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Fate and Transport of Pharmaceuticals in Soil and Aquatic Systems

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Abstract: The main goal of this study is to analyze import, transfer, fate of PPCPs as trace pollutants in situ and ex situ. This study attempts to examine the fate and transport of PPCPs in small fields using LC-ESI-MS/MS as a tool to monitor. In addition, transport and sorption of selected PPCPs in undisturbed soil columns will be evaluated with bromide tracer and HYDRUS software. Contribution of preferential flow and colloid-facilitated transport to the overall PPCPs movement to subsurface drain will also be featured in field studies and column experiments in this project. The output of this project will extend our knowledge of PPCPs and other emerging pollutants which are likely to affect organisms as well as human beings.

Keyword: *pharmaceuticals and personal care products (PPCPs), transport, monitoring, HYDRUS, LC-ESI-MS/MS, preferential flow, colloid-facilitated transport*

1. Introduction

Pharmaceuticals and personal care products (PPCPs) has also been synthesized for industrial uses as well as for medicinal purposes. Some PPCPs released into the environment bring about adverse effects on aquatic and terrestrial organisms as well as on human beings, such as malfunctions in physiological systems and the induction of specific diseases. Especially, surface water, groundwater and farmland using manure as fertilizer are likely to be contaminated by these pollutants owing to industrial wastewater, municipal sewage and agricultural sources.

In general, pharmaceutical drugs include all the medicines used for the diagnosis, treatment, and prevention of disease. The use of PPCPs continues to grow worldwide along with many agrochemicals. Unlike agrochemicals, they are disposed or discharged into the environment on a continual basis via domestic/industrial wastewater and runoff (Chad et al, 2006). PPCPs are in part subjected to the metabolism of the user; then, excreted as metabolites plus some unaltered parent compounds.

Recently, pharmaceuticals and Personal Care Products (PPCPs) used for human health and in the livestock industry were frequently detected in water sources and in soil (Martin et al., 2003, Kolpin et al., 2002). While several studies reported on detection frequency and the development of detecting methods using analytical facilities, the fate of PPCPs discharged into aquatic systems is not well understood because of complexity of environment(Brown et al., 2006; Campagnolo et al., 2002). Therefore, these issues need more investigation. Moreover, some PPCPs may be refractory to biodegradation or may undergo chemical transformations leading to nontoxic or less toxic forms.

The overall objective of our current research is to clarify and broaden our knowledge of the fate and transport of PPCPs, based on well-established analysis in environmental research fields as well as undisturbed soil column.

2. Research Area Description

Haean catchment is located within Soyang river catchment in northern region of South Korea, between longitude 128° 5' to 128° 11' E and latitude 38° 13' to 38° 20' N, and the range of altitude is about 500 to 1000m. The annual precipitation in the region is up to 1200mm, and 50% of total precipitation is concentrated on monsoon season from June to August. Two small experiment fields were chosen to describe transport of 3 sulfonamides under different storm events in situ. The size of each experiment field was ca. 20m^2(Width; 2.5m, Length: 8m) and had different slope (2.5° and 7.5°).

3. Materials and Methods

3.1 Chemicals and Reagents

3 sulfonbamide antibiotics (sulfamethazine, sulfamethozaxole and sullfadimethoxine) were purchased from Sigma (St. Louis, MO, USA). Acetonitrile and deionized water for HPLC were obtained from Th. Geyer GmbH (Renningen, Germany). Sulfamethazine-d4, sulfamethozaxole-d4, sulfadimethoxine-d4 were from Toronto Research Chemicals Inc. (Toronto, Canada). OASIS HLB extraction cartridge (60 mg, 3 mL) were purchased from WATERS (Milford, USA).

3.2 Batch and Column Experiments

Soil and weak salted water (0.01M $CaCl_2$) were added to 30ml small, respectively. The soil mass for each batch experiment were identical. The batch equilibrium experiments were done using various concentrations of 3 sulfonamides. The compounds were added to triplicate vials to create solution various concentrations (ppb level). The soil-water mixtures were agitated by rotation of the vials. After 1,2,4,8,12,24,48, and 96h, the bottles are centrifuged, and aliquots are removed and then assayed for HPLC-ESI-MS/MS (1200L High performance liquid chromatography-mass spectrometry, Varian, Darmstadt, Germany).

Undisturbed and homogeneous soil columns (D 20cm, H 30cm) were taken from agricultural lands in Haean and botanic garden in University of Bayreuth. Each column was slowly wetted over a 24-h period using a weak salt solution (0.01M $CaCl_2$). This was done to reduce the amount of entrapped air and to maintain soil structure. Both KBr and sulfonamides were passed through the soil column. The steady-state was essentially constant for both bromide ion and PPCPs experiments (average coefficient of variability <5%). The column effluents were collected every 10 min, and each fraction was analyzed for bromide ion and sulfonamides using the ion selective electrode and HPLC-ESI-MS/MS described earlier for the batch experiment.

3.3 Batch and Soil Column Model

Freundlich sorption isotherms were used to describe the batch equilibrium experiments and help identify the effects of various soil fractions on sorption. In the Freundlich sorption isotherm, the concentration of solute adsorbed on the soil matrix is related nonlinearly to the aqueous concentration in the soil solution:

$$S = k_d C^n$$

where K_d is the Freundlich distribution coefficient and n is an empirical constant that controls the deviation from linearity. A nonlinear, least-squares approximation method is used to obtain the best-fit equation to the observed data by optimizing the unknown parameters. The coefficient of determination was determined to measure the goodness of the fit.

To describe the dynamic fate and transport, a two-site convection-dispersion model (Van Genuchten and Wagenet, 1989) with transformation and Freunlich kinetic sorption was chosen. The following is the partial differential equation that governs the none-equilibrium transport for homogeneous systems during one-dimensional and steady-state flow:

$$\theta \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \theta V \lambda \frac{\partial^2 C}{\partial x^2} - \theta V \frac{\partial C}{\partial x} - \mu_w \theta C - \mu_s \rho_b S$$

where t is time (h), ρ_b is soil bulk density, λ(cm) is the dispersivity, x is depth (cm), and μ_w and μ_S are first-order degradation/transformation rate constants for the liquid and sorbed phases. For a stable nonsorbing solute such as the chloride ion, $S= \mu_w= \mu_S= 0$.

The model is considered that included transformations or production of the various PPCPs metabolites. PPCPs may undergo rapid transformation in agricultural soils. The chemical non-equilibrium, convective-dispersive model that is considered includes transformation in both aqueous and dissolved phases and is governed by the specific partial differential equations.

3.4 Field Experiments

The size of each experiment field was ca. 20m^2(W: 2.5m, L: 8m) and had different slope (2.5° and 7.5°). The same management has been adopted in the field, including tillage. The small fields had two furrow (width: 20cm) in order to drain runoff, respectively. At the end of the furrows, runoff collecting system was installed. The apparatus consists of two 20L buckets and 4 pressure sensor designed for measuring water level in the bucket. To estimate soil water content under storm events, 8 TDR probes were inserted at ridges and furrows at depth of 15, 30, 50, 70 cm. Soil-water was collected by suction candle.

4. Expected Results

4.1 Batch and Column Experiments

Within 48 hours, the batch experiments for 3 sulfonamides appeared to be at equilibrium. Freundlich isotherm was used to determine sorption rates between 3 selected sulfonamides and soil. Organic carbon content, cation exchange capacity, specific surface area and mineral particle distribution were strongly related to sorption rates and capacities. Additionally, the amount of sulfonamides in the supernatant decreased after the ultracentrifugation experiment. It suggested that 3 selected antibiotics were found on colloids in the supernatant. This result point out that colloid facilitated transport may play in a rule to determine the fate and transport of sulfonamides in environment.

In column experiments, fate and transport mechanisms of sulfonamides were evaluated. The target antibiotics can easily move in undisturbed soil column because of preferential flow and colloid-facilitated transport. In contrast, the sulfonamides remained at top of homogeneous soil system.

4.2 Field Experiment

The amount of runoff was affected by precipitation intensity, slope and soil structure. Both two research fields have similar physical properties of soil and adapted to same tillage method. Slope of the experiment field would be a main factor of runoff in this experiment. With increasing slope value, runoff could be generated easily and the amount of runoff during heavy storm event was strongly correlated to slope.

During precipitation, sulfonamides in top soil were redistributed in soil, soil-water and runoff. Heavy storm events would change the distribution of the antibiotics in the small soil system because it could generate seepage and runoff, which contain organic matters, soil particles and other materials derived from agricultural land as well as target antibiotics. Analysis of soil-water, soil and runoff obtained after every precipitation could be useful to describe the transport phenomena of the antibiotics in various storm events.

5. Conclusion

Comparing to other hydrophilic compounds, the solubility of 3 sulfonamides is relatively low, up to several mg/L. Owing to the low solubility of target compounds, the mobility of 3 sulfonamides (sulfamethazine, sulfamethozaxole and sullfadimethoxine) would be restricted in homogeneous soil system. In undisturbed soil column, preferential flow and colloid facilitate transport through the porous media would play an important role to increase mobility of the target antibiotics.

Distribution of sulfonamides in small agricultural land was affected by precipitation, the rate of runoff to seepage, soil structure and properties. With increasing the slope of field, more runoff would be generated, and also the antibiotics in top soil could easily move to surface water system, respectively.

From the research, fate and transport model of the pollutants which considers physico/chemical properties of PPCPs and structure of porous media can be developed. The achievements of this research include primary date of sorption and transport on the target PPCPs which have various physico/chemical properties and different soil system.

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