



Effect of pH and soil structure on transport of sulfonamide antibiotics in agricultural soils[☆]



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ABSTRACT

We investigated the effect of solution pH and soil structure on transport of sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) in combination with batch sorption tests and column experiments. Sorption isotherms properly conformed to Freundlich model, and sorption potential of the antibiotics is as follows; sulfadimethoxine > sulfamethoxazole > sulfamethazine. Decreasing pH values led to increased sorption potential of the antibiotics on soil material in pH range of 4.0–8.0. This likely resulted from abundance of neutral and positive-charged sulfonamides species at low pH, which electrostatically bind to sorption sites on soil surface. Due to destruction of macropore channels, lower hydraulic conductivities of mobile zone were estimated in the disturbed soil columns than in the undisturbed soil columns, and eventually led to lower mobility of the antibiotics in disturbed column. The results suggest that knowledge of soil structure and solution condition is required to predict fate and distribution of sulfonamide antibiotics in environmental matrix.

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1. Introduction

The presence of trace levels of antibiotics in the environmental system has concerned to developed regions as well as international organizations. These bioactive compounds have been found in various types of environmental matrices, such as soil, surface and ground water (Hirsch et al., 1999; Boxall et al., 2004; Andreozzi et al., 2004; Bartelt-Hunt et al., 2011). They can enter to the environment after excreted by animals and accidentally released during manufacturing and discarding. In general, veterinary medicines cannot be fully metabolized by physiological pathways in animals. For several veterinary antibiotics, metabolite rates are very low (<10%), and the non-metabolite antibiotics are directly excreted through urine and feces (Kümmerer and Henninger, 2003). Metabolites of the medical compounds can still have bioactivity, and may bring negative effects on aquatic and terrestrial ecosystems (Migliore et al., 1993; Froehner et al., 2000; Kilkkinen et al., 2008). The collected manure from husbandry is used as organic fertilizer, and is a major source of antibiotics in agricultural regions.

As an important group of veterinary pharmaceuticals,

sulfonamide antibiotics have intensively been studied with respect to their occurrence and fate in environmental matrices. The majority of studies have attested the general presence of sulfonamides in soils from ng/L up to µg/L level and at relatively low levels in water. For example, sulfadimethoxine was detected up to mg/kg level (Boxall et al., 2004). Sulfamethoxazole is as high as 1.9 µg/L in river water (Hirsch et al., 1999; Kolpin et al., 2002).

Understanding the fate and transport of sulfonamide drugs in environment plays a key role in accurate assessment of their behavior. Adsorption can be a limiting factor of subsurface transport and biodegradation by microorganisms in soil (Boxall et al., 2004; Thiele-Bruhn et al., 2004). The adsorption coefficients of sulfonamides vary with soil composition, texture, and natural organic matter (Thiele-Bruhn et al., 2004; Gao and Pedersen, 2005). The sorption of sulfonamides tends to be higher with increasing cation exchange capacity (CEC) of soils (Leal et al., 2013; Maszkowska et al., 2015). Some previous studies showed an increase in sorption with elevated ionic strength due to the replacement of protons and aluminum ions by cation species from the soil surface (ter Laak et al., 2006; Maszkowska et al., 2015). The presence of natural organic carbon can enhance sorption of sulfonamide antibiotics due to higher affinity between the sulfonamides and natural organic carbon (Thiele-Bruhn et al., 2004).

For organic acid compounds such as sulfonamides, pH-dependent sorption is also important to explain their transport

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and distribution in soil-water interfaces (Tülp et al., 2009; Bronner and Goss, 2010). One of main entering route of sulfonamide antibiotics is application of manure in agricultural lands (Boxall et al., 2004; Thiele-Bruhn, 2003). pH of the pore water in agricultural lands vary, and are dependent on tillage and management (Blevins et al., 1983; Dick, 1983). The transport of the solutes is also largely governed by the structural components of the soils (McCarthy and Zachara, 1989; Isensee and Sadeghi, 1993). Effect of pH and soil structure on transport of the sulfonamides should be investigated in order to quantitatively describe fate and distribution of the sulfonamide antibiotics in agricultural lands. However, it is rare that quantitative studies on transport of sulfonamide antibiotics in agricultural soils under different pH values and soil structure.

The objective of this study is to improve the understanding of sorption and transport of sulfonamide antibiotics in Korean agricultural soils, using batch adsorption tests and column displacement experiments under different pH levels. Transport of the antibiotics was evaluated in disturbed and undisturbed soil columns in order to describe effect of soil structure on their movement and fate in different soil system. The process-based physical and chemical transport model, HYDURS-1D was used to estimate hydraulic and solute transport parameters by inverse modeling.

2. Materials and methods

2.1. Soil sampling area and soil description

Soil columns were taken in Haeon catchment located at northeast of Gangwon province, South Korea (Soil A: N 38° 16', E 128° 8'; Soil B: N 38° 14', E 128° 7'). Both of the sampling site represents one of the largest highland-farming regions in Soyang watershed. Soil properties shows in Table 1. The soil columns are typical sandy-loam, due to adding sandy soil to the top soil layer of the crop fields to compensate for soil loss. Soil A was taken from typical corn farmland. Soil B was collected from fallowing land, where no agricultural activities were performed for about 1 year in order to recover soil nutrients. We analyzed residual concentration of the target sulfonamides (sulfamethoxazole, sulfadimethoxine and sulfamethazine) in the soil columns before applying the veterinary antibiotics. No pharmaceuticals were detected at the soils.

2.2. Chemicals and reagents

Sulfamethoxazole, sulfadimethoxine and sulfamethazine were purchased from Sigma–Aldrich (Seelze, Germany). Isotope-labeled compounds (sulfamethoxazole-D₄, Sulfadimethoxine-D₄ and Sulfamethazine-D₄) were obtained from Toronto Research Chemicals Inc. (North York, Ontario, Canada). Methanol, acetonitrile and water for HPLC-MS-MS analysis were purchased from Sigma–Aldrich and Th. Geyer GmbH (Renningen, Germany).

Table 1
Physical and chemical soil properties of two fields.

	Soil A	Soil B
Texture (%) ^a	Sand: 74.5 Silt: 20.0 Clay: 5.5	Sand: 65.2 Silt: 26.7 Clay: 8.1
Bulk density(g/cm ³)	1.42	1.34
Organic carbon (%)	2.21	3.97
pH	5.7	5.5
CEC (mmol/kg)	45.1	60.5

^a According to soil texture classification system from USDA(United States Department of Agriculture).

2.3. Analysis of antibiotics

The target sulfonamides in leachate were analyzed using high-performance liquid chromatography with tandem mass spectrometry (Quattro micro TM API, Waters, Milford, MA). Sulfamethoxazole-D₄, sulfadimethoxine-D₄ and sulfamethazine-D₄ were used as internal standard. Before analysis, the aqueous sample was filtered through a 0.22 μm PES membrane (Millipore, Billerica, MA) to separate suspended particles in sample.

2.4. Batch sorption experiments

The soils taken from the field sites were transported to the laboratory, and were dried in 60 °C. Properties of the soils were measured, such as soil texture, carbon contents and pH. Soil texture measurement was performed by laser diffraction analyzer (Mastersizer S MAM5004, Malvern Instrument GmbH, Herrenberg, Germany).

Target chemical solutions were prepared using sulfamethoxazole, sulfadimethoxine and sulfamethazine dissolved in methanol. Sorption studies were conducted in 30 ml glass tubes operated as completely mixed batch system. Three replicate tubes were prepared for each treatment by adding 2 g of dry soil and 10 ml of working solution (pH 4.0–8.0) containing 0.01 M CaCl₂ to pre-weighed tubes. The initial concentrations ranged from 10 μg/L to 5 mg/L for all target antibiotics. Losses caused by sorption were quantified with control tubes that contained no soil materials. The contents of the tubes were homogenized with a shaker at room temperature for 24 h. At the end of the contact time, the tubes were centrifuged for 20 min at 1500 rpm and then the aliquots were filtered with 0.22 μm PES membrane (Millipore, Billerica, MA). The antibiotics remaining in the aqueous aliquot is measured by HPLC-MS-MS.

The experimental data of the equilibrium adsorption isotherm for the sulfonamides were represented by Freundlich isotherm model considering multilayer adsorption over heterogeneous surface. Freundlich isotherm is given as:

$$q_e = K_f C_e^{1/n}$$

where q_e is amount of adsorbate in the adsorbent at equilibrium (mg/g), and C_e represents equilibrium concentration (mg/L). K_f is Freundlich isotherm constant (mg/g), and $1/n$ is adsorption intensity related to adsorption capacity.

2.5. Column transport experiment

Undisturbed soil columns were taken from the mentioned field sites using same stainless cylinder with 15 cm inner diameter and 30 cm length. Disturbed soil columns were packed with the same soils sieved with 2 mm mesh, using cylinders of the same dimensions. 0.02 M calcium chloride was applied for 24 h onto top of the soil columns at a rate of 3.6 ml/min to maintain steady-rate flow. After the wetting, aqueous solutions with each sulfonamide antibiotic (1 mg/L) and KBr (1 g/L) were applied to disturbed and undisturbed soil columns. Application of aqueous solution into soil columns was controlled by a peristaltic pump with 3.6 ml/min. Leachate from the bottom of each soil column was automatically collected every 5 min in 30 ml glass vial. Residual concentrations of the sulfonamides and conservative tracer, bromide in the aqueous sample were determined with HPLC-MS-MS and an ion-selective electrode (Metrohm, Zofingen, Switzerland) in combination with a reference electrode.

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