Report for 2001IA1261B: Predicting Sorption, Mobility, Accumulation, and Degradation Potential of Antibiotics in Iowa's Soil/Water Environment

There are no reported publications resulting from this project.

Report Follows:

Research problem:

Approximately fifty million pounds of antibiotics per year are released into the environment. About half of the total antibiotics produced are given to farm animals, fish, and trees for disease prevention and growth promotion at dosages below those recommended for fighting bacterial infections (Levy, 1997). These lower dosages are believed to be more conducive to building antibiotic resistance by pathogenic bacteria. Most of the antibiotics given to farm animals are not metabolized in the body, rather they are excreted in the active form (Lee et al., 2000). The fate of antibiotics introduced into soil and aquatic environments with manure and other animal wastes is largely unknown. However, there is much concern that the presence and persistence of antibiotics in soil and aquatic environments could encourage the buildup of existing and potentially the development of new antibiotic-resistant bacterial populations (Henry, 2000).

In Iowa, Earthen Waste Storage Structures (lagoons) are widely used for temporary storage of liquid animal wastes with the intent of protecting surface and ground water from contamination and allowing farmers to use the wastes in a timely fashion. The liquid animal wastes are generally spread on agricultural soils both as a means of disposal of the wastes and as a nutrient source for crop production. Recent data for lagoon liquid wastes in Iowa (Unknown author, Iowa Dept. of Public Health, 1998) showed relatively high concentrations of antibiotics. For example, chlortetracycline concentrations ranged from 11 to 540 µg/L and erythromycin concentrations ranged from 10 to 275 µg/L. The report also shows that many of the 18 *E. coli* isolates, all three Salmonella species and isolate of Enterococcus demonstrated resistance to a particular antibiotic or combination of antibiotics.

The antibiotics most commonly added to livestock feed as growth promoters (1 to 100 mg per head per day) are chlortetracycline (Aureomycin), oxytetracycline (Terramycin) and macrolide (erythromycin) (Sewell, 1993; FAC, 1998; Herman et al., 1995). The fate of these compounds in Iowa soils will depend on sorption and desorption of the antibiotics on soils, leaching, and the rates of chemical, photochemical, and microbial decomposition of the antibiotics. The basic hypothesis of the study is that the behavior of antibiotics in soil environments with respect to sorption/desorption, leaching, and decomposition is predictable from a knowledge of the chemical structure of the antibiotics.

Specific objectives:

1) Evaluate the potential of the antibiotics tetracycline, chlortetracycline, oxytetracycline and erythromycin to sorb onto soil surfaces involving organo-surfaces (humic substances) and clay mineral surfaces.
2) Evaluate the potential of the selected antibiotics to mobilize through the soil profile under various compositions of the soil solution and soil exchange phase.

3) Evaluate the potential of the selected antibiotics to persist in the soil environment: quantify the half-life for these antibiotics in soil and elucidate for modeling purposes abiotic and biotic cooperative/anti-cooperative effects of sorption on half-life.

Methodology:

Surface (0-15 cm) and subsurface (≥ 15 cm) soil samples were collected from three sites representing three different soil series. The soils were selected to represent a range of physical properties and because these soils and general locations had been previously characterized (McBride et al., 1987). Based on interviews with the landowner or operators, specific sampling sites that had never received manure applications were selected. The soils were characterized using standard analytical procedures to determine pH in $CaCl_2$, pH in KCl, pH in water, organic C, organic H, organic N, % sand, % coarse silt, % fine silt, % clay and extractable cations (Ca, Mg, Na, and K).

Preliminary chemical characterization of tetracycline, chlortetracycline, and oxytetracycline were performed. UV-vis absorbance spectra of the antibiotics dissolved in water, and various concentrations of KCl, $CaCl_2$, $MgCl_2$, and $AlCl_3$ were obtained using a UV-vis spectrophotometer (Varian Instruments, Cary 50 Bio model, Walnut Creek, CA, USA). Calibration curves for quantifying concentrations of the various antibiotics dissolved in water were developed for two wave lengths, near 270 nm (W1) and 370 nm (W2). Solubility of the oxytetracycline in water was measured by determining the concentration where the absorbance-concentration relationship deviates from Beer's-law. Work on developing an HPLC method for quantifying antibiotics was initiated.

Principal Findings and Significance:

Work on the project to date has focused on collecting and characterizing soil samples, characterizing chemical properties of the antibiotics, and the development of analytical methods for antibiotic quanitation.

The soils sampled for this study are listed in Table 1. Clay content of the sampled soils ranged from 19.2 % in the Nicollet surface sample to 34.6% in the Clarinda subsoil sample. Organic C content ranged from 0.44% for the Fayette subsoil sample to 1.65 for the Fayette surface soil sample. Total exchangeable cation ranged from 13.6 $cmol_c\ kg^{-1}$ for the Nicollet surface soil to 19.7 $cmol_c\ kg^{-1}$ for the Fayette subsoil. The pH values in KCl ranged from 4.5 in the Clarinda subsoil sample to 6.5 in the Fayette surface soil sample. In general, the properties of the sampled soils are sufficiently diverse to allow a reasonable assessment of the influence of soil properties on the fate of antibiotics.

Table 1: Soil sampled for the study.

Sample Site	Soil Series	Classification
Tama Co.	Fayette	Fine-silty mixed superactive mesic, Typic Hapludalfs
Boone Co.	Nicollet	Fine-loamy mixed superactive mesic, Aquic Hapludolls
Clarke Co.	Clarinda	Fine smectitic mesic, Vertic Argiaquolls

Potentiometric titrations indicate two and possibly three pKa's for the tetracyclines. The solubility of oxytetracycline was found to be approximately 300 mg L^{-1}. UV-VIS spectroscopy revealed two prominent absorption maxima near 280 and 360 nm for oxytetracycline and tetracycline and two prominent sorption maxima near 280 and 370 nm for chlortetracycline. Absorption spectra for all three tetracyclines were only slightly affected by background $CaCl_2$ (0 to 50 meq L^{-1}) and $MgCl_2$ (0 to 40 meq L^{-1}) concentrations. By contrast, the presence of as little as 2 meq L^{-1} $AlCl_3$ substantially altered the absorbance spectra for all three tetracyclines. The cause of change in the absorbance spectra in the presence of $AlCl_3$ is not clear, but may indicate either a pH effect or the formation Al-tetracycline complexes. More work is needed to resolve the cause of this effect. The results demonstrate that tetracycline, chlortetracycline, and oxytetracycline concentrations in water and both $CaCl_2$ and $MgCl_2$ solutions can be quantified by UV-VIS spectroscopy with linear response for the 0 to 20 mg L^{-1} concentration range. The presence of Al in aqueous solution, however, may cause problems with spectrometric analysis. Preliminary work on developing an HPLC technique for analysis of the oxytetracycline resulted in an r^2 of 0.98. This is not satisfactory for most analyses, and indicates that more work is needed to develop HPLC methods.

It is too early in the study to draw conclusions about the fate of antibiotics in soils. However, the work performed to-date has provided critical background information necessary for successful completion of the proposed research. Future work will focus on building on this foundation and focus on quantifying interactions between the antibiotics and soils.

References

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