

Removal of 2,4,6-trichlorophenol from a solution by humic acids repeatedly extracted from a peat soil

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Abstract

Humic acid (HA) is one of the major components of soil organic matter. It strongly affects the sorption behavior of organic and inorganic contaminants in soils. To obtain a better understanding of the interactions of contaminants with HA, a repeated extraction technique has been applied to a peat soil to obtain HA fractions with varying aliphaticity and aromaticity, which were subsequently correlated to the sorption properties of 2,4,6-trichlorophenol (TCP). HA fractions were extracted repeatedly using an alkaline solution and each HA fraction was separated into two portions with an air-drying or re-suspending (denoted as RSHAs) process. Solid-state ¹³C NMR and elemental analysis demonstrated that the aromaticity and polarity of HAs decreased with extractions. Kinetic results indicated that air-dried HAs exhibited two-step first order sorption behavior with a rapid stage followed by a slower stage. The slower sorption is attributed to the diffusion of 2,4,6-TCP in the condensed aromatic domains of HAs. Conversely, sorption of 2,4,6-TCP on RSHAs was extremely rapid and could not be fitted with any kinetic model. For air-dried HAs the sorption capacity (K_{oc}) was weakly correlated with the chemical compositions of HAs. However, a positive trend between K_{oc} and aromaticity was observed for RSHAs. Compared with the results of air-dried HAs with their counterparts of RSHAs, it is therefore concluded that air-drying may alter the structure of HAs through artificially creating a more condensed domain in HAs. The structural alternation may result in an incorrect interpretation of the relationship between sorption capacity and chemical composition of HAs and a misjudgment of the transport behavior of 2,4,6-TCP in soils and sediments.

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1. Introduction

Chlorophenols are a group of phenolic compounds that have been widely used in paper, biocide, cosmetic and public health industries [1,2]. These compounds have been discharged into the environment and hence frequently found in wastewaters, and surface and ground waters. In addition to the anthropogenic sources, some natural processes, such as chlorination of humic acid [3] and chemical or biological degradation of several pesticide groups (e.g., phenoxy, organophosphorus, and carbamate compounds) [4] can also pro-

duce chlorophenols. Because of high toxicity, carcinogenicity, yet poor biodegradability, chlorophenols are among the priority contaminants of major environmental concern. The stable C–Cl bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity and persistence in the biological environment. Among the chlorinated phenols, 2,4,6-TCP is of special interest because of its potential carcinogenicity.

The sorption behaviors of chlorophenols by soils and sediments play an important role in determining their transport, fate, and potential biological effects. For chlorophenols, organic matter has been recognized as an important sorbent in soils and sediments [5,6]. Generally, the sorptions of chlorophenols and other hydrophobic organic compounds (HOCs) by SOM exhibit linear isotherms [5,7], ascribed to the unlimited diffusion of

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Table 1
The chemical properties of Kuaikuan peat soil

Elevation (m)	Horizon	Depth (cm)	Texture	Bulk density (Mg/m ³)	pH		O.C. ^a (g/kg)	CEC ^b (cmol (+)/kg soils)	Sum cations (cmol (+)/kg soils)	Base ^c satu. (%)	Free Fe (%)
					H ₂ O	KCl					
35	O/A	0–20	L	1.35	4.5	3.8	115	14	3.7	26	1.42

^a Organic carbon.

^b Cation exchangeable capacity.

^c Base saturation percentage (%) = (exchangeable bases/CEC) × 100%.

HOCs into SOM structures in accordance with the solid-phase dissolution model [8,9]. The model was developed based on homogeneous binding-site energy distributions with noncompetitive sorption processes between HOCs and SOM sorbents. However, some sorptive phenomena, such as competitive sorption and sorption–desorption hysteresis, were also observed for HOC sorption by SOM, indicating energetic and structural heterogeneity for SOM [10].

Organic matter in soils and sediments (SOM) is derived from the decomposed residues of living organisms. Previous studies have shown that SOM is a biopolymer with diverse physical structures and chemical compositions, depending on its origin [11,12] and sampling depth [13], and the age of the source materials [14,15]. Recent application of solid-state nuclear magnetic resonance spectroscopy (NMR) to characterization of SOMs revealed that the structures of SOMs consist of two domains of aromaticity (0–112 ppm) and aliphaticity (112–163 ppm) [16]. The sorption of HOCs was then correlated to the two parameters to simplify detailed descriptions of the interactions between sorbates and adsorbents. For instance, a positive correlation of pyrene sorption with the aromatic contents of humic acids (HAs) was reported in Chin et al. [17]. In contrast, polycyclic aromatic hydrocarbons (PAHs) sorption exhibited a positive correlation with the aliphatic fraction of SOM [16,18]. In view of these inconclusive results regarding the sorption behavior of HOCs in humic substances, we found that the method of sample preparation (i.e., whether humic adsorbents are subjected to a drying process or not) may lead to different conclusions. For example, we reviewed previous reports and found that the aliphatic moieties of adsorbents, which were dried following extraction, controlled the sorption reactions of HOCs [16,19]. In cases where the extracted adsorbents were maintained in suspension, however, the aromatic carbon in SOM appeared to control HOC sorption [17,20].

The SOM used in each of the previous studies varied with respect to sampling location, chemical composition, and physical conformation, which may have contributed to the disparate results. Therefore, in this study a peat soil from a single location was collected and subjected to repeated extraction. Eight HA fractions were obtained with the extraction and both drying and nondrying variants were tested for them. The objective was to clarify the influence of these different preparative methods on (i) the variations in structure and compositions of each HA fraction; (ii) the sorption of TCP to HAs; (iii) the relationship between sorption and chemical structures of HAs, including aromaticity or aliphaticity.

2. Materials and methods

2.1. Soil samples

A Kuaikuan peat soil located in Changhua County, middle Taiwan (24°00'N, 120°38'E) was collected. Organic carbon contents and selected physical/chemical properties for the peat soil are listed in Table 1. The pedological classification of Kuaikuan soil is coarse-loamy, mixed, hyperthermic, Typic Sulfisaprist [21].

2.2. HAs extraction

HAs were repetitively extracted from the peat soil eight times following a standard procedure recommended by IHSS and outlined by Swift [22] and Li et al. [23] with slight modification. The solid HA obtained from each extraction was then separated into two parts. One was re-suspended in a solution (denoted RSHAs) with 0.005 M CaCl₂ and 200 mg/L HgCl₂ at pH 4. The other was air-dried, gently ground to grain passing through a 100-mesh sieve, and stored prior to the characterization and sorption experiments.

2.3. Characterization of the HAs

The C, H, N, and O contents of the HAs were determined using a Heraeus CHNOS Rapid F002 Elemental Analyzer. FTIR spectra were acquired for solid HAs randomly distributed in a KBr pellet, using a ThermoNicolet Nexus FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector and a KBr beamsplitter. Spectra were obtained by co-addition of 64 individual scans with an optical resolution of 4 cm⁻¹. ¹³C CP-MAS NMR spectra of the samples were collected on a Bruker DSX400WB NMR spectrometer. The magic angle spinning (MAS) rate was 6.5 kHz. For each scan, a pulse with a carrier frequency of 100 MHz was applied and the recycle time was 1.5 s.

2.4. Sorption experiments

Sorption experiment was conducted at room temperature using a batch method. Ten mg of air-dried HAs was placed into glass vials with 0.005 M CaCl₂ and 200 mg L⁻¹ HgCl₂ to suppress the dissolution of organics and to eliminate microbial activity, respectively [24]. Various amounts of a 100 mg L⁻¹ 2,4,6-TCP solution at pH 4 was added into each vial. Additional 0.005 M CaCl₂ solution was further added to bring the final vol-

Table 2
Yield, elemental compositions, atomic ratios, and E_4/E_6 ratios of Kuaikuan humic acids

Sample	Yield (%)	C ^a (%)	H (%)	N (%)	O (%)	Total	H/C	O/C	(N + O)/C	E_4/E_6
KF1 ^b	15.4	50.7	4.5	2.6	42.0	96.8	1.05	0.62	0.67	4.91
KF2	14.3	50.8	5.4	2.3	41.2	99.7	1.28	0.61	0.65	5.48
KF3	13.0	53.4	5.7	2.1	38.2	99.4	1.29	0.54	0.57	6.17
KF4	15.0	53.3	5.7	2.1	38.1	99.2	1.29	0.54	0.57	6.86
KF5	9.5	53.1	5.6	1.1	39.8	99.6	1.26	0.56	0.58	8.18
KF6	13.0	53.1	5.8	2.3	38.5	97.0	1.31	0.54	0.58	8.16
KF7	7.4	53.0	6.3	1.9	38.4	99.6	1.42	0.54	0.57	8.12
KF8	12.3	53.6	6.6	2.1	37.4	98.7	1.48	0.52	0.56	9.29

^a Values are on ash-free basis. H/C: atomic ratio of hydrogen to carbon. O/C: atomic ratio of oxygen to carbon. (N + O)/C: atomic ratio of sum of nitrogen and oxygen to carbon. E_4/E_6 : the ratio of the absorbance at 465 nm to that at 665 nm.

^b Number is the sequence of extraction.

ume of suspension in each tube to 20 mL. As a result, the initial 2,4,6-TCP concentrations were in a range of 0–20 mg L⁻¹ and the solid-to-solution ratio was 0.5 g L⁻¹. The samples for each 2,4,6-TCP concentration were triplicate. The vials were sealed tightly with screw caps with Teflon liners and then mechanically agitated at 150 rpm for 72 h. Afterwards, the suspensions were passed through a 0.45 mm PVDF filter to collect the filtrates. The remained 2,4,6-TCP concentration in the filtrates was determined using a Varian ProStar 210 high performance liquid chromatography (HPLC) equipped with a UV detector and a C18 column (SUPELCO, 23 cm × 4.6 cm × 5 μm). The wavelength of detection was set at 287 nm. The mobile phase was a mixture of 70% methanol and 30% water at a flow rate of 1 mL min⁻¹.

A separated set of the sorption experiment was conducted for RSHAs with a similar procedure. Twenty millilitres aliquot of the RSHAs suspensions with a solids concentration of 1 g L⁻¹ was placed in each of a series of 50-mL amber glass centrifuge tubes with Teflon-lined caps. Various amounts of 100 mg L⁻¹ of 2,4,6-TCP stock solution were added into the vials and the volume was then brought to 40 mL with background solution. In the samples, the initial 2,4,6-TCP concentration was ranged from 0 to 140 mg L⁻¹ and the solids concentration was 0.5 g L⁻¹. The remaining steps were described previously. A control experiment was also conducted by extracting 20 mL RSHA stock suspension without the addition of 2,4,6-TCP to evaluate the true weight of RSHA solids in each vial. After agitation for 3 days, the sample suspensions were passed through a filter, which was oven-dried at 30 °C and weighed in advance. RSHA solids collected on each filter were washed with a small amount of de-ionized water, oven-dried at 30 °C, and weighed. Solid weight of RSHA on each filter was determined by subtracting the filter weight from that containing RSHA. Using this process, we found that the variation of solid weight in each vial was less than ±5% of the estimated value (10 mg of HAs). We therefore neglected the variation and assumed a suspension density of 0.5 g L⁻¹ in each vial.

Sorption data was fitted to the logarithmic form of the Freundlich equation:

$$\log S = \log K_F + N \log C_e \quad (1)$$

where S and C_e are the equilibrium concentrations of CP in the adsorbed and liquid phases in mg g⁻¹ and mg L⁻¹, respectively;

K_F and N are the Freundlich coefficients related to the adsorption capacity and an indicator of isotherm nonlinearity, respectively, and can be calculated from the intercept and slope of the linear plot with $\log S$ versus $\log C_e$.

3. Results and discussion

3.1. Characterization of the HAs

The elemental compositions of HAs in repeated extractions from the peat soil are present in Table 2. The number in the sample names indicated their number in the extraction sequence. With increasing number of extractions, the C and H contents of HAs increased while the O content decreased. The H/C atomic ratio increased gradually from 1.05 for KF1 to 1.48 for KF8. In contrary, the O/C atomic ratio decreased from 0.62 for KF1 to 0.52 for KF8. The polarity index [(N + O)/C] also decreased with increasing number of extractions (Table 2). Accordingly, the HAs appear to become more aliphatic and less polar with

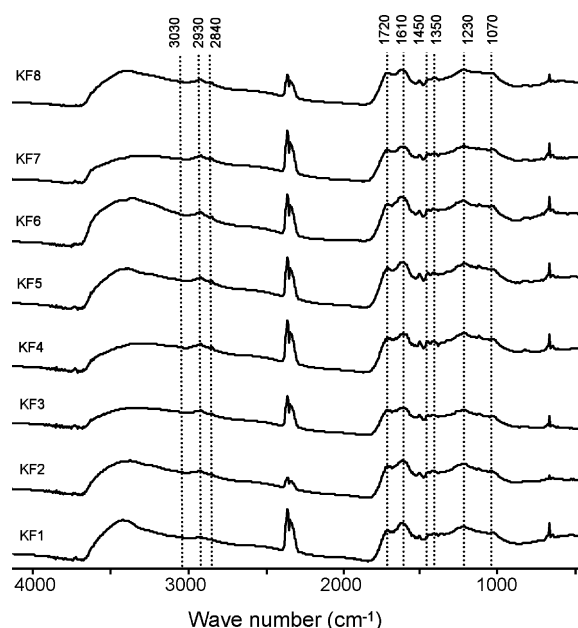


Fig. 1. FTIR spectra of humic acids repeatedly extracted from Kuaikuan peat soils.

Table 3
Selected assignments for Fourier-transformed infrared (FTIR) absorbance bands

Band (cm ⁻¹)	Assignment
3250–3350	Stretching vibration of hydroxyl functional groups ^a
3030	Aromatic CH stretch ^b
2930	Asymmetric CH stretch of –CH ₂ – ^b
2840	Symmetric CH stretch of –CH ₂ – ^b
1720	–C=O stretch of –COOH ^b
1610	Aromatic C=C stretch and/or asymmetric –COO ^{-b}
1450	Vibration of aliphatic C–H ^c
1350	Symmetric –COO ⁻ stretch and/or –CH bending of aliphatics ^b
1230	–C–O stretch and OH deformation of –COOH ^b
1070	C–C stretch of aliphatic groups ^b

^a Chen et al. [36].

^b Baes and Bloom [28].

^c Stevenson [29].

increasing number of extraction, which was consistent with the observations of Li et al. [23] and Kang and Xing [25].

The FTIR spectra of HA fractions are presented in Fig. 1, and the assignments for the selected peaks are listed in Table 3. The peaks at 2930 and 2840 cm⁻¹ correspond to aliphatic C–H, i.e. –CH₂ and –CH₃ stretching [26]. The increase in the relative intensities of these two peaks with progressive extractions indicates an increase in aliphatic carbon in the later extracted HAs. The results are in agreement with elemental and NMR (see below) analyses. With progressive extractions, the decreases in the intensities of the peaks at 1720 cm⁻¹ and those between 1230 and 1210 cm⁻¹ were attributed to the decreasing contents of oxygen containing functional groups, especially –OH and –COOH groups [27–29]. These results were consistent with the decreasing O/C atomic ratio and indicated that the HAs in the earlier extracts were more polar than those in the later extracts.

The ¹³C CP-MAS NMR spectra of HAs showed peaks corresponding to alky C (0–50 ppm), O-alky C (50–112 ppm), aromatic C (112–145 ppm), phenolic C (145–163 ppm), carboxyl C (163–190 ppm), and carbonyl C (190–215 ppm) [16]. Within the aliphatic C region of 0–112 ppm, the C content increased from 55.1% for KF1 to 63.8% for KF8, mirroring

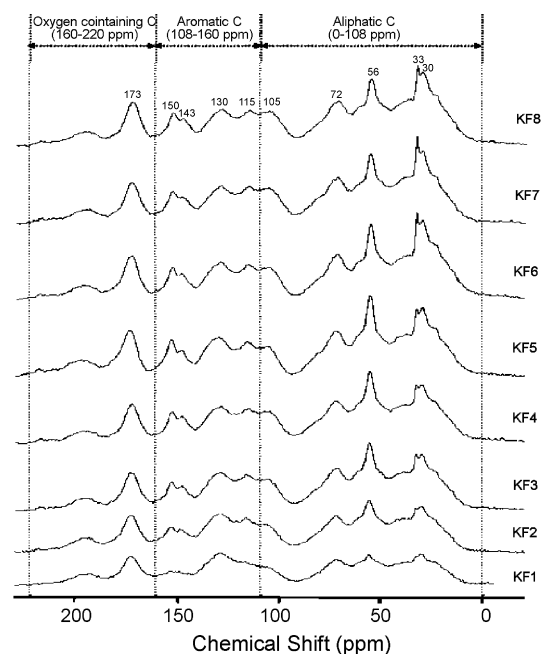


Fig. 2. Solid-state ¹³C NMR spectra of Kuaikuan humic acids.

the increase in aliphaticity from 66.5% to 74.0% with increasing extractions (Table 4). In contrast, the aromatic C (112–162 ppm) and aromaticity of HAs decreased with progressive extractions (Table 4). Kang and Xing [25] suggested that the hydrophobic characteristics of paraffinic carbons with a low aqueous solubility may contribute partially to the high contents of aliphatic carbons with later extractions. Two sharp peaks at 30 and 33 ppm, shown in the region of 0–50 ppm in the NMR spectra (Fig. 2), were assigned to amorphous aliphatic carbons and crystalline aliphatic carbons, respectively. These aliphatic components may derive from the microbial- and chemical-resistant biopolymers such as cutin or suberin [30,31]. Since the region of paraffinic carbons (0–50 ppm) constituted the major aliphatic domains of HAs, aliphatic carbons (both amorphous and crystalline) can potentially influence 2,4,6-TCP sorption. Again, the NMR data provided further evidences to the heterogeneity of HAs extracted from a single soil.

Table 4
Integration results of solid-state ¹³C NMR spectra of Kuaikuan HAs

Sample	Distribution of C chemical shift, ppm (%)						Aliphatic C (%)	Aromatic C (%)	Polar C (%)	Phenolic C (%)	Aromaticity ^a	Aliphaticity ^b
	0–50	50–112	112–145	145–163	163–190	190–215						
KF1 ^c	24.6	30.5	21.4	6.3	11.9	5.2	55.1	27.7	54.0	6.3	33.5	66.5
KF2	25.0	32.7	19.9	7.0	10.6	4.7	57.8	26.9	55.0	7.0	31.8	68.2
KF3	27.5	34.9	18.0	6.5	9.2	3.8	62.4	24.6	54.4	6.5	28.2	71.8
KF4	28.3	35.3	17.3	6.7	8.8	6.7	63.6	24.0	54.4	6.7	27.4	72.6
KF5	28.7	32.2	16.6	6.9	10.1	5.5	60.9	23.5	54.8	6.9	27.8	72.2
KF6	32.5	31.9	15.7	6.2	9.3	4.4	64.3	21.9	51.8	6.2	25.4	74.6
KF7	29.7	34.5	16.3	6.6	8.9	4.0	64.2	22.9	54.0	6.6	26.3	73.7
KF8	30.6	33.2	15.7	6.7	9.4	4.3	63.8	22.4	53.7	6.7	26.0	74.0

^a Aromaticity was calculated by expressing aromatic C (112–163 ppm) as percentage of the aliphatic and aromatic regions (0–163 ppm).

^b Aliphaticity was calculated by expressing aliphatic C (0–112 ppm) as percentage of the aliphatic and aromatic regions (0–163 ppm).

^c Number is the sequence of extraction.

Table 5
First-order kinetic model of 2,4,6-TCP adsorption on representative air-dried Kuaikuan humic acids

Sorbent	k_1^a (h^{-1})	First order regression equation	r^2	k_2^b (h^{-1})	First order regression equation	r^2
KF1	1.7×10^{-2}	$y = -0.0073x - 1.355$	0.994	1.2×10^{-3}	$y = -0.0005x - 1.374$	0.903
KF3	2.6×10^{-2}	$y = -0.0111x - 1.3777$	0.922	9.2×10^{-4}	$y = -0.0004x - 1.4093$	0.933
KF5	2.8×10^{-2}	$y = -0.0122x - 1.3501$	0.969	4.6×10^{-4}	$y = -0.0002x - 1.3928$	0.964
KF8	6.9×10^{-3}	$y = -0.003x - 1.3619$	0.977	1.2×10^{-3}	$y = -0.0005x - 1.3698$	0.932

^a The rate constant for the first step of first order kinetics within 0–3 h.

^b The rate constant for the second step of first order kinetics within 3–48 h.

3.2. Sorption kinetics

Sorption of 2,4,6-TCP on selected air-dried HA samples generally follows the two-step first order kinetic model and the corresponding rate constants are listed in Table 5. A rapid sorption (with rate constants from 6.9×10^{-3} to $1.7 \times 10^{-2} \text{ h}^{-1}$) followed by a relatively slow sorption (with rate constants from 4.6×10^{-4} to $1.2 \times 10^{-3} \text{ h}^{-1}$) of 2,4,6-TCP on HAs was observed. Dual mode models, which had been used to describe the complicated HAs structures [32,33], may explain the kinetic sorption of TCP. These models suggest that SOM is a composite of expanded/aliphatic and condensed/aromatic domains, which are analogous to rubbery and glassy polymers, respectively. The sorption of HOCs in expanded domain had been found to be fast as compared to that in the condensed domain [34]. Therefore, in the current study, the rapid sorption of 2,4,6-TCP may be attributed to its rapid interaction with aliphatic components. Conversely, more rigid aromatic structures of HA may decrease 2,4,6-TCP sorption rate due to the competitive sorption of solutes on the sites or slow diffusion of solutes through the condensed/glassy phase [35].

During the first step of sorption, the rate of 2,4,6-TCP sorption in HAs generally increased with increasing extractions (Table 5). The increase in 2,4,6-TCP sorption with progressive extractions may be attributed to the increase in the contents of aliphatic carbons (Table 4), which provided a suitable conformation for rapid sorption of 2,4,6-TCP [35]. However, the portions of rigid crystalline components (i.e., 33 ppm shown in Fig. 2) in the region of aliphatic carbons of HAs also increased with increasing extraction. The crystalline aliphatic carbons may be accessed with difficulty, retarding 2,4,6-TCP sorption. Thus, the increment of 2,4,6-TCP sorption rate decreased with increasing extraction. In addition, the discrepant decrease in sorption rate of 2,4,6-TCP for KF8 (Table 5) may be also attributed to its relatively higher content of crystalline aliphatic carbons (Fig. 2).

Unlike the sorption behavior of 2,4,6-TCP in air-dried HAs, no kinetic models could be applied to 2,4,6-TCP sorption on RSHAs due to the extreme high reaction rate with respect to the experimental time frame. Since RSHAs were prepared through direct acidification and precipitation of HAs after extraction and stored as a suspension, a “fluffy” region may be created. As a result, more sorption sites were exposed or became accessible, and a much higher sorption rate associated with a large sorption capacity (more than fourfold as compared with air-dried samples, data not shown) was observed.

3.3. Sorption isotherms

Sorption isotherms of 2,4,6-TCP with the selected samples are presented in Fig. 3. To characterize the detail information of 2,4,6-TCP sorption on air-dried HAs and RSHAs, the data were fitted to the Freundlich model, and the fitted parameters were listed in Table 6. Each sorption isotherm was nonlinear as evidenced by the Freundlich N values. For air-dried HAs, the N values were independent of the extraction number (Table 6). The results were inconsistent with previous reports that N values increased with increasing extraction (i.e., increasing in aliphaticity) [25]. Since low variations in

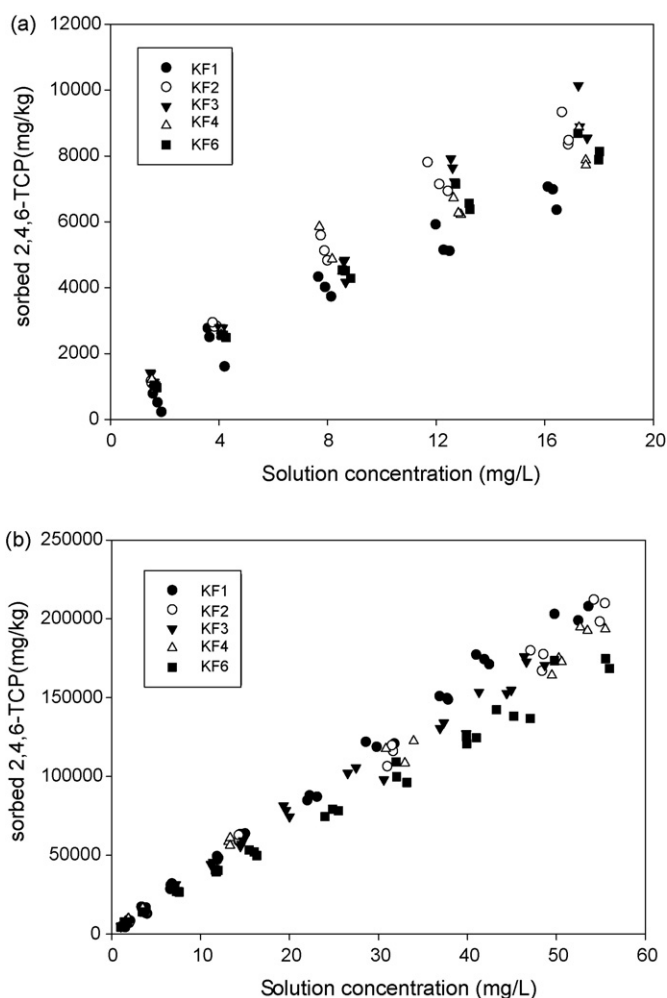


Fig. 3. Sorption isotherms of 2,4,6-TCP for (a) air-dried HAs and (b) RSHAs.

Table 6

Freundlich isotherm parameters and concentration-dependent organic carbon-normalized sorption coefficient ($\log K_{oc}$) for representative five Kuaikuan humic acids

	N	r^2	Concentration-dependent $\log K_{oc}$ ^a		
			C_e (mg L ⁻¹) = 4	C_e (mg L ⁻¹) = 8	C_e (mg L ⁻¹) = 16
Sorbent (air-dried)					
KF1 ^b	1.080 ± 0.009	0.976	2.93	2.96	2.98
KF2	0.884 ± 0.007	0.990	3.12	3.08	3.04
KF3	0.793 ± 0.006	0.991	3.12	3.06	2.99
KF4	0.824 ± 0.003	0.996	3.06	3.00	2.96
KF6	0.887 ± 0.004	0.997	3.03	3.00	2.97
Sorbent (RSHA)					
KF1	0.987 ± 0.003	0.995	3.91	3.91	3.90
KF2	0.950 ± 0.003	0.999	3.91	3.89	3.88
KF3	0.931 ± 0.002	0.999	3.91	3.88	3.86
KF4	0.891 ± 0.003	0.998	3.87	3.84	3.80
KF6	0.888 ± 0.006	0.999	3.86	3.83	3.79

^a $K_{oc} = (S/C_e)/F_{oc}$; S is sorbed concentration and C_e is equilibrium concentration.^b Number is the sequence of extraction.

aliphaticity among these extractions (Table 4), the contributions of aliphatic carbons to 2,4,6-TCP sorption may be approximate the same. Thus, we speculate that other chemical components of HAs, such as phenolic carbons or/and polar carbons, may become an essential factor influencing the overall 2,4,6-TCP sorption.

For RSHA samples, a negative relationship between Freundlich N value and aliphaticity of HAs was found (Tables 4 and 6). This suggested that the increase in aliphatic carbons of HAs would increase the isotherm nonlinearity of RSHAs. Since RSHAs were prepared without drying, the aromatic domains may be less condensation and become more susceptible to rapid diffusion of 2,4,6-TCP into inner sorption sites. In addition, due to the strong interactions between aromatic domain of HAs with 2,4,6-TCP, the amount of 2,4,6-TCP sorption on RSHAs was four times larger than that on air-dried HAs (data not shown). Therefore, the increase in nonlinear sorption of 2,4,6-TCP on later extracted RSHAs may be attributed to the competitive sorption of solutes on aromatic domain of HAs, which decreased gradually with increasing extraction.

Because the units of K_F are based on N values, which vary from sample to sample, comparisons of K_F values cannot be made between different isotherms. Therefore, the concentration-dependent organic carbon-normalized sorption coefficients (K_{oc}) at three concentrations ($C_e = 4, 8, 16$ mg L⁻¹) were used to compare the sorption capacity among HA samples. The K_{oc} values were derived from the procedures as described below. Briefly, by plotting $\log S$ versus $\log C_e$, the K_F and N values were first obtained from the intercept and slope of the plot. Then the sorbed concentration (S) at 4, 8, 16 mg L⁻¹ could be calculated using Freundlich model (Eq. (1)). Finally, the concentration-dependent K_{oc} was obtained based on the following equation [25]:

$$K_{oc} = \frac{S/C_e}{F_{oc}} \quad (2)$$

where S is sorbed concentration and C_e is equilibrium concentration. 2,4,6-TCP sorption (K_{oc}) on air-dried HAs was independent

of the number of extractions (or aliphaticity) (Fig. 4). However, a positive trend between the aliphaticity and $\log K_{oc}$ values was observed for the sorption of 2,4,6-TCP on RSHAs (Fig. 5). Moreover, with the same number of extraction, RSHAs had higher $\log K_{oc}$ values (1.26–1.33 times higher) than those of air-dried HAs (Table 6). These results demonstrate that the aromatic moieties of HAs dominated 2,4,6-TCP sorption when the aromatic sites became more accessible. There exist controversies over whether aromatic or aliphatic domains of HAs control HOCs sorption [16,18,19,25]. According to the current study, these arguments may result from differing methods of sample preparations, which created different conformations of HAs, leading to the exposure of various levels of chemical components of HAs, particularly, the aromatic domain. As a result, 2,4,6-TCP sorption in HAs was greatly affected when HAs were “loosened” to expose more deeply located aromatic sites. Thus, even if the Kuaikuan HA has a comparable lower aromaticity, the aromatic carbons still exhibited a high affinity to 2,4,6-TCP.

In addition to aromatic carbons, the polarity [(N + O)/C] of HAs may also affect the sorption behavior of HOCs, and such

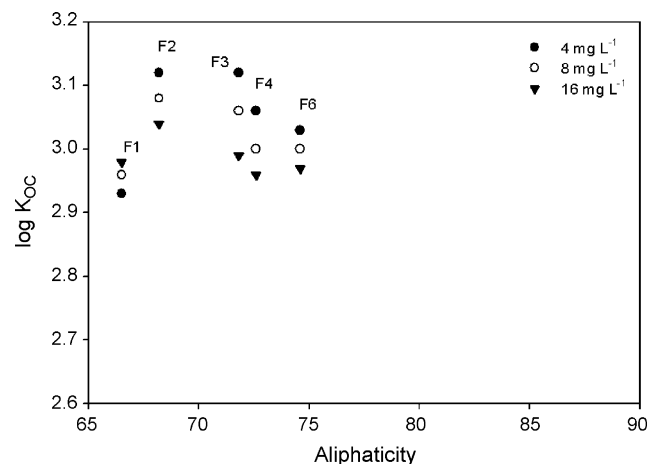


Fig. 4. Relationship between the $\log K_{oc}$ and the aliphaticity of HAs. $\log K_{oc}$ was obtained from the sorption of 2,4,6-TCP on air-dried HAs.

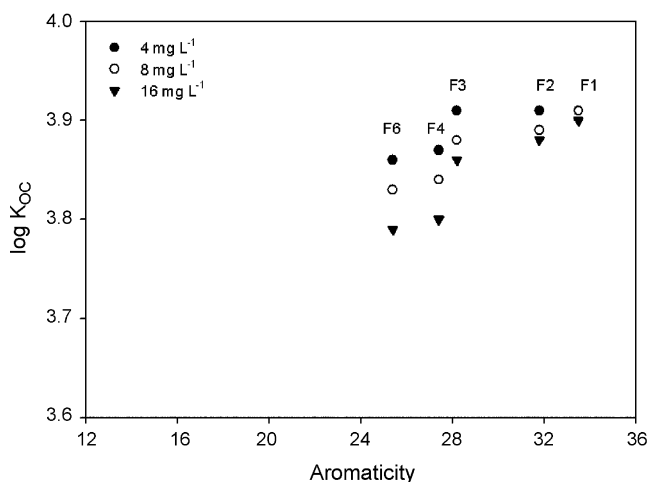


Fig. 5. Relationship between the $\log K_{oc}$ and the aromaticity of HAs. $\log K_{oc}$ was obtained from the sorption of 2,4,6-TCP on RSHAs.

effects have been previously reported in the literature [25,36]. In the current study, there was no significant relationship between the polarity and $\log K_{oc}$ for both air-dried HAs and RSHAs (Fig. 6). Nonetheless, it was clear that the $\log K_{oc}$ derived from

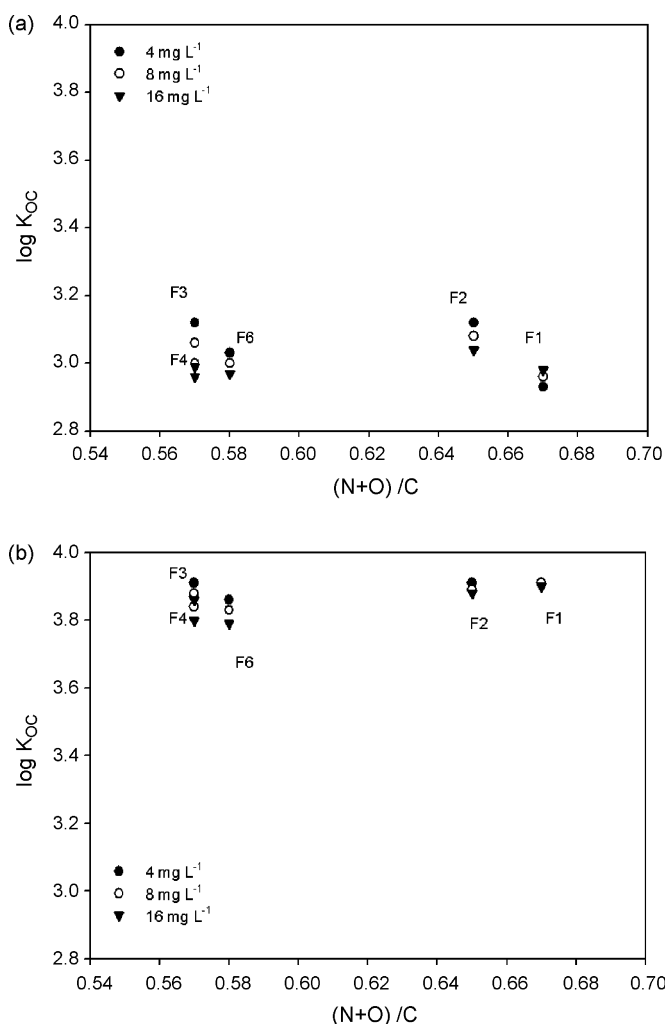


Fig. 6. Relationships between the $\log K_{oc}$ and the polarity of HAs. $\log K_{oc}$ was obtained from the sorption of 2,4,6-TCP on (a) air-dried and (b) RSHAs.

air-dried HAs was lower than that from RSHAs. This suggests that a portion of polar groups of HAs may have become accessible for interacting with 2,4,6-TCP in the case of RSHAs. Since both aromaticity and polarity decreased in consecutive extractions, it was difficult to assess the relative effects of these factors on 2,4,6-TCP sorption. Therefore, the two main compositional parameters of HAs, i.e. aromaticity and polarity, probably had a combined influence on 2,4,6-TCP sorption.

4. Conclusions

This study demonstrates the heterogeneous nature of different HA fractions extracted from a single soil sample. The NMR study indicated that HAs from Kuaikuan peat soil was aliphatic-rich. With increasing extractions the aliphaticity of HAs increased while the aromaticity and polarity index decreased. The sorption of 2,4,6-TCP by air-dried HAs exhibited two-step first order kinetics; on the contrary, no kinetic models could be applied to the sorption of 2,4,6-TCP in RSHAs. Sorption isotherms showed that the nonlinearity and $\log K_{oc}$ of different air-dried HA fractions did not correlate with the corresponding aliphaticity. In contrast, 2,4,6-TCP sorption by RSHAs appeared a positive correlation between the aromaticity and $\log K_{oc}$. The discordant results may be attributed to the differences in physical conformations of HAs caused by different preparation processes. Air-drying might result in shrinkage of the sponge-like structures of HAs, which subsequently hinder the access of TCP to the sorption sites or increase diffusion pathway for 2,4,6-TCP. Consequently, the sorption of 2,4,6-TCP in air-dried HAs proceeded more slowly with a lower sorption capacity (K_{oc}) compared with RSHAs. The exposure of polar groups in RSHAs to aqueous environment may also contribute significantly to 2,4,6-TCP sorption. There are several environmental implications to the results of this study. If HAs was prepared through different drying processes, the resulting variations in the chemical and physical properties of HAs may result in differences in the sorption behaviors of organic contaminants by HAs. Misinterpretation of organic contaminants sorption in SOM and the relationship between the chemical compositions of HAs and sorption capacity (K_{oc}) may be caused. The mobility of HOCs in soil may be incorrectly evaluated due to the utilization of air-dried HAs as a model adsorbent.

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