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SOC Effects on Diethyl Phthalate Sorption to Four Soils in China

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Abstract

Purpose: Phthalate esters (PAEs) are commonly detected in agricultural soils of China, which can post potential threats to human health. Understanding their sorption to soils is important in assessing their transport and bioavailability in environment. Limited research focuses on the influence of soil organic carbon (SOC) on PAEs adsorption to soils at different depths and increased dissolved organic carbon (DOC) after adsorption. **Materials and Methods:** Batch sorption experiments of diethyl phthalate (DEP) to four types of soils were conducted in this study, including black soil, fluvo-aquic soil, paddy soil, and red soil. Total concentration of solute DEP and the concentration of free DEP not sorbed to DOC were measured with HPLC. The UV absorbance of supernatant was measured and specific UV absorbance at 254 nm was calculated for DOC aromaticity. Sorption isotherms of DEP to soil particles were fitted to the Langmuir model and the Freundlich model. **Results and Discussion:** Partial SOC can dissolve to DOC in solution, and 47.4-89.4% of total DEP can be sorbed to DOC. Increasing DEP in solution can enhance aliphatic SOC dissolving. The sorption coefficients of DEP are higher to fluvo-aquic soils (K_{∞} for surface soils 1820 L kg⁻¹ and subsurface soils 1388 L kg⁻¹) than to other soils (<520 L kg⁻¹), which indicates that SOC fractions of different soils have varied affinity to DEP. **Conclusions:** SOC plays an important role in DEP sorption to soil particles. Soil samples from surface layers have higher affinity than those from subsurface layers. DOC from SOC in solution is important for DEP transport in soil, and organic pollution can accelerate SOC dissolving.

Keywords: Phthalate esters; Specific UV absorbance; Soil organic carbon; Sorption

Introduction

Phthalate esters (PAEs) are important additives in plastics industry, which can increase plastics flexibility, transparency, durability, and longevity [1]. PAEs can easily leach into soils [2], water [3], and air [4,5], because there is no covalent bond between PAEs and polyvinylchloride polymers. PAEs have been commonly detected in agriculture soils in China and their concentrations are in the range of 0.195-33.6 mg kg⁻¹ [6-9]. High levels of PAEs' exposure might pose health threats to human [10]. It has been reported that PAEs, especially di(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DnBP), have environmental endocrine-disrupting effects and might cause antiandrogenic, teratogenic, or mutagenic effects on young kids and fetus and carcinogenic toxicity [11-13]. The U.S. Environmental Protection Agency (U.S. EPA) has classified dimethyl phthalate, diethyl phthalate (DEP), DnBP, benzyl butyl phthalate, DEHP and di-n-octyl phthalate as priority environmental pollutants in 1979. Phthalate esters are relatively stable in soils, and their half-lives are varied from 1 d to several months depending on their side-chain lengths and structures [14-16]. The recently-published study of Cai et al. [17] showed that rice (Oryza sativa L.) could accumulate and translocate DEHP to its root, stem, shoot and grain, and the concentration range was from 0.26 to 11.8 mg kg 1. The study of Zhang et al. [18] showed the accumulation of DnBP in cucumber seedlings could decrease root protein content, and DnBP concentration (>50 mg L⁻¹) in soil changed the abundance, structure and composition of rhizosphere bacteria. Increasing DnBP concentration from 0.01 mg L⁻¹ to 1 mg L⁻¹ can cause the damage of the ultra-structures in Arabidopsis thaliana leaves [19].

Understanding the sorption of PAEs in soils is important to assess their transport and transformation in environment. The study of Murillo-Torres et al. [20] showed higher contents of soil organic carbon (SOC) and clays would sorb more PAEs, in which the adsorption coefficient $K_{\rm d}$ of DEHP was in the range of 1.8×10^4 to 4.2×10^4 L kg 1 . In the study of Yang et al. [21], batch sorption experiments were conducted with

17 PAEs and four soils. Their results showed the sorption of PAEs was positively correlated to their hydrophobicity. However, limited research examined effects of SOC in different soils; no research examined the effects of DOC on the sorption of PAEs, which would be an important factors for the adsorption of organic contaminants [22,23].

The preliminary objectives of this study were to investigate effects of soil type, soil depth, SOC content and DOC on the sorption of DEP to soil particles. Diethyl phthalate was selected as a model compound of PAEs due to its high solubility (4.86 mM), which had been commonly detected in soils [18] and surface waters [24]. Batch sorption experiments were conducted with four common soils in China, including black soil, fluvo-aquic soil, paddy soil and red soil. Black soil belongs to Isohumisols, which has high content of SOC, usually found in Northeast China; fluvo-aquic soil belongs to Cambisols and found in alluvial plains, which usually has high pH and sand content; paddy soil belongs to Anthrosols and is usually formed during long-term rice farming in a flooding-draught condition; red soil belongs to Ferrosols, which is widely distributed in South China with high contents of Fe/Al oxides and clay minerals.

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Materials and Methods

Chemicals

Diethyl phthalate ester was purchased from Sigma-Aldrich Chemical (St Louis, MO). The structure and its properties were listed in Table 1. Sodium hydroxide, hydrochloric acid, and methanol were obtained from National Medicines Corporation Ltd (Beijing, China). The purities of all chemicals in this study were >99%. Ultrapure water (18.2 M Ω ·cm $^{-1}$) from Synergy UV ultrapure water system with Millipak-40 Filter Unit (Millipore Corporation Merck KGaA, Darmstadt, Germany) was used to make solutions in the study.

Soil sampling and characterization

In this study, soil samples were collected at four sites, including black soil at E126.64, N45.72 in Haerbin, Heilongjiang Province, fluvoaquic soil at E114.54, N35.00 in Fengqiu, Henan Province, paddy soil at E116.13, N31.88 in Lu'an, Anhui Province, and red soil at E116.93, N28.21 in Yingtan, Jiangxi Province. At each site, soil samples at a depth of 0-20 cm and 20-40 cm were collected. After collection, big stones and visible plant residues were removed by hand. Then soil samples were airdried in hood, passed through a 2 mm sieve and stored in glass bottles at room temperature. The content of SOC was measured with the potassium dichromate titrimetric method [25]. Iron content in soil particles was measured with a Hitachi Z-2000 Atomic Absorbance Spectrometer after total digestion in HNO3-HF-HClO4 mixture. The specific surface area of soil particles was followed the method of Brunauer-Emmett-Teller (B.E.T.) and measured by the Analysis Center of Nanjing University. Soil texture and cation exchangeable capacity (CEC) was measured by the Soil Analysis Laboratory in the Institute of Soil Science, CAS. The mineral compositions of soil samples were analyzed with an X-ray Rigaku D/max-Ultima IV diffractometer (Rigaku Corporation, Tokyo, JP), using a CuKα radiation and 0.02° step scanning from 2° to 60° at a rate of 2° min⁻¹.

Batch sorption experiments

Batch sorption experiments of DEP to soil particles were conducted in 15 mL 5 mM ${\rm CaCl}_2$ background solutions for 5 d at a solid-to-solution ratio of 1:50 in dark. The initial DEP concentrations were from 0.02 mM to 0.90 mM, and 0.01% ${\rm NaN}_3$ was added to suppress microbial activity in solution before sorption experiments. The preliminary experiments showed that sorption equilibrium would be arrived within 5 d. After equilibrium, the suspension was centrifuged at 6000 rpm for 20 min.

Then, 1 mL supernatant was taken and passed through 0.22 μ m syringe filter and stored in a 2 mL vial for later analysis. Another 5 mL supernatant was taken and added on a methanol pretreated solid phase extraction column (LC-C18, 500 mg, 6 mL) and eluted with methanol 3 times to get free DEP in solution [26]. The collected elution was N₂-purged till dry and re-dissolved in 1 mL methanol for later analysis. The DOC-sorbed DEP was calculated by subtracting free DEP concentration from the total DEP concentration in supernatant.

Control experiments without soil particles were conducted in parallel to account for unknown degradation during the sorption process, and all experiments were conducted in triplicates. After sorption and centrifugation, 10 mL methanol was added to soil particle pellets, and the recovery rate of DEP was in the range of 15-73%, which indicated interactions between DEP and soil particles were complicated and desorption was not completely reversible.

DOC aromaticity analysis

The 1 mL supernatant of soil suspension after sorption was scanned from 200-900 nm with a UV-2700 spectroscopy (Shimadzu, Kyoto, JP). Both DOC and DEP molecules in supernatant can absorb UV light. It has been reported that the aromaticity of DOC is corresponded to DOC reactivity [27], which can be indicated with the specific UV absorbance at 254 nm ($SUVA_{254,DOC}$) and the ratio of UV absorbance at 465 nm (UV_{465}) and 665 nm (UV_{665}). The value of $SUVA_{254,DOC}$ (L mg $_{\rm c}^{-1}$ m $^{-1}$) could be estimated by dividing the UV absorbance of DOC at 254 nm ($UV_{254,DOC}$) with the concentration of DOC ([DOC] $_{\rm e}$). Because the intensities of $UV_{254,DOC}$ and the UV absorbance of DEP ($UV_{254,DEP}$) were additive (Figures S1 and S2), $UV_{254,DOC}$ could be calculated by subtracting $UV_{254,DEP}$ from the total absorbance of supernatant $UV_{254,DOC}$ The value of $SUVA_{254,DOC}$ at equilibrium could be calculated as follows (equation 1):

$$SUVA_{254,DOC} = \frac{UV_{254,\text{total}} - UV_{254,\text{DEP}}}{[DOC]_{e}}$$
(1)

where $[DOC]_e$ (mg_c L⁻¹) was DOC concentration in supernatant at equilibrium, in which DOC contributed from DEP was excluded. Total organic carbon (TOC) of the supernatant was analyzed with a Shimadzu TIC-500 Total Organic Carbon Analyzer (Kyoto, Japan). Preliminary data showed calculated DOC contributed from DEP measured with HPLC had a good linear correlation (ρ =0.99, R²=0.91) with the value measured with TOC analyzer (Figure S2).

Diethyl phthalate (DEP)					Solubility: 4.86 mM [†] log K _{ow} : 2.31 [‡] MW: 222.24			
Soil	Depth	pН	CEC	BET	soc	Fe	Clay	Texture
	cm		cmol _c ·kg⁻¹	m²⋅g⁻¹	g kg ⁻¹	%	%	
Disabasil	0-20	7.5	27.3	19.2	44.3	2.39	30.7	Clay loam
Black soil	20-40	7.6	29.6	25.5	37.9	2.48	38.6	Clay loam
Fluvo-aquic soil	0-20	7.8	7.55	8.34	10.1	2.24	14.0	Sand loam
	20-40	8.2	11.3	18.6	6.0	2.81	28.9	Clay loam
Paddy soil	0-20	6.6	19.7	19.5	23.9	2.69	28.6	Silt loam
	20-40	7.8	18.0	22.2	6.4	2.35	29.3	Silt loam
Red soil	0-20	6.6	16.1	29.0	8.3	3.38	42.8	Clay
	20-40	6.7	14.8	22.5	9.3	3.07	44.4	Clay

[†]The Solubility of DEP was measured at 20°C; [‡]data from Yang et al. [21]

 Table 1: Physicochemical properties of diethyl phthalate and soils in this study.

High Performance Liquid Chromatography (HPLC)

DEP concentration in supernatant was analyzed by direct injection of 20 μL supernatant onto a 4.6 \times 250 mm SUPELCOSIL LC-18 (5 $\mu m)$ column in Agilent 1260 high performance liquid chromatography with a Diode Array Detector VL at 224 nm. The flow rate was 1 mL min $^{\text{-}1}$ for each run.

Data analysis

The batch sorption data were fitted to the Langmuir Model and the Freundlich model. The Langmuir model was followed equation 2:

$$\frac{1}{q_s} = \frac{1}{q_m} + \frac{1}{K_I \cdot q_m} \cdot \frac{1}{C_c} \tag{2}$$

where $q_{\rm s}$ (mmol kg⁻¹) and $q_{\rm m}$ (mmol kg⁻¹) were the soil-sorbed DEP concentration at equilibrium and the maximum soil-sorbed DEP concentration, $C_{\rm e}$ (mM) was the concentration of free DEP in solution at equilibrium, and $K_{\rm L}$ (L mmol⁻¹) was the Langmuir constant, which could be used to calculate a dimensionless parameter, Hall separation factor $(R_{\rm L})$, as follows:

$$q_{\rm s} = K_{\rm f} \cdot C_{\rm e}^{\rm n} \tag{3}$$

where C_0 (mM) is the initial concentration of DEP in solution. When $R_L < 0$ or >1, the sorption was unfavorable; when $0 < R_L \le 1$, the sorption was favorable; when $R_T = 0$, the sorption was irreversible.

The Freundlich model was followed equation 4, as follows:

$$q_{\rm s} = K_{\rm f} \cdot C_{\rm e}^{\rm n} \tag{4}$$

where $K_{\rm f}$ (mmol¹⁻ⁿ·Lⁿ·kg⁻¹) was the Freundlich affinity coefficient, and n is the Freundlich nonlinearity index.

Based on preliminary data, the sorption of DEP to quartz or metal oxide was smaller than to clay minerals and SOC. The total sorbed DEP (q_s) to soil particles included SOC-sorbed DEP ($q_{s,SOC}$, mmol kg⁻¹) and clay-sorbed DEP ($\Sigma q_{s,clay}$ mmol kg⁻¹), as follows:

$$q_{\rm s} = q_{\rm s \ SOC} + q_{\rm s \ clay} = q_{\rm s \ SOC} + \Sigma (f_{\rm clay,i} \cdot K_{\rm f \ clay_i} \cdot C_{\rm e}^{n_{\rm clay_i}}) \tag{5}$$

Combined equations 4 and 5, we got equations 6 and 7 as follows:

$$q_{\text{sSOC}} = K_{\text{f}} \cdot C_{\text{e}}^{\text{n}} - \sum (f_{\text{clay,i}} \cdot K_{\text{f clay,i}} \cdot C_{\text{e}}^{n_{\text{clay,i}}}) = f_{\text{o}} \cdot K_{\text{0}} \cdot C_{\text{e}}$$
(6)

$$K_{\rm OC} = (K_{\rm f} \cdot C_{\rm e}^{\rm n-1} - \Sigma (f_{\rm clay,i} \cdot K_{\rm f, clay_i} \cdot C_{\rm cday_i}^{\rm n-1})) / f_{\rm oc}$$
 (7)

where $f_{\rm oc}$ (%) and $f_{\rm clay,i}$ (%) were the fractions of SOC and ith clay mineral contents in soil particles; $K_{\rm oc}$ (L kg $^{-1}$) was sorption coefficient of SOC in soil particles; $K_{\rm f,clay}$ (mmol $^{1-n}\cdot {\rm L}^n\cdot {\rm kg}^{-1}$) and $n_{\rm clay}$ were the Freundlich affinity coefficient and the Freundlich nonlinearity index of the ith clay mineral.

Results and Discussion

Soil properties and soil organic carbon

The pH range of these soil samples was from 6.6 to 7.8 (Table 1); soil particles from surface layers (0-20 cm) had higher SOC contents

than those from subsurface layers (20-40 cm), except red soils. Black soils had the highest SOC contents around 41.1 g kg⁻¹; red soils had the lowest SOC contents around 8.8 g kg⁻¹, and the highest clay and iron contents, around 43.6% and 3.23%, respectively; surface layer of fluvoaquic soil had the lowest clay content of 14.0%, and the subsurface soil of fluvo-aquic soil had increased clay content (28.9%) but lowest SOC content (6.0 g kg⁻¹), which was related to the alluvial formation process of soil

Partial of SOC can dissolve into solution to form DOC when soil particles were suspended into solution. The concentration of DOC was positively correlated with SOC contents in soils. The values of $SUVA_{254,\mathrm{DOC}}$ (Table 2) for the soils were in the range of 3.59-5.28, which were consistent with previous reported data (0.6-5.3) of Weishaar et al. [28]. Higher value of $SUVA_{\rm 254,DOC}$ means higher aromaticity of DOC. The results indicated that DOC from red soil had the highest aromaticity among DOCs from these soil samples, and Fluvo-aquic surface soil had the lowest aromaticity. These results were further confirmed by the ratio of UV_{465} and UV_{665} (Table 2), which was inversely correlated with DOC aromaticity [29-31]. More DEP in solution can cause more SOC dissolve to form DOC at sorption equilibrium (Figure 1), especially for black soil (0-20 cm) and red soils (0-20 cm and 20-40 cm), which indicate that organic contaminants in solution can facilitate SOC dissolution. It is also observed that $SUVA_{245, DOC}$ is decreasing as higher DEP concentration in solution (Figure 2), which indicates that either sorbed DEP or DEP in solution can induce more aliphatic SOC dissolving to form DOC. The sorbed DEP only added 0.00034%-0.022% of organic carbon to soil particles, while the fraction of DOC is 0.0067%-0.11% of SOC. The results indicate organic contaminants can accelerate SOC dissolve from soil particles.

The sorption of DEP to DOC

The intensities of UV absorbance at 254 nm for DEP and DOC are additive (Figure S1), which suggests the interaction between DEP and DOC may not happen between aromatic rings, but rather between the functional groups of -C=O in DEP and O-H in DOC. Similar results were reported in the research of Xu et al. [32]. The further investigation of the interactions between DOC and DEP should be conducted with 3-D fluorescence spectroscopy [33].

In suspension, DEP molecules was sorbed to DOC and soil particles. The results showed that 47.4-89.4% of DEP was sorbed to DOC, 2.1-18.3% of DEP was sorbed to soil particles, and 3.2-34.3% of DEP existed as free DEP in suspension when the initial concentration of DEP [DEP]₀ was 0.045 mM. When [DEP]₀ increased to 0.90 mM, the fractions of free DEP in suspensions increased to 51.6-91.9%, while the fractions of DOC-sorbed DEP decreased to 6.41- 46.5% and the fractions of soil-sorbed DEP decreased to 1.4-4.5%. The results indicate that DOC-sorbed DEP is one of the main forms of DEP and plays an important role in DEP transport. There was no clear correlation between DOC aromaticity and the sorption of DEP to DOC.

The sorption of DEP to DOC was not fit to the Langmuir model nor the Freundlich model. Figure 3 shows that the sorption of DEP ($q_{\rm e,DOC}$) is highest to DOCs from fluvo-aquic soils, then Paddy soils, black soils and red soils. DOCs from subsurface layers had twice higher affinity to DEP than DOCs from surface layers, except red soils.

Sorption of DEP to soils

The sorption isotherms of DEP to soil particles were fitted well to the Langmuir model with R^2 of 0.70-0.99. From Table 3, the q_m values of black surface soil (16.72 mmol kg⁻¹) and paddy surface soil (10.85 mmol

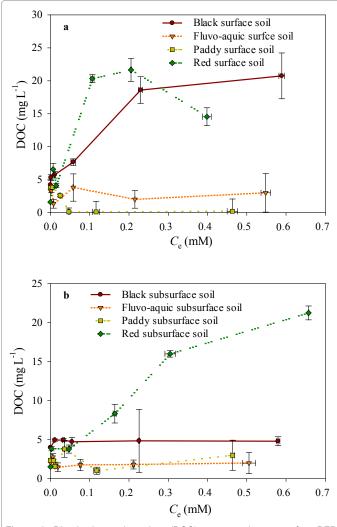


Figure 1: Dissolved organic carbon (DOC) contents change as free DEP concentration increasing at sorption equilibrium. **(a)** DOCs formed from 0-20 cm surface soils; **(b)** DOCs formed 20-40 cm subsurface soils.

kg⁻¹) were 10.3 and 8.1 times of their subsurface soils, while fluvo-aquic subsurface soil (1.52 mmol kg⁻¹) and red subsurface soil (0.76 mmol kg⁻¹) were 1.6 and 1.3 times as the surface soils. The subsurface layer soil of fluvo-aquic soil had twice more of clay mineral content and B.E.T surface area than surface layer, which might cause the higher sorption of DEP in subsurface layer. The $R_{\rm L}$ values in this study were in the range of 0-1, which indicated that sorption of DEP to soil particles happened spontaneously and partially irreversible. Based on values of $q_{\rm m}$ (Table 3), the sorption capacities of the four surface layer soils were in the sequence: black soil>paddy soil>fluvo-aquic soil>red soil, however, there was limited difference among those subsurface layer soils. The results were consistent with the SOC contents in these soils.

The sorption isotherms of DEP to soil particles (Figure 4) were also well fit to the Freundlich model (R^2 0.88-0.97). The range of n values was 0.25-0.86, which indicated heterogeneous sorption sites for DEP in soil particles (Table 3). The subsurface soils had higher linearity than the surface soils, except red soil. Based on soil component analysis, clay contents in soil samples were in the range of 14.0-44.4% (Table 1). The results (Table S1) showed that the mineral parts of soils contained 48-81% SiO₂, 1-37% feldspar, 7-16% hydromica, 1-6% kaolinite and

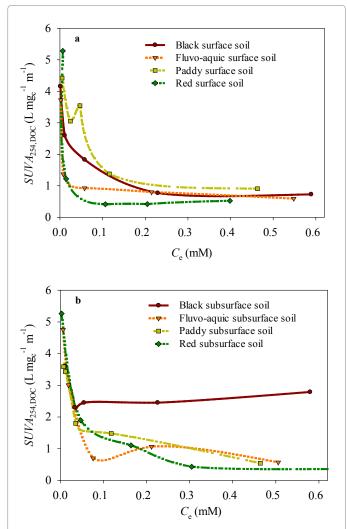
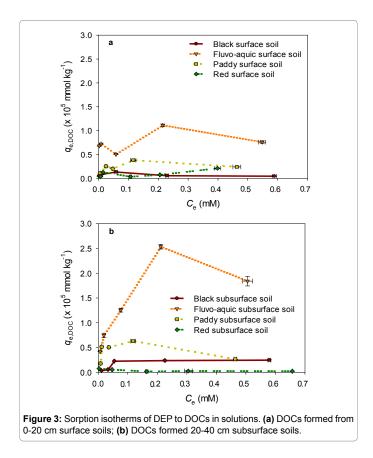


Figure 2: Changes of $SUVA_{254,DOC}$ with changed DEP concentrations at equlibrium. (a) surface soils; (b) subsurface soils.

chlorite, and 1% vermiculite based on XRD spectroscopies [34]. The previous research of clay adsorption [35] showed that $n_{\rm clay}$ and $K_{\rm f,clay}$ of K+ saturated kaolinite or K+ saturated montmorillonite were 1.1 and 3.31 mmol $^{-0.1}\cdot L^{1.1}\cdot kg^{-1}$ or 2.4 and 1000 mmol $^{-1.4}\cdot L^{2.4}\cdot kg^{-1}$, respectively. There was no detectable montmorillonite in these soils. The ratios of sorbed DEP to Kaolinite to the total sorbed DEP by soil particles were 0.135-4.57%. There was negligible sorption of DEP to SiO $_2$. The sorption of DEP to clay minerals was negligible in this study, thus equation 7 could be simplified to equation 8.

$$K_{\rm OC} = K_{\rm f} \cdot C_{\rm e}^{n-1} / f_{\rm o} \tag{8}$$

Table 3 showed $K_{\rm OC}$ values of SOC from fluvo-aquic surface (1820 \pm 115 L kg $^{\rm I}$) and subsurface soils (1388 \pm 226 L kg $^{\rm I}$) were 3.5-5.7 times or 2.1-4.7 times as those of the other soils at $C_{\rm e}$ =0.045 mM. The research of Yang et al. [21] showed that $K_{\rm OC}$ values (44.7 L kg $^{\rm I}$ for NC soil, 26.9 L kg $^{\rm I}$ for NJ soil and 35.5 L kg $^{\rm I}$ for JX soil) were smaller than the values in this study. The possible reason was that they did not consider DOC-sorbed DEP in solution, and overestimated free DEP at sorption equilibrium. The values of $K_{\rm OC}$ for Soil particles was much smaller than those of DOC. The value of $K_{\rm OC}$ for paddy surface soil was about half



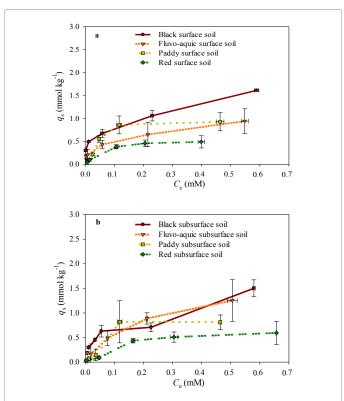


Figure 4: Sorption isotherms of DEP to these soils, (a) 0-20 cm surface soils; (b) 20-40 cm subsurface soils.

	Depth	DOC			
Soil				SUVA _{254,DOC} †	UV ₄₆₅ /UV ₆₆₅ ‡
	cm	mg L ⁻¹	UV ₂₅₄		
Black soil	0-20	4.28	0.178	4.16	3.5
	20-40	3.99	0.178	4.46	3.0
Fluvo-aquic soil	0-20	3.33	0.124	3.72	3.0
	20-40	2.02	0.096	4.75	2.0
Paddy soil	0-20	3.80	0.168	4.42	3.0
	20-40	2.37	0.085	3.59	2.5
Red soil	0-20	1.59	0.084	5.28	1.3
	20-40	1.52	0.080	5.26	1.5

 † SUVA_{254,DOC}: specific UV absorbance at 254 nm as a measurement of the relative DOC aromaticity, calculated by $SUVA_{254}$ =(UV₂₅₄/DOC) 100 [28,36]; $^{\ddagger}UV_{465}$ /UV₆₆₅, the ratio of UV absorbance at 465 and 665 nm, which had inverse correlation with DOC aromaticity [29-31].

Table 2: Aromaticity of DOC from soils in this study.

Soil	Depth cm	n	log <i>K</i>	R²	κ _{oc} (L·kg ⁻¹)‡	
				, A	C =0.045 mM	
Black soil	0-20	0.25 ± 0.03	0.21 ± 0.04	0.97	383 ± 46	
	20-40	0.37 ± 0.06	0.20 ± 0.08	0.92	297 ± 49	
Fluvo-aquic soil	0-20	0.32 ± 0.02	0.34 ± 0.03	0.99	1820 ± 115	
	20-40	0.50 ± 0.08	0.24 ± 0.11	0.93	1388 ± 226	
Paddy soil	0-20	0.64 ± 0.14	0.38 ± 0.20	0.88	319 ± 72	
	20-40	0.86 ± 0.17	0.41± 0.26	0.89	650 ± 137	
Red soil	0-20	0.59 ± 0.08	0.043 ± 0.104	0.95	518 ± 72	
	20-40	0.58 ± 0.09	-0.062 ± 0.12	0.93	389 ± 62	

[†]The sorption experiments were conducted at 25°C at solution to solid ratio of 150:1. [‡]The value of $K_{_{\rm OC}}$ (L kg⁻¹) was calculated with the equation of $K_{_{\rm OC}}$ = $K_{_{\rm C}} \times C_{_{\rm e}}^{(n-1)}/f_{_{\rm oc}}$, where $K_{_{\rm f}}$ (mmol^{1-n-L n -kg⁻¹) and n were obtained from the Freundlich model, and $C_{_{\rm e}}$ (mM) was the free DEP concentration at sorption equilibrium; $f_{_{\rm oc}}$ (%) was the fraction of SOC in soil particles.}

 $\textbf{Table 3:} \ Sorption \ parameters ^{\dagger} \ of \ DEP \ to \ four \ soils \ fitted \ with \ the \ Langmuir \ model \ and \ Freundlich \ model.$

of paddy subsurface soil, which indicated that DEP had higher affinity to SOC in paddy subsurface soil than surface SOC. The varied values of $K_{\rm OC}$ are attributed to the different origins of SOC in different soils, which have varied structure and composition. The fluvo-aquic soil is derived from alluvial sediments of the Yellow River and SOC is mainly from anthropogenic activities and crop residues (maize or wheat); paddy soil is developed from flooding field with rice agriculture, and black soil is a humic-rich soil under forest or grassland [36,37].

Conclusions

The fraction of SOC in soils is an important constituent for DEP sorption. Soils with higher SOC contents sorb more DEP than those with lower SOC contents, which could explain why surface soils had higher DEP sorption than subsurface soils, except red soil. DOC dissolved from SOC had higher sorption of DEP than SOC. Increasing DEP in solution or sorbed to SOC could enhance more aliphatic DOC dissolving. The sorption isotherms of DEP to these soils greatly departed from linearity, which indicated heterogeneous sorption sites in soil particles. Fluvo-aquic soils have lower SOC contents, but the values of sorption coefficients ($K_{\rm OC}$) were higher than other SOCs, which indicated that SOC composition was important in DEP sorption.

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