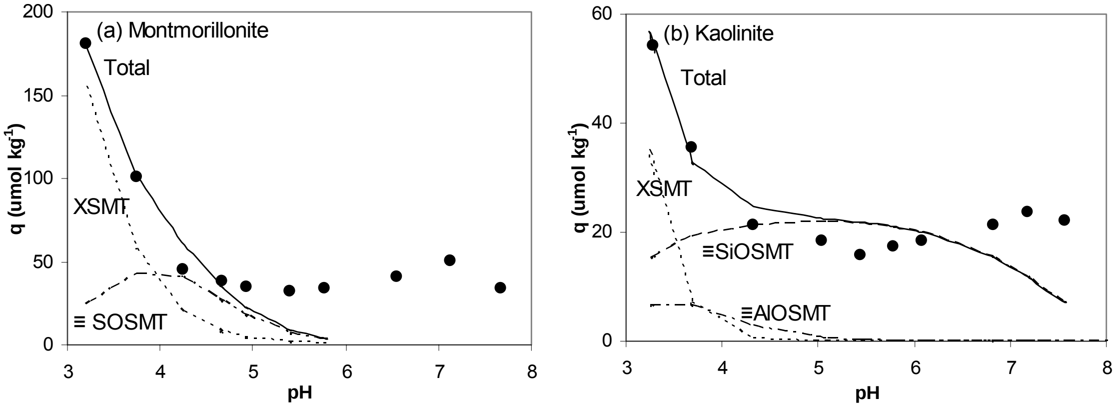

Figure 3.8. Effect of pH on sulfamethazine (SMT) sorption. Closed circles represent experimental data and lines represent modeled complexes. The sorption data were obtained by equilibrating 6.5 g L^{-1} of Na^+-saturated montmorillonite or 20 g L^{-1} of Na^+-saturated kaolinite in 0.01 M $NaNO_3$ containing 0.005 mM SMT. The suspensions were equilibrated for 24 h at 20 to 22°C.

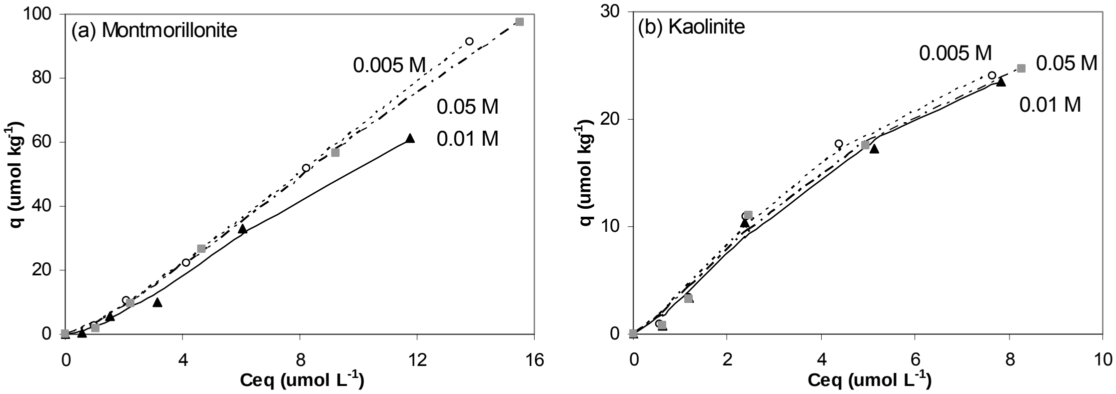

Figure 3.9. Ionic strength effect on sulfamethazine (SMT) sorption. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.9. The sorption data were obtained by equilibrating 6.5 g L^{-1} of Na^+-saturated montmorillonite or 20 g L^{-1} of Na^+-saturated kaolinite in 0.005-0.05 M $NaNO_3$ containing 0.0006-0.016 mM SMT. Solution pH values were 4.9 (montmorillonite) and 5.7 (kaolinite). The suspensions were equilibrated for 24 h at 20 to 22°C.

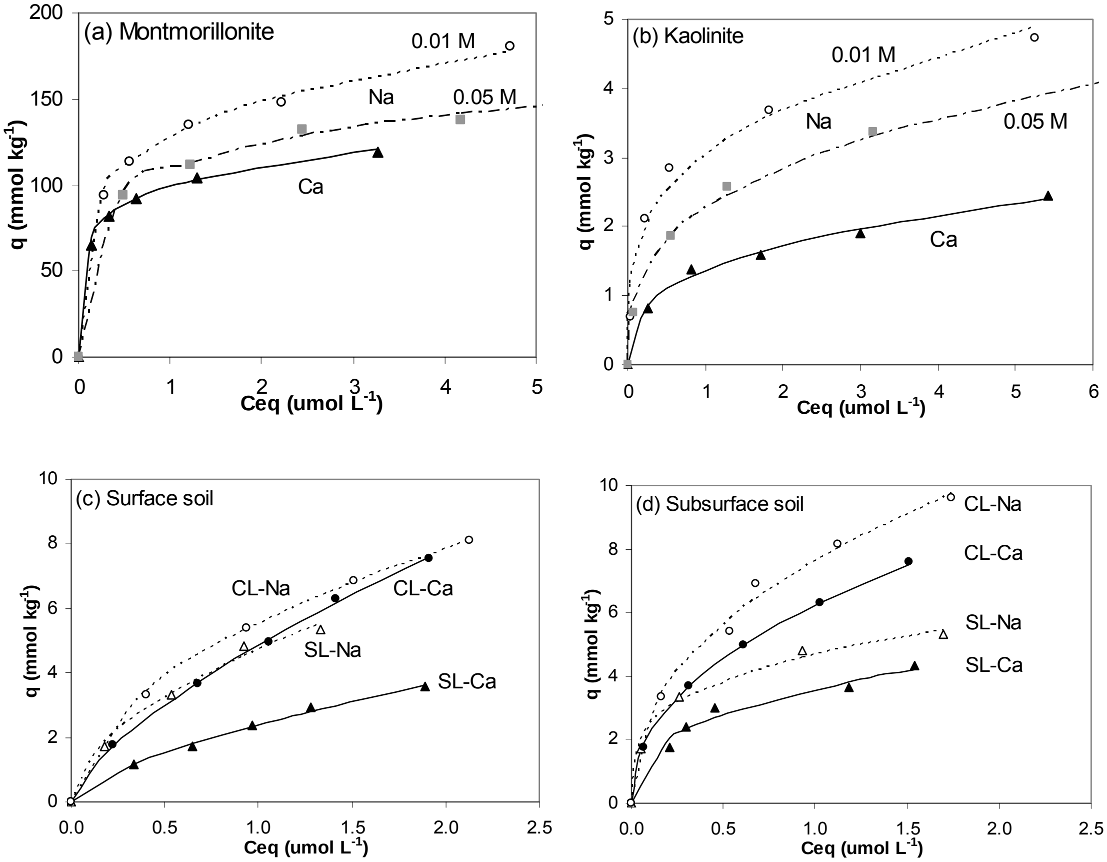

Figure 3.10. Effect of background electrolyte cation type on chlortetracycline (CTC) sorption. SL= sandy loam, CL= clay loam. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.7. The sorption data were obtained by equilibrating 0.45 g L^{-1} of Na^{+}- or Ca^{2+}-saturated montmorillonite, 3.6 g L^{-1} of Na^{+}- or Ca^{2+}-saturated kaolinite, or 17 g L^{-1} of soils in 0.01 M $NaNO_3$ or $Ca(NO_3)_2$ containing 0.003-0.087 mM CTC. For clays, sorption data and isotherm models in 0.05 M $NaNO_3$ were also shown. Solution pH values were 4.4 (montmorillonite), 5.3 (kaolinite), 5.7 (CL-S), 5.8 (CL-SS), 5.8 (SL-SS), and 5.8 (SL-SS) for Na systems and 4.3 (montmorillonite), 5.1 (kaolinite), 5.2 (CL-S), 5.2 (CL-SS), 5.2 (SL-S), and 5.4 (SL-SS) for Ca systems. The suspensions were equilibrated for 48 h at 20 to 22°C.

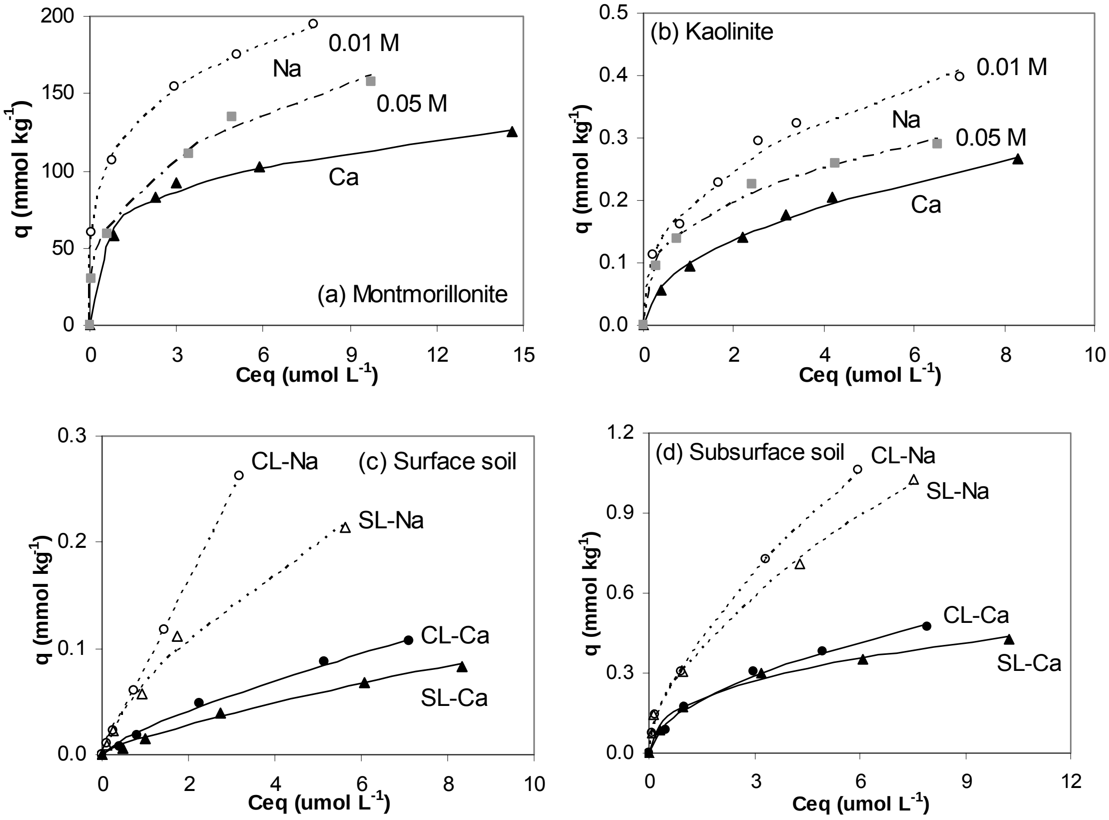

Figure 3.11. Effect of background electrolyte cation type on tylosin (TYL) sorption. SL= sandy loam, CL= clay loam. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.8. The sorption data were obtained by equilibrating 0.30 g L^{-1} of Na^{+}- or Ca^{2+}-saturated montmorillonite, 6.0 g L^{-1} of Na^{+}- or Ca^{2+}-saturated kaolinite, or 50 g L^{-1} of soils in 0.01 M $NaNO_3$ or $Ca(NO_3)_2$ containing 0.0008-0.059 mM TYL. For clays, sorption data and isotherm models in 0.05 M $NaNO_3$ were also shown. Solution pH values were 5.6 (montmorillonite), 5.7 (kaolinite), 5.8 (CL-S), 5.9 (CL-SS), 6.0 (SL-S), and 6.0 (SL-SS) for Na^{+} systems and 5.0 (montmorillonite), 5.2 (kaolinite), 5.3 (CL-S), 5.4 (CL-SS), 5.4 (SL-S), and 5.6 (SL-SS) for Ca^{2+} systems. The suspensions were equilibrated for 24 h at 20 to 22°C.

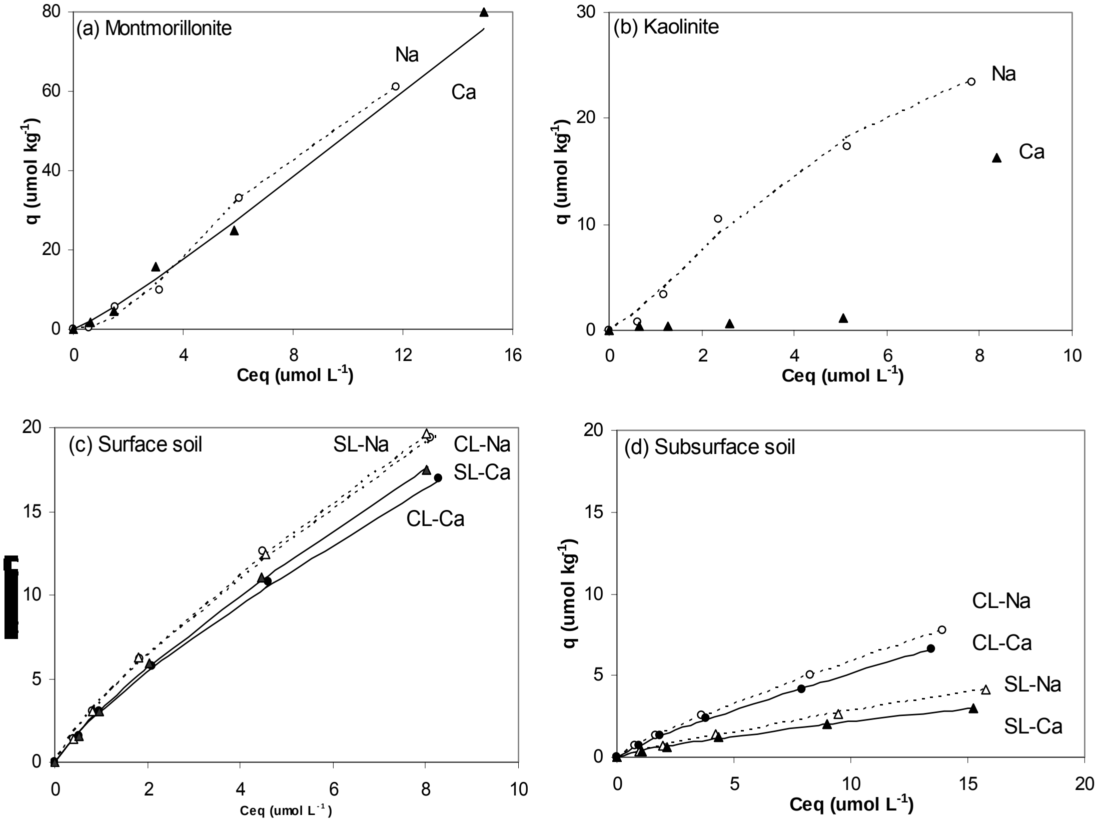

Figure 3.12. Effect of background electrolyte cation type on sulfamethazine (SMT) sorption. SL= sandy loam, CL= clay loam. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.9 and Table 3.10. The sorption data were obtained by equilibrating 6.5 g L^{-1} of Na^{+}- or Ca^{2+}-saturated montmorillonite, 20 g L^{-1} of Na^{+}- or Ca^{2+}-saturated kaolinite, or 500 g L^{-1} of soils in 0.01 M $NaNO_3$ or $Ca(NO_3)_2$ containing 0.0006-0.016 mM SMT. Solution pH values were 4.9 (montmorillonite), 5.7 (kaolinite), 5.5 (CL-S), 5.6 (CL-SS), 5.7 (SL-S), and 5.8 (SL-SS) for Na^{+} systems and 4.2 (montmorillonite), 5.2 (kaolinite), 5.2 (CL-S), 5.3 (CL-SS), 5.4 (SL-S), and 5.5 (SL-SS) for Ca^{2+} systems. The suspensions were equilibrated for 24 h at 20 to 22°C.

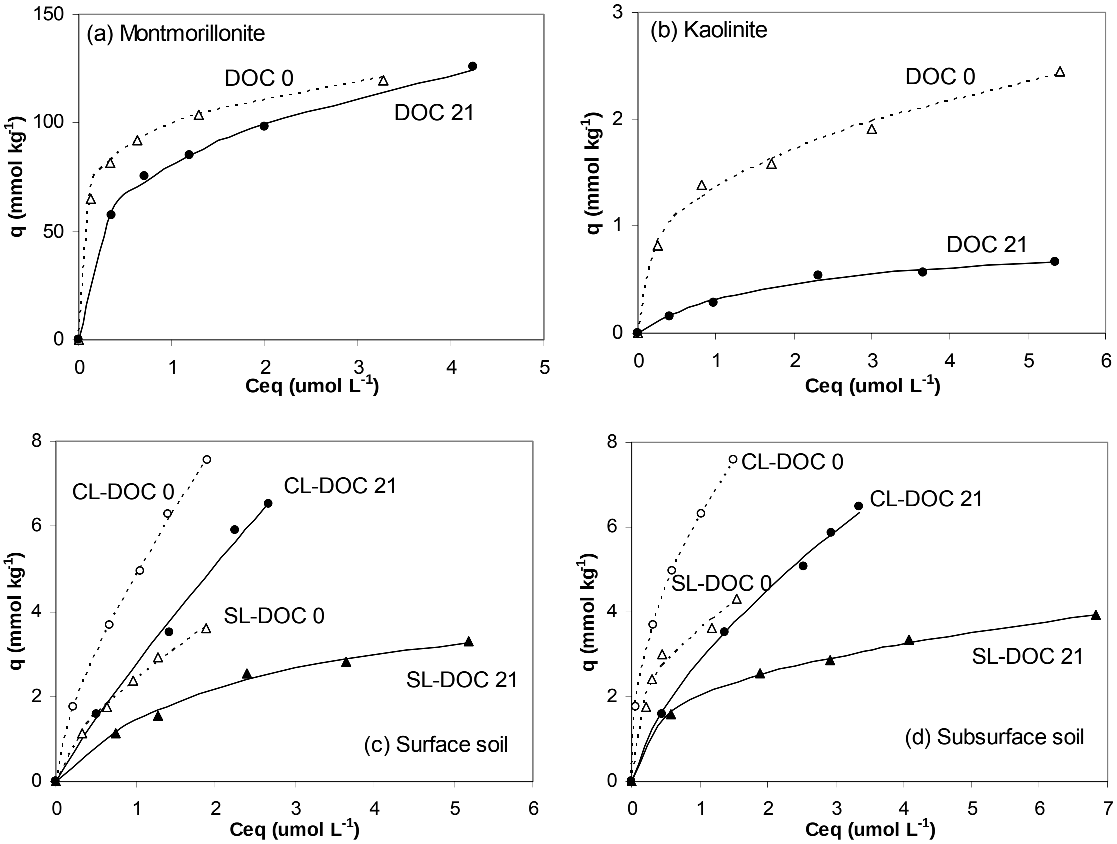

Figure 3.13. Dissolved organic carbon (DOC) effect on chlortetracycline (CTC) sorption. DOC= 21 mg L^{-1}. SL= sandy loam, CL= clay loam. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.7. The sorption data were obtained by equilibrating 0.45 g L^{-1} of Ca^{2+}-saturated montmorillonite, 3.6 g L^{-1} of Ca^{2+}-saturated kaolinite, or 17 g L^{-1} of soils in 0.01 M $Ca(NO_3)_2$ containing 0.003-0.087 mM CTC. Solution pH values were 4.3 (montmorillonite), 5.1 (kaolinite), 5.2 (CL-S), 5.2 (CL-SS), 5.2 (SL-S), and 5.4 (SL-SS) in the absence of DOC and 4.7 (montmorillonite), 5.6 (kaolinite), 5.3 (CL-S), 5.4 (CL-SS), 5.3 (SL-S), and 5.4 (SL-SS) in the presence of dairy manure DOC. The suspensions were equilibrated for 48 h at 20 to 22°C.

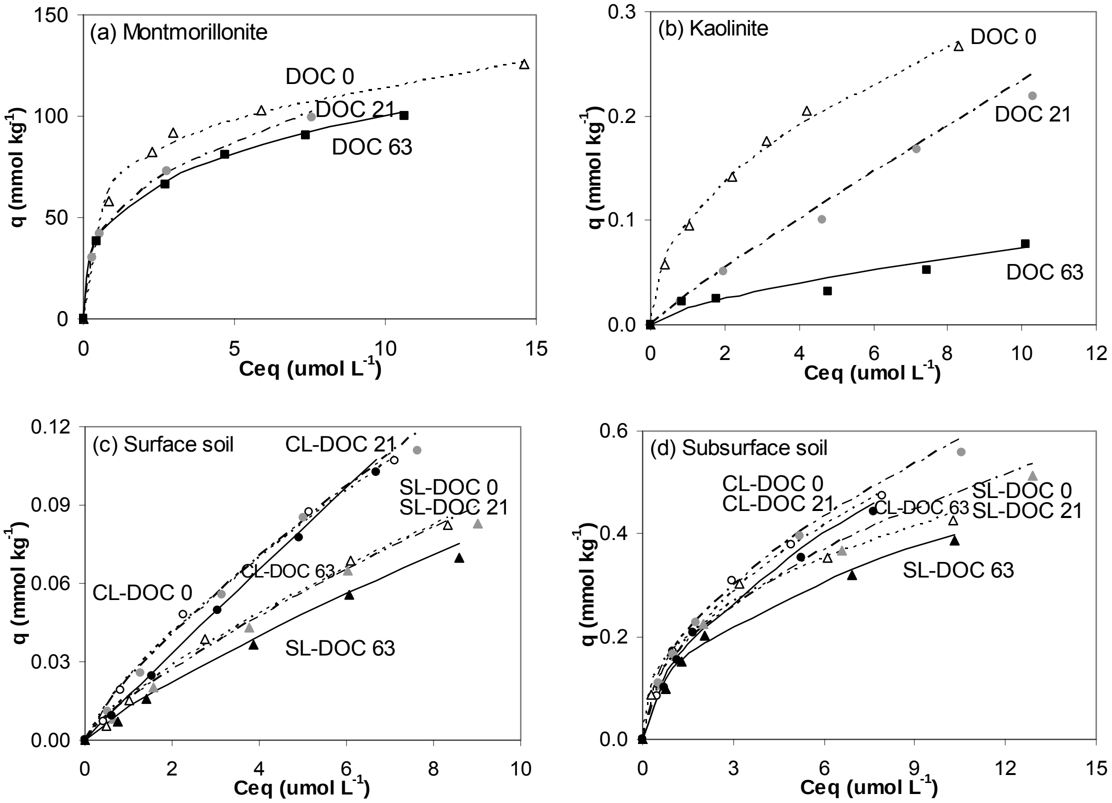

Figure 3.14. Dissolved organic carbon (DOC) effect on tylosin (TYL) sorption. DOC= 21 and 63 mg L^{-1}. SL= sandy loam, CL= clay loam. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.8. The sorption data were obtained by equilibrating 0.30 g L^{-1} of Ca^{2+}-saturated montmorillonite, 6.0 g L^{-1} of Ca^{2+}-saturated kaolinite, or 50 g L^{-1} of soils in 0.01 M $Ca(NO_3)_2$ containing 0.0008-0.059 mM TYL. Solution pH values were 5.0 (montmorillonite), 5.2 (kaolinite), 5.3 (CL-S), 5.4 (CL-SS), 5.4 (SL-S), and 5.6 (SL-SS) in the absence of DOC and 5.6 (montmorillonite), 5.3 (kaolinite), 5.3 (CL-S), 5.5 (CL-SS), 5.5 (SL-S), and 5.6 (SL-SS) in the presence of dairy manure DOC. The suspensions were equilibrated for 24 h at 20 to 22°C.

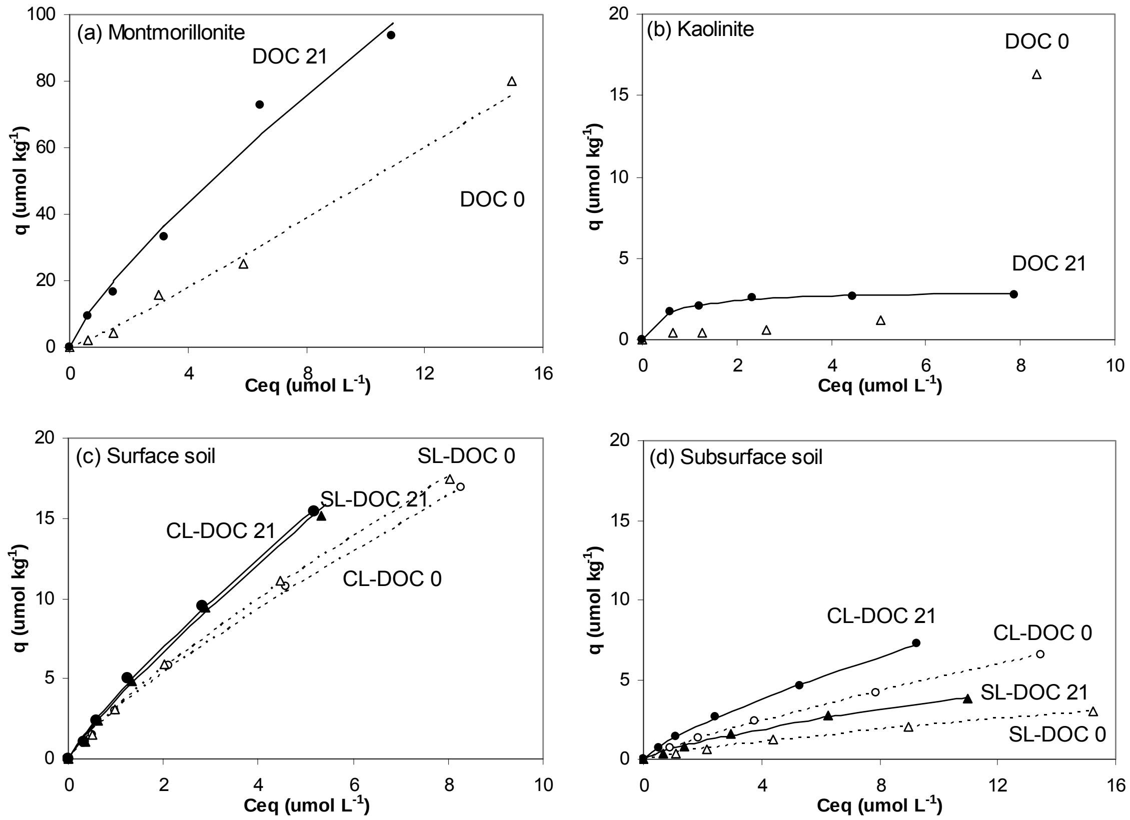

Figure 3.15. Dissolved organic carbon (DOC) effect on sulfamethazine (SMT) sorption. DOC= 21 mg L^{-1}. SL= sandy loam, CL= clay loam. Symbols represent experimental data and lines represent isotherm models for which parameters are listed in Table 3.9 and Table 3.10. The sorption data were obtained by equilibrating 6.5 g L^{-1} of Ca^{2+}-saturated montmorillonite or 500 g L^{-1} of soils in 0.01 M $Ca(NO_3)_2$ containing 0.0006-0.016 mM SMT. Solution pH values were 4.2 (montmorillonite), 5.2 (kaolinite), 5.2 (CL-S), 5.3 (CL-SS), 5.4 (SL-S), and 5.5 (SL-SS) for both in the absence and in the presence of dairy manure DOC. The suspensions were equilibrated for 24 h at 20 to 22°C.

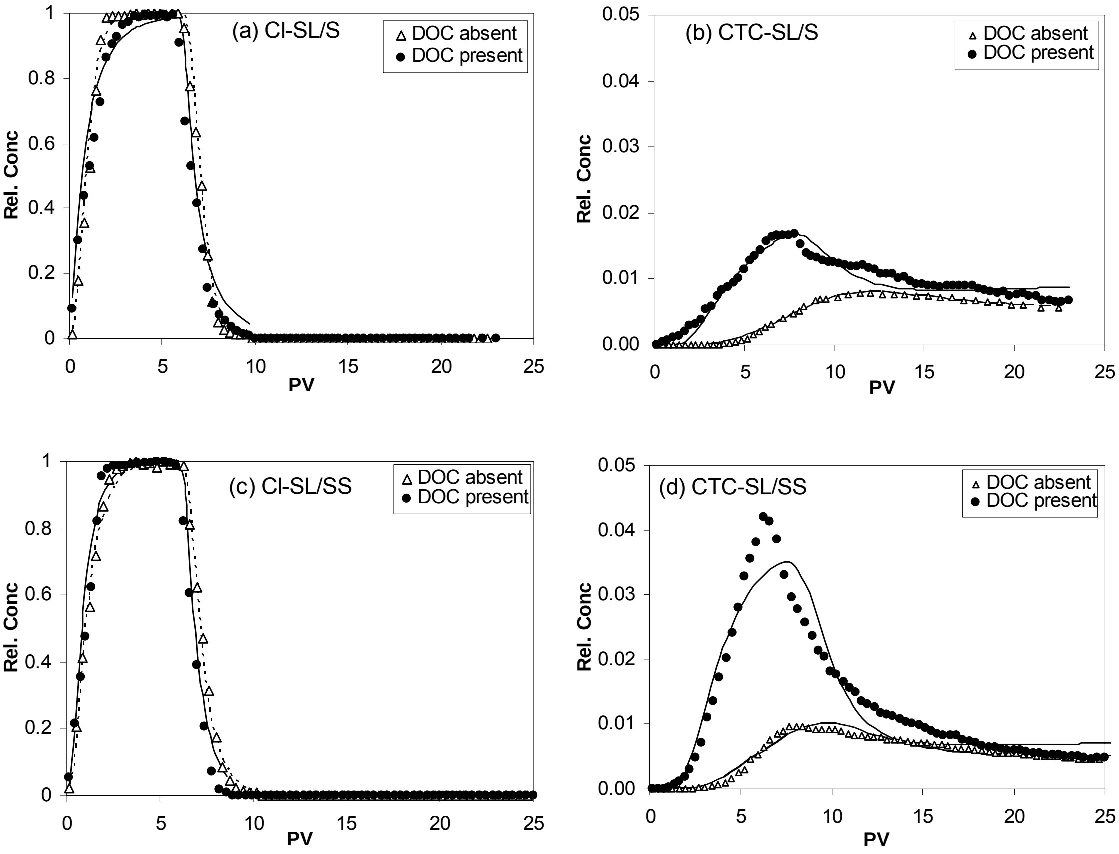

Figure 3.16. Dissolved organic carbon (DOC) effect on chlortetracycline (CTC) mobility. Cl^- and CTC are chloride and chlortetracycline, respectively. SL/S and SL/SS are Captina sandy loam surface and subsurface soil, respectively. Concentrations of DOC added to input solution were 63 mg L^{-1} for surface soil and 21 mg L^{-1} for subsurface soil. Symbols represent measured breakthrough curves (BTCs) and lines represent fitted BTCs for which transport parameter estimates are listed in Table 3.11.

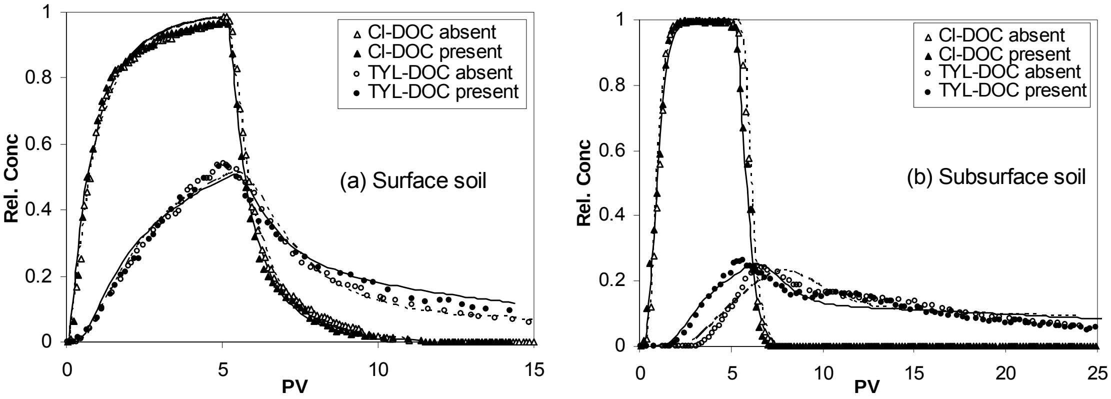

Figure 3.17. Dissolved organic carbon (DOC) effect on tylosin (TYL) mobility for Captina sandy loam. Concentration of DOC added to input solution was 63 mg L^{-1}. Symbols represent measured breakthrough curves (BTCs) and lines represent fitted BTCs for which transport parameter estimates are listed in Table 3.12.

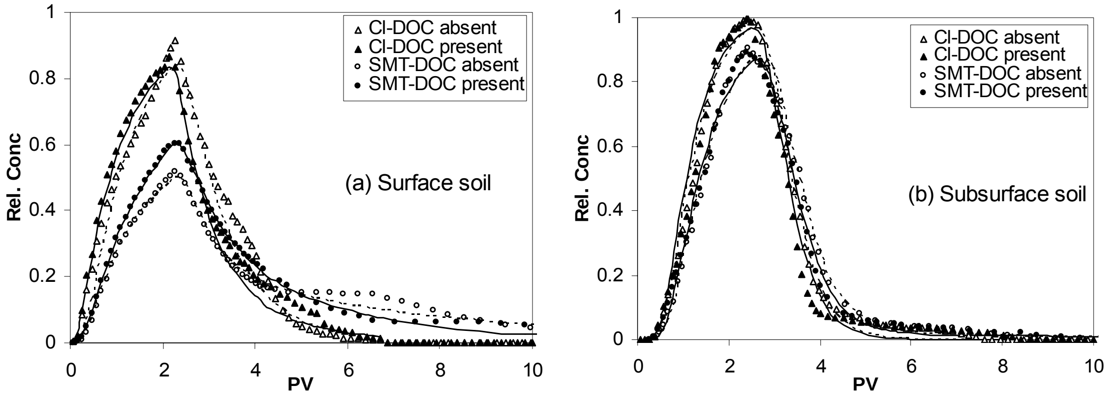

Figure 3.18. Dissolved organic carbon (DOC) effect on sulfamethazine (SMT) mobility for Captina sandy loam. Concentration of DOC added to input solution was 63 mg L^{-1}. Symbols represent measured breakthrough curves (BTCs) and lines represent fitted BTCs for which transport parameter estimates are listed in Table 3.13.

VITA

Youngho Seo was born in Gimje, Republic of Korea. After graduating from high school in 1988, he joined the undergraduate program in the Seoul National University, Republic of Korea with a major in agricultural chemistry. In 1992, he received the Bachelor of Science degree and started the graduate program in the Seoul National University. He obtained his Mater of Science degree in agricultural chemistry in 1994 with a research concentration in Plant Ecology and Soil Science. After serving his military duty, he joined the doctoral program in Agricultural Chemistry, Seoul National University in 1996, and finished the course works in 1999. He had been working as a Researcher in the Gangwon-do Agricultural Research and Extension Services, Republic of Korea since 1996 before joining the doctoral program in Biosystems Engineering and Soil Science, University of Tennessee, Knoxville in Fall, 2002. He was supported as a graduate research assistant. He presented the results of his research in annual meetings of Soil Science Society of America in 2003-2005.