A Hydrobiological Mechanism Controlling the Synergistic Effects of Unsaturated Flow and Soil Organic Matter on Degradation of Emerging Organic Contaminants in Soils

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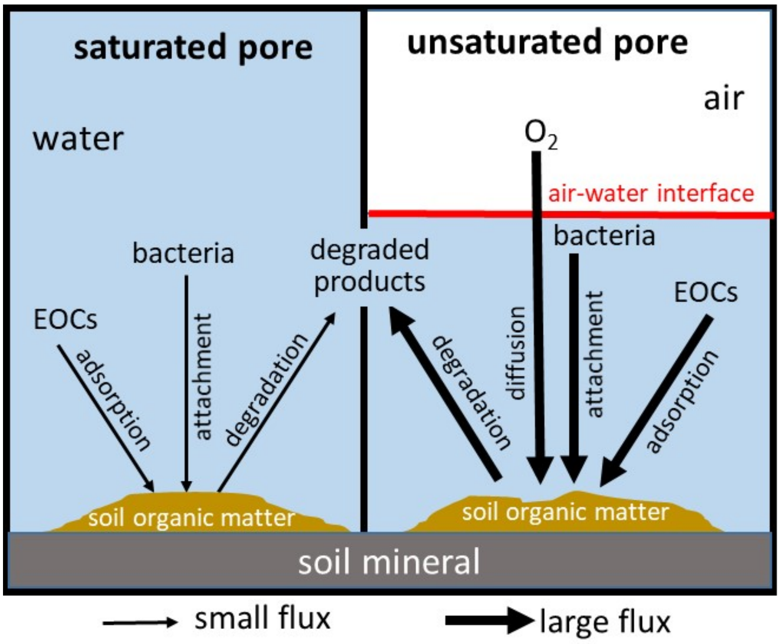
Abstract: Hydrology is a key factor influencing microbial degradation of emerging organic contaminants (EOCs) in soils, but the underlying mechanisms are not clear. In this study, biotic and abiotic column experiments were performed to investigate the removal and degradation of five EOCs in soils with different soil organic matter (SOM) contents under saturated and unsaturated flow conditions. In biotic experiments, 54-90% of bisphenol A (BPA) and 9-22% of ibuprofen (IBU) were removed from the aqueous phase of saturated columns due to adsorption and biodegradation. The biodegradation removed 26-65% of BPA and 1-22% of IBU. Decreasing soil pore water saturation from 100% to 80% increased BPA removal to 97-100% and IBU removal to 42-43% due to increased biodegradation (67-81% for BPA and 36-39% for IBU). No significant removal of BPA and IBU was observed in SOM-removed soils under saturated and unsaturated flow conditions. The desaturation did not influence sorptive losses of BPA (<27%) and IBU (<7%), suggesting negligible adsorption of them at air-water interfaces, but increased biodegradation of BPA and IBU sorbed at SOM-water interfaces. The study shows that soil drying and SOM can synergistically degrade BPA and IBU but have no effect on recalcitrant carbamazepine, tetracycline, and ciprofloxacin.

Keywords: emerging organic contaminant, unsaturated transport, biodegradation, soil organic matter, soil water content

Synopsis:

Air intrusion and organic matter content synergistically increase the degradation of organic contaminants in soils.

Graphical Abstract:



1. Introduction

Continued usage and release of organic additives for domestic and industrial purposes have introduced emerging organic contaminants (EOCs) into soils at μg to mg levels.[1,2] Many EOCs persist in surface soils (e.g., 0-20 cm) for years or even decades.[3,4] Fate studies have demonstrated transport of certain EOCs through the vadose zone (an unsaturated soil profile) into aquifers,[5,6] causing ecological and health risks to soil, groundwater, and human health.[7-11] To date, few studies have addressed the impact of unsaturated flow conditions on the environmental fate of EOCs.

As one of the key attenuation processes, the aerobic microbial degradation of EOCs in unsaturated surface soils is critical for ecological risk reduction. The degradation of EOCs has been investigated in water-saturated soils (i.e., without air phase and redox dynamics),[12-14] but rarely in unsaturated soils (i.e., with air-water interface [AWI] and redox dynamics).[15] Transport and degradation of EOCs in partially saturated soils is perhaps of greater importance, since EOCs that are retained in surface soil areas must pass through an unsaturated vadose zone before entering groundwater. In unsaturated soil, both solid-water interface (SWI) and AWI exist, which influence the adsorption and transport of EOCs.[16] Under steady state flow conditions, the AWI can act as interfaces retaining organic contaminants.[17] Meanwhile, decreased water content leads to the longer flow paths and residence time and increases dispersion and retention.[18] Many studies investigated adsorption and transport of organic contaminants in the vadose zone;[10,19-20] however, it is not clear how AWI and SWI interact to influence the degradation of EOCs.

Soil organic matter (SOM) affects the degradation of EOCs through three mechanisms. First, SOM plays a key role for adsorption of EOCs[6,21] and can increase the retention of organic contaminants.[22,23] Second, SOM can provide nano/micro-pores or promote aggregate formation to reduce the diffusion of EOCs by decreasing pore water connectivity.[3,24] This pore structure change can increase the residence time and promote the microbial degradation of EOCs. Third, SOM is a carbon and nutrient resource for microorganisms that can degrade EOCs.[25] Our previous studies demonstrated that SOM can increase the removal of EOCs, and the removal could be further enhanced by pore water desaturation.[20] It was assumed that the air phase in unsaturated soil could increase the adsorption of EOCs; however, the relative contributions of SWI and AWI to the adsorption of EOCs are unclear. Furthermore, it is unknown to what extent microbial degradation contributes to the overall removal of ECOs under unsaturated flow conditions.

Therefore, this study aimed to elucidate the effects of unsaturated flow on the degradation of EOCs during transport through soils with different SOM contents. Based on our previous work studying the adsorption and transport of EOCs in heterogeneous soils, five EOCs with a range of physico-chemical properties and environmental behaviors, including bisphenol A (BPA), ibuprofen (IBU), carbamazepine (CBZ), tetracycline (TTC), and ciprofloxacin (CPF), were selected. Biotic and abiotic attenuation processes were measured to distinguish their relative contributions to the fate of EOCs in the saturated and unsaturated soils. In addition, the impact of SOM on the extent of biodegradation and transport processes was evaluated. These new findings demonstrate that unsaturated flow and SOM exert a coupled effect on the environmental behavior of EOCs in soils, and that the effect varies with the physico-chemical characteristics of EOCs. The new findings suggest that improved irrigation strategies (e.g., applying deficit irrigation and limiting it to SOM-rich soil layer) could reduce the risks associated with EOCs in farmland receiving reclaimed water or organic wastes.

2. Materials and Methods

2.1 Chemicals

Five EOCs, including bisphenol A (BPA), carbamazepine (CBZ), ibuprofen (IBU), ciprofloxacin (CPF), and tetracycline (TTC) were selected to represent a wide range of physical and chemical properties and environmental behaviors of EOCs (Table 1). The five EOCs have been frequently detected at elevated concentrations in soils.[26] The EOCs were purchased with >98% purity from Sinopharm Chemical Reagent Co., Ltd (Shenyang, China). A mixed stock solution of the five EOCs (1,000 mg L^{-1} each) was prepared in HPLC grade methanol and stored at 4 °C. Methanol was purchased from Sigma-Aldrich (St. Louis, MO, USA). Deionized water was supplied by a Milli-Q purification system (Millipore, Barnstead, Boston, USA). NaCl and NaN_3 were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2 Soils and property analysis

The soil was collected from a long-term fertilization experimental site at a depth of 5-15 cm. The site was maintained by Shenyang Agricultural University, China, located at a latitude of 41°49', a longitude of 123°34', and an elevation of 75 m. The region has an average annual temperature of 8 °C and an annual precipitation of 705 mm. The field received annual surface application of fermented swine manure (containing organic matter at 150 g kg^{-1}) since 1987 at a low level (M1, equivalent to 2,025 kg C ha y^{-1}) and a high level (M2, equivalent to 4,050 kg C ha y^{-1}). The soil is loamy brown earth developed on the Loess matrix, and is classified as a Hapli-Udic Cambisol (FAO Classification). The soil contains 37% sand, 33% silt, and 30% clay.[27] After collection of the soil samples, plant roots and debris were removed manually, and then the soils were air-dried, ground, and sieved through a mesh of 2 mm. To investigate the effect of SOM on the degradation of EOCs, we depleted SOM from a portion of the M2 soil by thermal treatment at 375 °C for 26 h according to an established method.[28] This treatment can remove a majority of SOM without destroying the soil pore structure. The treated soil was designated OXM2. SOM associated with the three soils was measured using the potassium dichromate oxidation method,[29] and the contents were 8.03, 19.81, and 24.17 g kg^{-1} for OXM2, M1, and M2 soils, respectively. The Brunauer-Emmett-Teller (BET) surface area of the soil samples was measured with a Micromeritics ASAP 2460 Surface Area and Porosity Analyzer (Micromeritics Instrument Corporation, Norcross, George, USA) using nitrogen gas (ISO 9277) after preheating at 150 °C for 18 h. The specific surface areas of the OXM2, M1, and M2 soils were 17.67 ± 0.02, 24.55 ± 0.01, and 20.17 ± 0.10 m^2 g^{-1}, respectively. The cation exchange capacities were determined by the means of oscillating exchange and vacuum filtration. Briefly, the soils were treated with ammonium acetate, and the cations were quickly exchanged by shaking, collected by centrifugation, adsorbed by soil colloids, and measured by a fully automatic Kjeldahl nitrogen analyzer (K9840, Jinan, China). The CEC values of OXM2, M1, and M2 soils were 13.7, 19.5, and 21.7 cmol kg^{-1}, respectively. Soil pH values measured at a soil-to-water ratio of 1:2.5 (v:v) were 6.82, 6.54, and 6.76 for the OXM2, M1, and M2 soils, respectively.

2.3 Column system and experimental procedure

A series of column experiments was conducted with replicates under saturated and unsaturated flow conditions to investigate the removal and degradation of EOCs during their transport through soils. The experiments followed a previously reported procedure.[20] Schematics of the saturated and unsaturated column experiments are shown in Figure S1. Specifically, the saturated column system consisted of a stainless steel column (11 cm in length and 5.5 cm in inner diameter), a piston pump (LC-16, Shimadzu Corporation, Kyoto, Japan) connected to the inlet of the column for injecting input solution, and an automated fraction collector (CF2, Spectrum Chemical Mfg. Corp, CA, USA) to collect effluent. The inner surface of the column was roughened by sand paper prior to use in order to avoid potential sidewall flow. Stainless steel tubing was used for the entire experimental system. Air-dried soil samples (~10 g) were packed into the column and tapped down after each 1-cm increment with a stainless steel rod to avoid soil layering. A thin layer (~0.5 cm) of quartz sand (0.07-0.18 mm, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was placed on the top of the soil to facilitate commingling of the effluent across the soil surface at the outlet of the column during the saturated experiments. Prior to use, the quartz sand was washed with 1 M HNO_3 at 80 °C for 8 h and rinsed with deionized water three times before drying at 105 °C for 4 h. In addition, a nylon membrane (10 μm pore size, Sterlitech Corporation, Washington, USA) was used as a capillary boundary at the bottom of the column to horizontally distribute input solution. The saturated experiment was initiated by flushing the dry-packed column upward with CO_2 gas for ~8 h for trapped air replacement.[6,23,30] Then, the soil column was flushed with the deaerated background solution for 15 pore volumes at a rate of 1.0 mL min^{-1} to leach tiny impurities from the soil and establish steady flow and physical-chemical equilibrium conditions. The upward flow direction ensured water saturation and avoided any entrapment of gas bubbles.[30] After the equilibrium was established, ~22 pore volumes (3,000 mL) of an experimental input solution were injected into the column at 0.5 mL min^{-1} to observe the breakthrough of EOCs. Subsequently, the injection was switched back to the deaerated background solution to elute the soil for ~15 pore volumes at 0.5 mL min^{-1}. During the entire course of the experiment, effluent samples (7 mL) were continuously collected from the top of the columns into 10-mL glass test tubes using the fraction collector every 14 minutes. The liquid samples were stored at 4 ^{o}C for 12-24 h prior to analysis. The experimental input solution was prepared by dissolving bromide (44.6 mg L^{-1} KBr) and EOCs (BPA, IBU, CBZ, TC, and CIP at 1 mg L^{-1} each) into the deaerated background solution (10 mM $CaCl_2$, pH 6.7). These relatively high EOC concentrations (1 mg L^{-1} of each EOC) were required for effective detection and quantification in the column experiments, considering variable removal efficiency [20]. Still, the concentrations of EOCs were in the range of polluted soils irrigated with wastewater.[26] Soil-free control column experiments with injection of EOCs were performed to determine the abiotic losses of the EOCs due to hydrolysis, volatilization, and adsorption in the experimental system, while soil-packed control column experiments without input of EOCs were carried out to determine the release of the EOCs from soil in the experimental system.

The unsaturated column system consisted of the same column, piston pump, and fraction collector as used in the saturated column system in addition to a peristaltic pump (Longer Pump, Baoding, China) and a sprinkling system. The peristaltic pump was connected to the outlet of the column to regulate soil water content by controlling outflow rate. The sprinkling system consisted of a completely enclosed input solution reservoir (5.5 cm in inner diameter and 4 cm in height) to evenly distribute the solution onto soil surface via nineteen 26-gague hypodermic needles that were uniformly positioned across the bottom of the reservoir. The needles penetrated a parafilm that was placed above the soil surface to avoid water evaporation during the experiment. A short portion of Tygon tubing was used for the peristaltic pump, while stainless steel tubing was used for the rest of the experimental system including the piston pump. In addition, an electronic balance (YHC-L01, Yingheng Weighing Co., Ltd., Shanghai, China) was used to gravimetrically monitor soil water content of the unsaturated column. It was assumed that the hydrological conditions were stable once the total weight of the column remained constant during the experiment. The column was packed with the same procedure as used for the saturated columns, including a thin layer (~0.5 cm) of the quartz sand on the top and a nylon membrane at the bottom of the column. The unsaturated experiment was initiated by flushing the soil column upward with 10 pore volumes of the deaerated background solution at a rate of 1.0 mL min^{-1} under steady-state saturated flow conditions. Immediately after the flush, the top plate of the column was removed, and the deaerated background solution was introduced by the piston pump onto the open top of the column at 1.0 mL min^{-1} via the sprinkling system. Meanwhile, the peristatic pump connected to the outlet was adjusted to reach an outflow rate of 1.1 mL min^{-1} for draining water from the saturated soil column. Once the soil water content stabilized at a pore water saturation of 80% according to the balance reading, ~28 pore volumes (3,000 mL) of the experimental input solution was injected through another set of the sprinkling system with both inflow and outflow rates adjusted to 0.5 mL min^{-1} for maintaining a steady unsaturated flow. Subsequently, ~18 pore volumes of the background solution were infused to the unsaturated column to elute the soil at 0.5 mL min^{-1}. During the input solution injection and column elution stages, effluent samples were continuously collected from the bottom of the columns into 10-mL glass test tubes every 14 minutes and stored at 4 ^{o}C for 12-24 h prior to analysis.

The calculated pore velocities were 2.1-2.2 cm h^{-1} for the saturated columns and 2.6-2.7 cm h^{-1} for the unsaturated columns (Table 2). The pore velocities differed slightly due to the necessary flow rate adjustment for achieving 80% water saturation. Such minor differences in flow rate were not expected to cause significant difference in the transport and retention of EOCs.[31,32,33] These pore water velocities were in the range of saturated hydraulic conductivity (1-3 cm h^{-1}) measured with these soils under field conditions.[34] The downward flow direction more effectively achieved different degrees of saturation and allows percolation through the unsaturated zone.[30] To assess microbial degradation of EOCs, 100 mg L^{-1} sodium azide (NaN_3) was added to the input solution. NaN_3 prevents microbial activity by inhibiting respiratory electron transport.[35] The removal of EOCs in the soil columns without NaN_3 (i.e., biotic experiments) was assumed to be the total of adsorption and degradation of EOCs, while the removal in the presence of NaN_3 (i.e., abiotic experiments) was considered adsorption only. The difference between EOC removal in biotic versus abiotic column experiments was ascribed to microbial degradation.

2.4 Sample analysis

Bromide concentrations in the effluent were analyzed using an ion chromatograph equipped with an IonPac AS11-HC 4-mm anion-exchange column (Dionex ICS 600, California, USA), which was eluted with 100 mM KOH at a flow rate of 1 mL min^{-1}. The concentrations of the five EOCs were measured using a high-performance liquid chromatograph (HPLC) (Agilent 1260 Infinity, California, USA) with a ZORBAX SB-C18 column (4.6×150 mm, 5 μm). The eluent gradient was established by mixing two mobile phases: phase A, methanol, and phase B, millipore water (0.12% [w/v] ammonium dihydrogen phosphate). The pH of the mobile phase was adjusted to 3.6 using 0.1% phosphoric acid. The chromatographic separation was achieved with the following gradient: 0-5 min 5% A, changing to 60% A in 15 min, changing to 80% A in 16 min, changing to 85% A in 9 min, and return to initial conditions in 5 min. The injection volume was 30 μL. The five EOCs were detected using a UV detector by absorbance readings at 227 nm. External standards were used in the range of 100-2,000 μg L^{-1} to quantify the concentration of EOCs. The calibrations were performed as a multi-step internal standard calibration. The limit of detection was taken as signal-to-noise ratio 5:1 in ~50 μg L^{-1}. Data were acquired and processed using Agilent OpenLAB CDS Chemstation software. Each sample of the replicate column experiments was analyzed twice, and the data represent the mean values of two independent column experiments.

2.5 Data modelling

A Hydrus-1D software was used to simulate the breakthrough processes of bromide and EOCs from the soil columns. Considering potential involvement of diffusion-limited process in this relatively low column length-to-diameter ratio (i.e., 2) in this study, the simulation was performed based on the one-dimensional advection-diffusion equation (ADE) with incorporation of the two-site chemical nonequilibrium sorption model as shown below:

$$\frac{\partial C}{\partial t}+\frac{\rho_b}{\theta}\frac{\partial(S_1)}{\partial t}+\frac{\rho_b}{\theta}\frac{\partial(S_2)}{\partial t}=-v\frac{\partial C}{\partial Z}+D\frac{\partial^2 C}{\partial Z^2}-\mu_w C \tag{1}$$

where C is concentration of each contaminant in aqueous phase (mg L^{-1}), t is time (h), ρ_b is soil bulk density (g cm^{-3}), θ is volumetric water content (cm^3 cm^{-3}), v is pore water velocity (cm h^{-1}), z is distance (cm), μ_w is a first-order degradation rate constant (h^{-1}), and D is diffusion coefficient (cm^2 h^{-1}). The D value was obtained by fitting bromide breakthrough data to Eq. (1) assuming the values of S_1, S_2, and μ_w are zero. A two-site adsorption model was selected to describe the transport of EOCs through soils. The model assumes that adsorption sites can be divided into two fractions: instantaneous (Type-1) and kinetic (Type-2) sites.[36]

$$S = S_1 + S_2 \tag{2}$$

where S is solute concentration in the solid phase (mg L^{-1}), S_1 and S_2 are solid phase concentrations associated with Type 1 and Type 2 sites, respectively. Considering Type-1 adsorption sites are always at equilibrium, S_1 is calculated as:

$$\frac{\partial(S_1)}{\partial t}=f\frac{\partial S}{\partial t} \tag{3}$$

The Type-2 adsorption sites are assumed to be a first-order kinetic rate process:

$$\frac{\partial(S_2)}{\partial t}=\alpha_2[(1-f)K_d C-S_2] \tag{4}$$

where α_2 is a first-order kinetic rate coefficient (h^{-1}), f is the fraction of instantaneous adsorption sites (Type-1), and K_d is soil-water distribution coefficient (L kg^{-1}). Retardation factor (R) represents effect of adsorption on the transport of EOCs, which is calculated as follows:

$$R=1+\frac{\rho_b K_d}{\theta} \tag{5}$$

3. Results and Discussion

3.1 Dependence of desaturation effect on microbial activity

Breakthrough curves of bromide (conservative tracer) obtained under both saturated and unsaturated flow conditions demonstrated good stability and reproducibility of the hydraulic conditions applied to all experiments (Figure S2). The soil-free control experiments showed no changes in the effluent concentrations of EOCs, indicating negligible release and abiotic losses of EOCs in the experimental system. In the biotic experiments (i.e., without NaN_3 in the input solution), BPA breakthrough was observed after ~2 pore volumes. This one pore volume slower breakthrough than bromide was attributed to adsorption of BPA to the soil.[6,23] In the columns with low SOM (e.g., M1 soil), 53.5% and 97.1% of the injected BPA were removed under the saturated and unsaturated flow conditions, respectively. In the biotic columns, the removal of EOCs is considered to be the sum of two processes, adsorption and microbial degradation.[37] However, in the abiotic experiments (i.e., with NaN_3 in the input solution), the mass percentage of removed BPA decreased to 27.2% and 30.4% under the saturated and unsaturated flow conditions, respectively. These two values represent the percentages of BPA adsorbed to the soil (Figure 1). The minor difference in the removal between the saturated and unsaturated flow conditions suggests a very limited role of the AWI in BPA adsorption.

We calculated the degradation by subtracting the removal in the presence of NaN_3 (i.e., adsorption only) from the removal without NaN_3 (i.e., sum of adsorption and degradation). The mass percentage of degraded BPA was 26.3% under the saturated flow conditions and 66.7%

under the unsaturated flow conditions (Figure 2). This 2.5-fold increase in degradation suggests a strong effect of the 20% desaturation. This finding was verified by the increase in mass recovery of BPA after soil microbial activities were inhibited by adding NaN_3 into the experimental input solution (Figure 1). The desaturation effect is also supported by the 5-fold increase in the value of μ_w (the first-order degradation rate constant) from 4.32 h^{-1} to 21.36 h^{-1} in M1 soil columns when pore water saturation decreased from 100% to 80% (Table 2).

The above desaturation-enhanced degradation of BPA is attributed to two processes. One is the attachment of microorganisms at the AWI under the unsaturated flow conditions.[16,38] The AWI existing under the unsaturated flow conditions serves as an interface additional to the SWI, the only interface available for microorganism adsorption and BPA degradation under saturated flow conditions.[17,39] The other process associated with degradation is oxygen diffusion. Desaturation increases diffusion and distribution of gas-phase oxygen in the pore space.[40] Under the unsaturated flow conditions, water flow becomes slow in the “wedge” regions formed by contacting soil grains, but fast along the AWI.[14] These differences in pore water configuration and flow velocity were favorable to oxygen diffusion.[41,42] As a result, unsaturated flow conditions enhance local oxygen availability for microbial activity, leading to increased degradation of BPA.

3.2 Dependence of desaturation effect on SOM

No significant degradation of BPA occurred in the SOM-depleted soil (OXM2) under both the saturated and unsaturated conditions (Figure 3). However, the presence of SOM (e.g., in the

M1 and M2 soils) greatly increased the degradation percentage under the saturated flow conditions, and the increase was enlarged when pore water saturation decreased from 100% to 80%. Specifically, SOM was responsible for 26.3% and 65.1% degradation of BPA under the saturated flow conditions in the M1 soil (low SOM) and M2 soil (high SOM), respectively (Figure 3). These degradation percentages further increased to 66.7% and 81.3% under the unsaturated conditions in the M1 and M2 soils, respectively. This SOM-prerequisite desaturation effect was consistently reflected by changes in the μ_w values fitted from the breakthrough curves with the ADE model (Table 2). Such dependence of a desaturation effect on SOM is attributed to the coupling of three processes. One is that SOM increases kinetic adsorption of BPA at SWI under both saturated and unsaturated flow conditions.[20] The second is that AWI existing in unsaturated soils enhances attachment of microorganisms at SWI.[38,39] The third is that properties and composition of SOM have been shown to favor microbial growth and activities.[43] As a result, these processes worked together to increase BPA accessibility by microbes, making a larger fraction of BPA degraded under lower water saturation in the soil with higher SOM content.[25,44] This SOM dependence is supported by the increase in the values of K_d and previous studies.[6]

3.3 Dependence of desaturation effect on EOC properties

TTC and CPF were not detected in the effluent under both the saturated and the unsaturated flow conditions with or without NaN_3 in the influent. Therefore, no experimental data and numerical simulation are provided in Table 2. The complete removal of these two positively charged EOCs is attributed to their strong electrostatic attraction to the negatively charged soil surfaces (e.g., SWI)[20,23,45] and their recalcitrant nature.[46,47]

BPA and IBU were detected in the effluent of columns packed with the OXM2, M1, and M2 soils. During the transport, the degradation of BPA (26.3-81.3%) was much higher than that of IBU (1.2-38.9%) (Figure 2). This difference was mainly due to the higher adsorption of non-dissociated BPA to soil surfaces via hydrophobic interactions compared to the negatively charged IBU, which was electrostatically repulsed on the soil surfaces.[6,23] The degradation of BPA and IBU increased 3-fold and 30-fold, respectively, when pore water saturation decreased from 100% to 80% in the M1 soil columns (Figure 2). This is consistent with their change in the μ_w value, which increased from 4.32 h^{-1} to 21.36 h^{-1} for BPA and from 0.48 h^{-1} to 2.88 h^{-1} for IBU in the M1 soil columns as a result of 20% desaturation (Table 2). These results suggest that desaturation was favorable to the degradation of non-dissociated and negatively charged EOCs (i.e., BPA and IBU), though it had no significant influence on their adsorption.

In comparison, CBZ exhibited much lower microbial degradation than BPA. Less than 10% of the injected CBZ was degraded under both the saturated and the unsaturated flow conditions. This result is in consistent with a prior study that reported a mass recovery of 86% and degradation rate of 10^{-8} d^{-1} in soils.[46] We attribute this insignificant removal to the persistency of CBZ to microbial degradation.[48]

3.4 Environmental implications

This study reveals a hydrobiological mechanism that controls the effects of soil hydrology on microbial degradation of different EOCs in soils with different SOM contents. The results demonstrate that a small desaturation (e.g., 20%) of soil pore water could greatly increase the degradation of biodegradable, non-dissociated, or negatively charged EOCs, such as BPA by 1.25-2.54 folds and IBU by 1.75-30 folds, depending on SOM content. However, the desaturation had no effect on the degradation of these compounds when microbial activity was inhibited and/or SOM was depleted from the soils. Comparison of SOM-differing soils indicated that the desaturation effect was larger in soils with higher SOM content. Dominant processes of the degradation include AWI-enhanced attachment of microorganisms and SOM-facilitated adsorption of EOCs at SWI, where SOM existed and biodegradation happened. However, pore water desaturation and SOM cannot influence the degradation of recalcitrant EOCs (e.g., CBZ, TTC, and CPF). These compounds could thus pose significant threats to the environment since compounds like CBZ exhibit high transport tendency and compounds like TTC and CPF can accumulate in the upper soil horizons.

It is worth noting that the repacked soils used in the study might result in less conductive and smaller pore structure compared to intact field soil and thereby increase retention of EOCs.[49] In addition, pre-treatments adopted in the experiments (e.g., soil air-drying, thermal oxidization of SOM, and CO_2 pre-flush) might potentially affect soil microbial community. However, these experimental procedures were necessary for distinguishing the coupled effects of unsaturated flow and SOM on the degradation of EOCs in real soil environment. Overall, this work implies that soil management practices (e.g., organic fertilization), which can increase SOM and soil microbial activities, could be effective ways to accelerate the degradation of biodegradable

EOCs (e.g., BPA and IBU). However, an optimal level of organic fertilization must be identified if the applied organic wastes (e.g., manure) contain contaminants (e.g. CBZ, TTC and CPF) that are toxic to microorganisms, recalcitrant to degradation, and/or mobile through preferential flow pathways. Future study should clarify how soil drying-wetting cycles under natural conditions or during deficit irrigation influence the degradation and transport of EOCs. These implications are valuable for optimizing hydrological and biologically conditions for minimizing the off-site risks of EOCs in farmland receiving reclaimed water and animal wastes.

Supporting Information

Schematic setup of saturated and unsaturated column systems; transport of bromide through different soil columns under steady-state and unsaturated flow conditions; results of replicated control column experiments

Acknowledgement

This work was financially supported by National Natural Science Foundation of China (Grant number: 41730858) and the National Key Research and Development Program of China (Grant number: 2018YFC1801200).

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Table 1. Physico-chemical properties of emerging organic contaminants (EOCs)

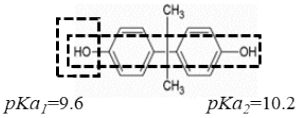
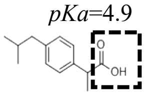
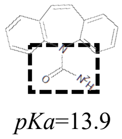
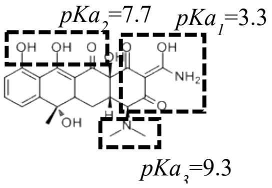
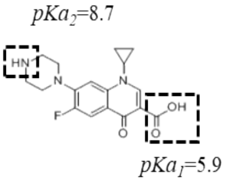
Compounds	Chemical structure	Molecular weight (g mol^{-1})	Water solubility (mg L^{-1})	LogK$_{ow}$	Half-life in soil (day)	Application
Bisphenol-A (BPA)		228.29	120	3.32	11-18[10]	Polycarbonate plastic, epoxy resins
Ibuprofen (IBU)		206.29	21	3.97	10-15[9]	Non-steroidal anti-inflammatory drug
Carbamazepine (CBZ)		236.28	17.7	2.45	∞[38]	Antiepileptic
Tetracycline (TTC)		444.44	231	1.30	1155[41]	Antibiotic
Ciprofloxacin (CPF)		331.35	30000	0.28	578[41]	Antibiotic

Table 2. Experimental and fitted model parameters of column experiments

EOCs	Soil	ρ_b (g cm^{-3})	v (cm h^{-1})	D (cm^2 h^{-1})	K_d (L kg^{-1})	f	R^2	μ_w (h^{-1})	R	Breakthrough (%)
Saturated										
BPA	OXM2	1.13	2.2	2.46	0.88	0.00	0.99	0.04	2.73	85.3±0.16
	M1	1.11	2.2	2.13	1.74	0.01	0.98	0.18	4.32	46.5±3.25
	M2	1.03	2.1	2.46	11.71	0.12	0.97	0.50	20.73	10.5±2.13
IBU	OXM2	1.13	2.2	2.46	0.29	0.00	0.99	0.00	1.57	100.0±2.33
	M1	1.11	2.2	2.13	0.65	0.02	0.99	0.02	2.24	91.5±4.17
	M2	1.03	2.1	2.46	1.22	0.02	0.98	0.06	3.06	77.8±3.54
CBZ	OXM2	1.13	2.2	2.46	0.82	0.01	0.99	0.02	2.62	93.7±0.14
	M1	1.11	2.2	2.13	1.33	0.24	0.98	0.02	3.54	92.5±0.21
	M2	1.03	2.1	2.46	3.42	0.12	0.98	0.01	6.76	93.2±2.05
Unsaturated										
BPA	OXM2	1.14	2.7	1.24	3.24	0.14	0.99	0.00	9.10	90.3±0.16
	M1	1.13	2.6	0.99	4.11	0.94	0.95	0.89	11.12	2.9±3.25
	M2	1.03	2.6	1.33	—	—	—	—	—	0.0±2.13
IBU	OXM2	1.14	2.7	1.24	0.38	0.48	0.99	0.00	1.95	100.0±2.33
	M1	1.13	2.6	0.99	0.91	0.61	0.99	0.12	3.24	57.3±4.17
	M2	1.03	2.6	1.33	2.71	0.05	0.96	0.09	6.71	56.8±3.54
CBZ	OXM2	1.14	2.7	1.24	1.17	0.62	0.99	0.00	3.93	96.9±0.14
	M1	1.13	2.6	0.99	2.00	0.66	0.97	0.01	5.93	92.1±0.21
	M2	1.03	2.6	1.33	1.56	0.26	0.97	0.01	6.60	94.1±2.05

M1: Soil with low level manure application;

M2: Soil with high level manure application;

OXM2: M2 soil with soil organic matter depleted;

ρ_b: Soil bulk density of experimental column;

v: Experimental pore water velocity;

D: Dispersion coefficient;

K_d: Fitted soil-water distribution coefficient;

f: The fraction of instantaneous adsorption sites (Type-1);

R^2: Coefficient of determination;

μ_w: Fitted first order degradation rate constant;

R: Fitted retardation factor (dimensionless);

"—" represents effluent samples without detection of bisphenol-A.

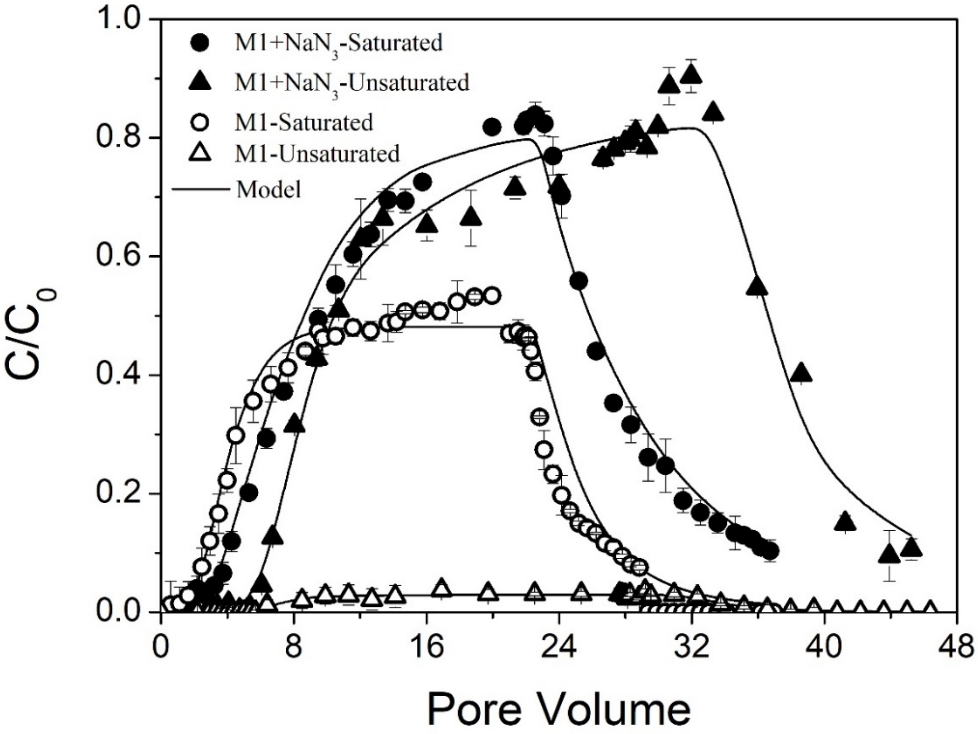


Figure 1. Transport of BPA through M1 soil columns with and without addition of NaN_3 under steady-state saturated (100% water saturation) and unsaturated (80% water saturation) flow conditions. M1: soil with low level application of swine manure; M1+NaN_3: M1 soil and input solution containing 100 mg L^{-1} NaN_3 to inhibit microbial reproduction.

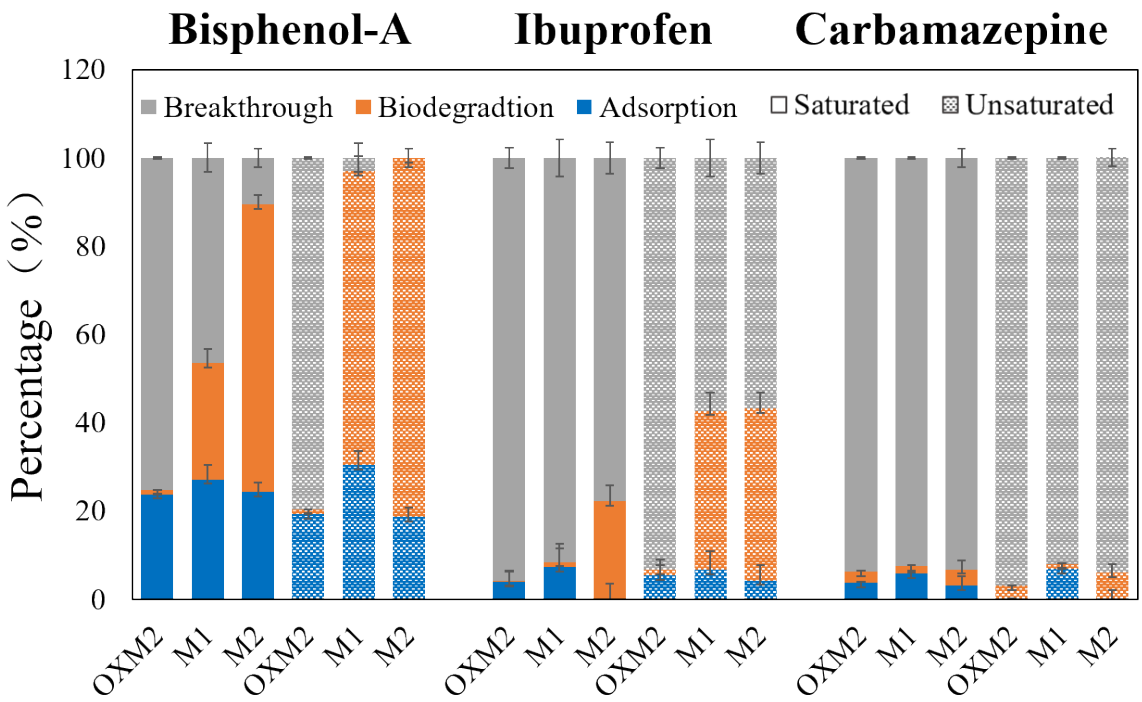


Figure 2. Mass balance of bisphenol-A (BPA), ibuprofen (IBU), and carbamazepine (CBZ) in different soil columns under steady-state saturated (100% water saturation) and unsaturated (80% water saturation) flow conditions. M1: soil with low level application of swine manure; M2: soil with high level application of swine manure; OXM2: M2 soil with soil organic matter removed by thermal oxidation.

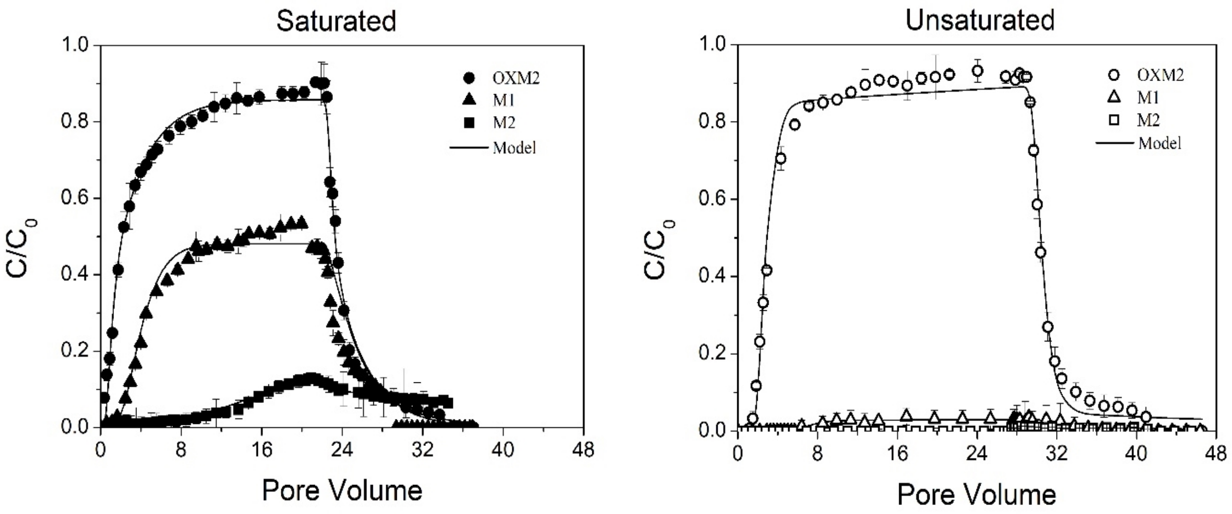


Figure 3. Effect of soil organic matter on the transport of BPA under steady-state saturated (100% pore water saturation) and unsaturated (80% pore water saturation) flow conditions. M1: soil with low level application of swine manure; M2: soil with high level application of swine manure; OXM2: M2 soil with soil organic matter removed by thermal oxidation.