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Sorption behavior of 17 phthalic acid esters on three soils: Effects of pH and dissolved organic matter, sorption coefficient measurement and QSPR study

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HIGHLIGHTS

- Sorption capacities of PAEs increased with the decreasing soil pH.
- The low concentration of DOM promoted the soil sorption of PAEs.
- The high concentrations of DOM affected the sorption more complicated.
- Soil partition coefficients ($\log K_{oc}$) were measured for 17 PAEs on three soils.
- Satisfactory QSPR models were established to predict $\log K_{oc}$ of PAEs.

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ABSTRACT

This work studies the sorption behaviors of phthalic acid esters (PAEs) on three soils by batch equilibration experiments and quantitative structure property relationship (QSPR) methodology. Firstly, the effects of soil type, dissolved organic matter and pH on the sorption of four PAEs (DMP, DEP, DAP, DBP) are investigated. The results indicate that the soil organic carbon content has a crucial influence on sorption progress. In addition, a negative correlation between pH values and the sorption capacities was found for these four PAEs. However, the effect of DOM on PAEs sorption may be more complicated. The sorption of four PAEs was promoted by low concentrations of DOM, while, in the case of high concentrations, the influence of DOM on the sorption was complicated. Then the organic carbon content normalized sorption coefficient ($\log K_{oc}$) values of 17 PAEs on three soils were measured, and the mean values ranged from 1.50 to 7.57. The $\log K_{oc}$ values showed good correlation with the corresponding $\log K_{ow}$ values. Finally, two QSPR models were developed with 13 theoretical parameters to get reliable $\log K_{oc}$ predictions. The leave-one-out cross validation (CV-LOO) indicated that the internal predictive power of the two models was satisfactory.

1. Introduction

Phthalic acid esters (PAEs) are the dialkyl or alkyl aryl esters of phthalic acid. They are mainly used as plasticizers in the plastics materials to increase the flexibility of polymers. In addition, they are also used in the products such as paints, lubricating oils, pharmaceutics, perfumes, glues and pesticides (Zeng et al., 2008). Since the PAEs are physically bound to the polymer chains, they are easily released into the environment during the manufacturing, using and disposal process (Roslev et al., 2007; Liang et al., 2008). It has been reported that PAEs were distributed all over the world and frequently detected in air, water, soil and food. Moreover, many researches show that PAEs have estrogenic effects on animals and human, i.e. they can interfere with the endocrine system and procreation ability (Gray et al., 2000; Moore, 2000; Duty et al., 2003; Higuchi et al., 2003). Therefore, the environmental behavior of PAEs has been become a hot area of research.

Soil sorption is considered as an important environmental process for organic compounds. This process plays a key role in the migration, degradation and bioavailability of contaminants. Hunter and Uchrin, 2000 have investigated the sorption behavior of PAEs in different soils and sediments. Li et al. (2010) studied the sorption of dimethyl phthalate (DMP) and diethyl phthalate (DEP) on two soils, and found that the soil organic carbon content plays a major role in the sorption and pH can affect the adsorption capacity. The study carried out by Xu and Li (2009) showed that the sorption behavior of benzyl butyl phthalate (BBP) on marine sediments could be attributed to the organic content and the sorption increased with an increase in salinity. However, to the best of our

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knowledge, little studies have focused on the effects of dissolved organic matter (DOM) on the PAEs sorption. In fact, many researches have shown that DOM can influence the sorption of hydrophobic compounds on soil, and the impact will be different depending on the intrinsic nature of DOM (Sablijic et al., 1999; Seol and Lee, 2000; Sun et al., 2008).

As a series of compounds, PAEs show different hydrophobicity (Cousin and Mackay, 2000) and sorption affinity with the type of ortho-position substitution (Lu, 2009). Therefore, systematic investigation of the soil sorption behavior of PAEs could be essential to the environmental risk assessment. The soil organic carbon content normalized sorption coefficient ($\log K_{oc}$) is a well-known constant used to describe the soil sorption affinity of organic compounds. In recent years, the computation-based quantitative structure property relationship (QSPR) method has been widely used to study the soil sorption and predict $\log K_{oc}$ of organic compounds (Hansen et al., 1999; Baker et al., 2001). Thomsen et al. (1999) predict the K_{oc} of seven phthalic acid esters using the molecular connectivity indices (MCIs) and electrotopological atomic state indices (EASIs) as descriptors. Besides, Lu (2009) built QSPR models for 11 PAEs with Lμ index. However, due to the lack of related experiment sorption data, up to now, the regularity of sorption coefficients based on a large number of PAEs have not been reported in detail.

Therefore, the objective of this study is to investigate the sorption behavior of 17 phthalic acid esters by experimental and theoretical methods. First, the influences of soil type, pH and external DOM on the sorption of PAEs (DMP, DEP, DAP, DBP) were investigated. Then, the $\log K_{oc}$ of 17 PAE congeners were determined by batch equilibration experiments. Finally, the QSPR models were established with the multiple linear regression method.

2. Experimental and calculation methods

2.1. Soils and chemicals

Three types of soils were collected (0–20 cm below the ground surface) from three representative regions of China: NanChang Honggutan (28.697′N, 115.858′W), NanJing Xianlin (32.104′N, 118.947′W) and JiaXing Xiuzhou (30.765′N, 120.764′W). All the soils in sample sites had negligible background levels of pollutants. After collection, the samples were air-dried, sieved (<2 mm), thoroughly mixed and stored in glass jars at 4 °C until further used. The physical and textural properties of the soils were presented in Table 1.

Phthalate esters were analytical reagents (>98% purity). Their stock solutions were prepared in methanol (HPLC grade) from Merck KGaA (Darmstadt, Germany). Ultrapure water was supplied by a Milli-Q water purification system (Millipore, Bedford, USA). All the other chemicals used in this study were of reagent grade.

2.2. DOM preparation

DOM was extracted from the rice straw (Nanjing Xianlin) according to the method described by Zarruk et al. (2007) and Chen et al. (2010). The straw was mixed with water (the straw/water ratio of 1:10) in a glass bottle, which was shocked in a vortex mixer for 24 h. Then the suspending liquid was centrifuged and filtered through a 0.45-μm membrane. The filtrate (stock solution) was stored at 4 °C before use. The pH was measured by a S20 pH meter (Mettler-Toledo Instruments (Shanghai) Co., Ltd., China). Total organic carbon content and element analysis was conducted by Shimadzu TOC 5000 and elementar vario MICRO (Germany), respectively. The results were shown in Table 1.

2.3. PAEs sorption experiment

Batch equilibrium experiments were carried out to determine the K_{oc} of 17 PAEs. At first, stock solution was prepared by dissolving the PAE sample in methanol. For each compound, we adopted three initial concentrations working solutions in order to determine the accurate K_{oc}. The stock solutions were diluted into the working solutions by ultrapure water with 0.01 M $CaCl_2$ and 0.05% $HgCl_2$ (as biocides). The volume fraction of methanol in working solutions was less than 0.1% in order to avoid the co-solvent effect.

For each experiment, after mixing the working solution with the air-dried soils, the glass bottle was placed in an rotary shaker with variable speed control at 22 ± 1.5 °C. Note that in experiments with a large soil/water ratio, magnetic stirrers were used. The soil mass (g) to solution volume (mL) ratios changed with the sorption percentage ranging from 20% to 80%. Before the equilibrium experiment, kinetic studies were conducted to determine the apparent equilibrium time. The results indicated that 72 h was sufficient for the 17 PAEs to reach the apparent equilibrium. Therefore, 72 h was used as the equilibrium time in this study. After shaking in dark for 72 h, the suspensions were centrifugated for 30 min at 6000 rpm and the aqueous concentrations were determined by HPLC. For those PAE samples with low water solubility, water phase was extracted with *n*-hexane. The recovery was measured by the standard recovery test and it was found to be in the range of 90–115%.

All the tests were conducted in triplicate and two blank tests (one without soil and the other one without samples) were performed simultaneously.

2.4. Effect of pH and DOM

The influence of pH and DOM on the sorption of four PAEs including: dimethyl phthalate (DMP), diethyl phthalate (DEP), diallyl phthalate (DAP) and di-n-butyl phthalate (DBP) was investigated in detail. The JX soil was chosen here. Six concentrations of

Table 1
Properties of the soil and straw DOM.

Depth interval			Soil texture			Soil organic carbon (%)	CEC (cmol/kg)	Total nitrogen (%)	Moisture content (%)
Soil	bgs (cm)	pH	Sand (%)	Silt (%)	Clay (%)				
Soil properties									
NC soil	0–20	4.88 ± 0.01	18.95	45.1	35.95	0.64 ± 0.01	10.07 ± 0.14	0.091 ± 0.001	1.73 ± 0.01
NJ soil	0–20	8.08 ± 0.01	6.06	61.15	32.79	0.83 ± 0.01	15.34 ± 0.19	0.065 ± 0.002	3.80 ± 0.02
JX soil	0–20	7.87 ± 0.01	11.85	28.35	59.8	2.91 ± 0.02	17.88 ± 0.24	0.032 ± 0.001	3.52 ± 0.02
pH	TOC(mg L^{-1})	Elemental composition (%)				Atomic ratio			
		C	H	N	O	H/C		O/C	
DOM properties									
7.91 ± 0.01	332.7 ± 13.9	13.24	2.570	1.000	12.43	2.329		0.7041	