



# The surface-pore integrated effect of soil organic matter on retention and transport of pharmaceuticals and personal care products in soils



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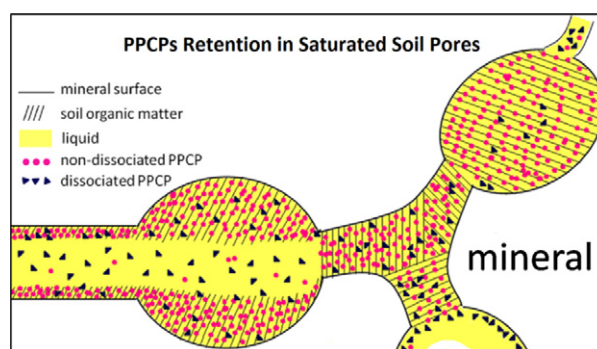
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## HIGHLIGHTS

- SOM controls PPCP transport by modifying surface and pore systems.
- Dissociated PPCPs have larger off-site risks in agricultural soils.
- Mineral surface reduces transport of dissociated PPCPs.
- Pore-filled SOM reduces transport of dissociated and non-dissociated PPCPs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study examines a surface-pore integrated mechanism that allows soil organic matter (SOM) to influence the retention and transport of three representative pharmaceuticals and personal care products (PPCPs)—ibuprofen, carbamazepine, and bisphenol A—in agricultural soil. A series of sorption-desorption batch tests and breakthrough column experiments were conducted using manured and non-manured soils. Results show that SOM could substantially influence the environmental behaviors of PPCPs via two mechanisms: surface-coating and pore-filling. Surface-coating with molecular SOM decreases the sorption of dissociated PPCPs (e.g., ibuprofen) but increases the sorption of non-dissociated PPCPs (e.g., carbamazepine and bisphenol A), while pore-filling with colloidal SOM enhances the retention of all the PPCPs by providing nano-/micro-pores that limit diffusion. The higher retention and lower mobility of PPCPs in soil microaggregates than in bulk soils suggest that SOM content and SOM-altered soil pore structure could exert a coupled effect on PPCP retention. Differences in the elution of PPCPs with low surface tension solution (i.e., 20% ethanol) in the presence and absence of SOM indicate that PPCPs prefer to remain in SOM-filled pores. Overall, ibuprofen has a high environmental risk, whereas carbamazepine and bisphenol A could be readily retarded in agricultural soils (with a loamy clay texture). This study implies that SOM accrual (particularly pore-filling SOM) has a high potential for reducing the off-site risks of PPCPs by increasing soil nano-/micro-porosity.

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## 1. Introduction

Soil organic matter (SOM) is a key sorption medium for organic contaminants in soils if its mass fraction is >0.1% (Schwarzenbach and Westall, 1981; Luo et al., 2008; Estevez et al., 2014). Sorption onto SOM is a process that determines the retention and transport of organic contaminants in the subsurface environment (Mitchell and Simpson, 2013). This mediation behavior of SOM generally depends on two mechanisms: (i) modifying soil surface chemistry (i.e., SOM polarity, aromaticity, aliphaticity) to affect retention (Mayer and Xing, 2001), and (ii) changing the soil pore system to affect transport (Balesdent et al., 2000; Mayer et al., 2004; McCarthy et al., 2008). Previous studies mainly focus on the first mechanism. For instance, Chefetz et al. (2008) investigated the effect of SOM chemistry on the sorption of organic compounds, and they found that non-polar SOM has stronger sorption interaction with carbamazepine than polar SOM. Ahangar et al. (2008) found that the values of organic carbon-normalized distribution coefficients ( $K_{oc}$ ) for diuron are positively correlated with aryl carbon and negatively correlated with O-alkyl carbon. A few studies have demonstrated that, in addition to polarity and aromaticity, aliphaticity of SOM (connected with aromaticity, SOM with high aliphaticity generally has low aromaticity, and vice versa) is unfavorable to the sorption of organic contaminants (Ahangar et al., 2009; Ding and Rice, 2011). These and other studies have well addressed the role of SOM in influencing the sorption of organic contaminants. Unfortunately, few investigations have been conducted to examine the second mechanism: the role of colloidal SOM in influencing the transport of organic contaminants from the perspective of pore structure change (Ji et al., 2010; Yang et al., 2011).

The role of colloidal SOM in altering the soil pore system is seldom addressed. McCarthy et al. (2008) found that certain agricultural management practices (i.e., manure application and no-till) could promote the encapsulation of colloidal SOM in soil pores, thereby creating SOM-filled pores that can reduce pore connectivity, retard diffusion, and increase pore water retention (Zhuang et al., 2008). Reduction in water movement in SOM-filled pores could slow solute transfer between sorption sites (Grathwohl and Reinhard, 1993), implying that pore-filling SOM might have a great potential for controlling the retention and transport of organic contaminants in soils. It is thus meaningful to verify this mechanism and establish a theoretical basis that guides the reduction of the environmental risks of soil contaminants.

As emerging organic pollutants, pharmaceuticals and personal care products (termed PPCPs) have gained increasing attention during the past decades because of their frequent detection in the agricultural soil environment and their long-term potential risks to soil organisms and aquatic systems (Qin et al., 2015). The main route of PPCPs entering agricultural soils is irrigation with reclaimed water, which is increasingly adopted in countries that experience water shortages (Kinney et al., 2006; Plumlee et al., 2012). Among the thousands of PPCPs, ibuprofen, carbamazepine, and bisphenol A are frequently detected in reclaimed water, soil, and even groundwater. Ibuprofen and carbamazepine are extensively used pharmaceuticals (Scheytt et al., 2005). Bisphenol A is a potential endocrine disruptor often detected in various human tissues and in leaching fluids from plastics and epoxy coatings on numerous foods and beverages (Willhite et al., 2008; Ballesteros-Gomez et al., 2009; Schecter et al., 2010). All of them have significant interactions with SOM. For instance, Durán-Álvarez et al. (2014) found that ibuprofen had lower sorption affinity in SOM-low soil. Carbamazepine exhibited higher sorption affinity in soils at 0–5 cm depth (high SOM) than at 15–25 cm depth (low SOM) (Chefetz et al., 2008). The distribution coefficients of endocrine disrupting chemicals, including bisphenol A and estrone, are positively related to SOM level (Sun et al., 2012). These studies suggest that SOM abundance could play a role in retention of PPCPs in agricultural soil. However, detailed retention mechanisms and sorption-based transport behaviors remain unclear.

The objective of this study was to examine the integrated role of SOM-affected surface and pore structures in the retention and transport

of PPCPs in agricultural soils that are subject to different levels of long-term manure treatments. The research hypothesizes that surface coating and pore filling with SOM exert a coupled effect on the environmental behavior of PPCPs in soils, and that the effect varies with the chemistry of PPCPs. The results are expected to provide mechanistic insights into how organic carbon sequestration could reduce the off-site risks of PPCPs in reclaimed water irrigated soils.

## 2. Materials and methods

### 2.1. Chemicals

Ibuprofen (>99% purity), carbamazepine (>98% purity), bisphenol A (>98% purity), and bromide ion standard solution ( $1 \text{ g L}^{-1}$ ) were purchased from Sinopharm chemical reagent (Shenyang, China). The chemical structures and characteristics of these compounds are provided in Table S1 of the Supporting Information. A mixed stock solution of these compounds ( $10 \text{ g L}^{-1}$ ) was prepared in methanol (HPLC grade) and stored in a refrigerator at  $-20 \text{ }^\circ\text{C}$ . Methanol, sodium bromide, and sodium chloride were purchased from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Deionized water was prepared in a Milli-Q purification system (Millipore, Barnstead, Boston, USA).

### 2.2. Preparation of soil and microaggregates

Bulk soil was collected from a depth of 0–15 cm in a maize field (*Zea mays* L.) located in Gongzhuling, Jilin, China ( $124^\circ48'\text{E}$ ,  $43^\circ30'\text{N}$ ). Field experimental treatments included surface application of three levels (0, 30, and  $60 \text{ t ha}^{-1}$  per year) of organic fertilizer (mature cattle manure after composting, pH 6.9–7.5) prior to tillage, designated as  $M_0$ ,  $M_{30}$ , and  $M_{60}$ , respectively. The annual manure application was started in 1979, 34 years before we collected the soil samples from replicate subplots. The soil was classified as Typic Hapludoll with a loamy clay texture (37% sand, 33% silt, and 30% clay). The soil secondary clay minerals were rich in illite and montmorillonite. Soil was sampled from five random locations in each treatment plot after crop harvest. Then, roots, rhizomes, and larger pieces of organic debris were removed by passing the soil through an eight-mm sieve. The sieved soils were then air-dried and passed through a two-mm sieve for experimental use or microaggregate extraction.

A 100-g subsample of soil from each plot was used to extract water-stable microaggregates (53–250  $\mu\text{m}$ ) following a procedure modified from the method of Cambardella and Elliott (1994), which is described briefly here. Soil was capillary-wetted overnight at  $4 \text{ }^\circ\text{C}$  prior to sieving. The prewetted soil samples were then suspended in room temperature water on the 250- $\mu\text{m}$  sieve stacked on the top of a 53- $\mu\text{m}$  sieve for 5 min before sieving. Aggregate disruption was accomplished by moving the sieve 3 cm vertically 50 times in 2 min, being careful to break the surface of the water with each stroke. The isolated microaggregates remaining on the 53- $\mu\text{m}$  sieve were backwashed into an aluminum pan and freeze-dried. The dried water-stable microaggregates were weighed and stored at room temperature ( $22 \pm 1 \text{ }^\circ\text{C}$ ) for use.

The physical and chemical properties of bulk soils and microaggregates were measured using the standard methods (Sparks et al., 1996) and provided in Table 1. Ratio of SOM-filled pore volume to total pore volume (termed SOM-filled porosity) shown in Table 1 were measured using small-angle X-ray scattering technique, and contrast variations in X-ray scattering before and after combustion ( $375 \text{ }^\circ\text{C}$ , 26 h) for the pores originally filled with SOM were used to estimate the pore volume of the SOM-filled pore (McCarthy et al., 2008).

### 2.3. Thermal oxidation of soil organic matter

To remove SOM from the pores of soil samples, the bulk soils and isolated microaggregates were combusted at  $375 \text{ }^\circ\text{C}$  for 26 h following the modified method of McCarthy et al. (2008).

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