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Effect of physical forms of soil organic matter on phenanthrene sorption

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Abstract

The sorption coefficient, K_{OC}, of phenanthrene (PHE) has been reported to vary with different types of organic matter, leading to uncertainties in predicting the environmental behavior of PHE. Among the studies that relate organic matter properties to their sorption characteristics, physical conformation of organic matter is often neglected. In this work, organic matter samples of different physical forms were examined for their sorption characteristics. Dissolved humic acids (DHA) showed significantly higher K_{OC} than the corresponding solid humic acids (SHA) from which the DHAs were made. The K_{OC} of DHAs was found to be related to polarity, whereas K_{OC} of SHAs increased with aliphatic carbon content. Soil particles were treated with H_2O_2 to remove organic matter, and humic acid was coated on H_2O_2-treated soil particles to make organo-mineral complexes at pH 4, 7 and 10. Although the nonlinear sorption was apparent for SHAs and H_2O_2-treated soil particles, the organo-mineral complexes formed using these two components at pH 4, 7 and 10 exhibited relatively linear sorption at organic carbon content, $f_{OC} > 0.5\%$. These results indicate that organic matter of the same composition may have different sorption properties due to different physical forms (or conformations). Nonlinear sorption for the complexes formed at pH 4 with lower f_{OC} ($< 0.5\%$) was also discussed.

Keywords: Soil organic matter; Physical conformation; Humic acid; Phenanthrene; PAHs; Organo-mineral complex

1. Introduction

Soil organic matter (SOM) primarily controls the sorption of hydrophobic organic compounds (HOCs) in soil. Thus K_{OC}, the organic carbon normalized sorption coefficient, was proposed to predict the behavior of HOCs in the environment regardless of physical conformation and chemical components of SOM. However, nonideal sorption was reported due to multi-domain sorption (Weber and Huang, 1996), and then researchers focused on establishing the relationship between properties of SOM and sorption characteristics. Some studies showed that sorption of HOCs by SOM was controlled by aromatic carbon (Chin et al., 1997; Perminova et al., 1999; Abelmann et al., 2005), while others showed that sorption was controlled by aliphatic carbon (Chefetz et al., 2000; Simpson et al., 2003; Kang and Xing, 2005). Moreover, polarity of SOM was reported to be a regulating factor for sorption of HOCs (Kang and Xing, 2005; Tanaka et al., 2005). Hence, it appears that each property of SOM has some reasonable contribution for affecting the behavior of HOCs, and no explicit conclusion could be drawn so far.

Another line of research has indicated that the humin fraction of SOM has a significantly higher sorption affinity with HOCs than other fractions (Ding et al., 2002; Gunasekara and Xing, 2003). Salloum et al. (2001) observed that the total amount of 1-naphthol sorbed by different soil

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fractions was higher than that by the whole soil sample. They proposed that the molecular structure was rearranged during the SOM fractionation procedure. According to Gunasekara and Xing's hypothesis (2003), several molecular layers of SOM at SOM–mineral interfaces may rearrange to a more condensed form due to the effect of mineral surface, leading to more nonlinear sorption of HOCs. Other studies also pointed out that sorbed molecules could rearrange the SOM matrix and change its sorption characteristics (Kan et al., 1998; Lu and Pignatello, 2002; Braida et al., 2003). Furthermore, the existence of glass transition temperature (T_g) indicates that sorption properties of SOM will change with temperature, without any alteration of chemical composition (Schaumann, 2006).

The above mentioned studies show that the physical conformation of SOM can be a key factor affecting the interaction between SOM and HOCs. In this study, sorption characteristics were examined between solid humic acid particles (SHA), dissolved humic acid (DHA) and organo-mineral complexes synthesized with DHA and H_2O_2-treated soil particles. We hope to shed light on how the different forms of SOM influence sorption of HOCs.

2. Material and methods

2.1. Chemicals and solutes

Phenanthrene (PHE, purity >98%) was purchased from Acros Co. and was dissolved in methanol to make stock solution. All other chemicals and solvents used were better than analytical grade (Beijing Chemical Reagent Co.). Hexane was distilled for purification and the fluorescence spectrum of purified hexane showed stable and low baseline in the wavelength range of PHE.

2.2. Humic acid (HA) purification and characterization

Four HAs were investigated in this study. Three of them were extracted from natural soils and the fourth one was from Fluka Company. Natural soils were collected from the northern outskirts of Beijing, far from any industrial area. The soils were sampled from the surface horizon (sandy in texture) with organic carbon (TOC) content of 0.7%, 2.9% and 7.9%, and pH of 7.8, 7.6 and 7.1 for soil 1, 2 and 3, respectively. The soil samples were sieved through a 2-mm sieve. All four HAs were purified using the method by Xing (2001). Briefly, a solution containing 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ was mixed with the soil or Fluka HA (50:1, v:w) to extract humic acid and fulvic acid. After 12 h of equilibration, the mixture was centrifuged at 1000*g* for 10 min and the supernatant was collected. The extraction procedure was repeated three times until a light yellow extract was obtained. The supernatants were filtered through a 0.45 μm filter and collected, and the HA was precipitated with HCl. The precipitated HAs were washed using distilled water until a negative test of chloride using $AgNO_3$, freeze-dried and ground to <500 μm particles. They are referred as solid humic acids (SHAs). The four SHAs were analyzed using an elemental analyzer (Elementar Vario EL, Germany) for C, H and N, and by ^{13}C NMR (Bruker DSX-300) (Kang and Xing, 2005) for the functional groups. The parameters used for running NMR were as follows: contact time, 1 ms; spinning speed, 5 kHz; 90° ^1H pulse, 5 μs; acquisition delay, 4 s; and the number of scans, from 5000 to 10000. Within the 0–220 ppm chemical shift range, C atoms were assigned to alky C (0–50 ppm), O-alky C (50–108 ppm), aromatic C (108–145 ppm), phenolic C (145–168 ppm), carboxyl C (168–192 ppm), and carbonyl C (192–220 ppm).

2.3. Preparation of dissolved humic acid (DHA)

An aliquot of each SHA was dissolved overnight in 2 ml of NaOH (0.5 M). One hundred ml NaN_3 solution (200 mg l^{-1}, used as biocide) was mixed with DHA. No visual particle or flocculation was observed during the whole experimental procedure. The concentration of DHA was measured using a TOC analyzer (5000 A, Shimadzu, Kyoto) and expressed as carbon content. The pH of DHA was adjusted using 0.1 M HCl or 0.1 M NaOH to pH 4, 7 and 10. No precipitation of DHA was observed at any pH during the experiment.

2.4. Preparation of organo-mineral complexes

After removal of humic and fulvic acids, the soil was soaked in 10% H_2O_2 to remove organic carbon. The upper two thirds of the supernatant were replaced with fresh H_2O_2 solution everyday. After 40-day treatment with H_2O_2, the residual particles were washed with distilled water, saturated with calcium by mixing with 0.5 M $CaCl_2$ for three times, and washed with distilled water until a negative test of chloride using $AgNO_3$. The particles were dried, ground and sieved.

Two grams of H_2O_2-treated soil particles were mixed with 2 ml DHA (about 500 mg C l^{-1}) stock solution, and the resulting sludge-like mixture was dried at 40 °C. The dried complex was ground (<0.5 mm) and 2 ml DHA solution was subsequently added. The wet–dry cycle was repeated until a desired amount of DHA was added. The dried samples were washed with distilled water until TOC in the water was below 5 mg l^{-1}. The experimental design was presented in Table 1.

2.5. Sorption experiments with SHAs and HA-mineral complexes

Sorption experiment procedure was similar to Pan et al. (2006). Briefly, the PHE stock solution was diluted sequentially to a series of concentrations distributed evenly on a log scale using 0.01 M $CaCl_2$ and 200 mg l^{-1} NaN_3 solution. The methanol:solute ratio was the same in all the

Table 1
Experimental design of organo-mineral complex in dry–wet cycle

Sample[a]	pH[b]	Expected carbon	Measured OC content[c]		The amount of the added DOM		
		%	%	Std. error	Volume (ml)	C (mg C l^{-1})	Times
A0	4	0.08	0.03	0.04	2	0	5
A1	4	0.50	0.22	0.02	2	1000	5
A2	4	1.00	0.37	0.07	2	1000	10
A3	4	1.20	0.93	0.06	2	1000	12
A4	4	1.50	1.54	0.07	2	1000	15
N0	7	0.08	0.03	0.00	2	0	5
N1	7	0.13	0.18	0.02	1	1000	1 + 4[d]
N2	7	0.50	0.40	0.01	2	1000	5
N3	7	0.80	0.49	0.02	2	1000	8
N4	7	1.00	0.75	0.10	2	1000	10
N5	7	1.20	0.66	0.01	2	1000	12
N6	7	1.50	0.85	0.09	2	1000	15
N7	7	2.00	0.76	0.09	2	1000	20
B0	10	0.08	0.03	0.05	2	0	5
B1	10	0.50	0.12	0.01	2	1000	5
B2	10	1.00	0.32	0.01	2	1000	10
B3	10	1.20	0.52	0.08	2	1000	12
B4	10	1.50	0.56	0.08	2	1000	15

[a] Samples A (acidic) are the organo-mineral complexes formed at pH 4, samples N (neutral) at pH 7, and samples B (basic) at pH 10.

[b] pH values of the DHA solution adjusted by HCl or NaOH.

[c] Organic carbon contents were measured in triplicate.

[d] The distilled water was added four times to ensure the five-times of wet–dry cycles.

sorption systems, and the volume ratio of methanol was below 0.001 to avoid co-solvent effect. The aqueous:solid ratios were 100 and 4000 for the complexes and SHAs, respectively. The vials containing the solution and solid were sealed with a glass stopper immediately. The stopper was tightly bound with the vial externally by parafilm, which was not in contact with solution. Headspace was kept minimal to reduce solute vapor loss. The tubes were kept in dark and rotated vertically on a rotator (30 rpm, Glas-Col lab rotator) for 5 d, and centrifuged at 1000*g* for 10 min. The supernatant was poured out carefully to prevent the loss of soil particles, and subjected to solute analysis. The reduction of the solute concentration in solution was in the range of 20–80%. Sorbed PHE was calculated by mass difference. All experiments including the blanks were run in duplicate.

2.6. Fluorescence quenching experiment for the association of PHE with DHA

Fluorescence quenching is a traditional method for investigating the binding of DOM with fluorescent compounds, and has advantages over other methods (Gauthier et al., 1986). In order to compare the sorption characteristics, the binding experiment between DHA and PHE was conducted using a fixed DHA concentration and various PHE concentrations (Laor and Rebhun, 2002). The background solution was purged for 30 min using nitrogen to avoid the static quenching induced by oxygen. A predetermined volume of DHA solution was mixed with PHE solution to reach a TOC concentration of 20 mg C l^{-1} in a total volume of 10 ml, and the tube was immediately sealed with a glass stopper. The tube was shaken by hand, and stored in dark for one day. The fluorescence was counted on a fluorescence spectrometer (F-2500, Hitachi, Tokyo), and the UV absorbance of the PHE–DHA solution was recorded for inner filter correction.

2.7. Measurement of the solutes

All the aqueous samples in sorption experiments of SHAs and organo-mineral complexes were subjected to solvent extraction by purified hexane (volume ratio of sample to hexane was 2:1). The water–hexane was mixed vigorously, and two drops of ethanol were added to diminish emulsification. The recoveries of the hexane extraction exceeded 98% for PHE (Pan et al., 2006).

Approximately 1 ml of the hexane was used for fluorescence analysis until the water–hexane interface was clear. The parameters of fluorescence photometer were as follows: silt 2.5 nm, voltage 700 V, emission wavelength 300–450 nm, excitation wavelength 293 nm, and the peak height at 365 nm was used to quantify PHE. For the binding experiment between DHA and PHE, all the liquids used were purged using N_2 to remove dissolved oxygen before adding PHE.

2.8. Data analysis

The inner filter effect was corrected using absorbance at excitation and emission wavelengths using the following equation (Gauthier et al., 1986):

$$f_{\mathrm{cor}} = \frac{2.3dA_{\mathrm{ex}}}{1-10^{-dA_{\mathrm{ex}}}} 10^{gA_{\mathrm{em}}} \frac{2.3sA_{\mathrm{em}}}{1-10^{-SA_{\mathrm{em}}}} \tag{1}$$

where, f_{cor} is the correcting factor, A_{ex} and A_{em} stand for the absorbance at excitation and emission wavelengths, respectively. The parameters of d, g and s are the geometric dimensions of the measuring cell, which are 1, 0.25 and 0.1 cm, respectively. Consequently, the true fluorescence intensity was calculated as follows:

$$F_{\mathrm{cor}} = f_{\mathrm{cor}} \times F_{\mathrm{obs}} \tag{2}$$

where F_{obs} and F_{cor} are the fluorescence intensity before and after correction. The corrected fluorescence intensity was calibrated and PHE concentration was obtained.

The super-cooled aqueous solubility reduced Freundlich equation was used to fit the sorption isotherms. The equation could be expressed as Eq. (3). In order to compare the parameters of sorption isotherms, the organic carbon normalized concentrations were used:

$$S_{\mathrm{OC}} = K_{\mathrm{FOC}} \times \left(\frac{C_{\mathrm{e}}}{C_{\mathrm{scl}}}\right)^{n} \tag{3}$$

where S_{OC} is the solid-phase concentration of PHE (μg kg C^{-1}), C_{e} represents the aqueous-phase concentration of PHE (μg l^{-1}), and C_{scl} is the super-cool solubility of PHE at 25 °C (5970 μg l^{-1}). K_{FOC} and n are the Freundlich sorption parameters.

Single point sorption coefficients were used widely for comparisons in literature due to isotherm nonlinearity (Wang et al., 2006). Therefore, the single point K_{OC} was calculated based on Freundlich equation at a given concentration (C_{i}).

$$K_{\mathrm{OC}} = \frac{S_{\mathrm{OC}}}{C_{\mathrm{i}}} = K_{\mathrm{FOC}} \times \frac{C_{\mathrm{i}}^{n-1}}{C_{\mathrm{scl}}^{n}} \tag{4}$$

In this study, the single point sorption coefficient for SHA was noted as K_{SHA}, while that of DHA was K_{DHA}.

3. Results

3.1. Composition of solid humic acids (SHAs)

Elemental composition of the four SHAs is presented in Table 2. Carbon contents were around 50%. The three SHAs from soils showed similar elemental composition, because of the close vicinity of soil samples. However, Fluka SHA had lower carbon and higher oxygen contents, and its atomic ratios of O/C and (N + O)/C were also higher than other three SHAs, indicating its higher polarity.

The NMR results provided the composition of structural carbon groups. As listed in Table 2, aliphatic and aromatic carbons accounted for 87–93% of total carbon for the four SHAs. Three soil SHAs were not different in their structural carbon distribution, with 53–55% aliphatic carbons and 33–35% aromatic carbons. Fluka SHA again showed a different composition with 22% aromatic carbons and more than 71% aliphatic carbons.

3.2. Sorption of PHE by solid humic acids (SHAs)

A typical sorption isotherm of PHE on SHA is presented in Fig. 1 and all fitting results are listed in Table 3. The four SHAs exhibited similar nonlinear sorption with PHE. The n values were 0.80–0.82 without any significant difference ($P < 0.01$). The single point K_{SHA} varied from 8230 l kg C^{-1} to 10300 l kg C^{-1} at $C = 0.1C_{\mathrm{S}}$ and 13200 l kg C^{-1} to 15700 l kg C^{-1} at $C = 0.01C_{\mathrm{S}}$. A positive relationship between K_{SHA} and aliphatic carbon contents of the four SHAs was observed (Fig. 2a).

Nonlinear sorption of HOCs by SOM has been widely reported in literature. According to the dual mode model (Xing and Pignatello, 1997), SOM contains both rubbery (soft) and glassy (hard) domains. Sorption of HOCs in rubbery domain occurs by dissolution, while in glassy domain by concurrent dissolution and hole filling mechanisms. Therefore, the apparent sorption of HOCs on SOM particles is nonlinear. For the SHAs in this study, the glassy domain could be generated during the acid precipitation and freeze-drying procedure. Nonlinearity was thus generally observed.

3.3. Interaction of PHE with dissolved humic acids (DHAs)

Interactions of PHE with DHA were investigated with the same concentration sequence as in the SHA sorption experiments; therefore, the Freundlich model could be used to fit the isotherms. A typical curve is shown in Fig. 1 and the overall fitting results are in Table 3. We observed nonlinear isotherms in this study, with n values from 0.81 to

Table 2
Elemental composition of SHAs used in this study

HA	N (%)	C (%)	H (%)	O (%)	Ash (%)	H/C[a]	O/C[a]	(N + O)/C[a]	Aliphatic C[b] (%)	Aromatic C[c] (%)
HA1	3.8	51.9	4.9	39.4	<0.1	1.14	0.57	0.63	0.54	0.33
HA2	2.9	54.7	4.9	37.5	<0.1	1.08	0.51	0.56	0.55	0.35
HA3	2.7	53.9	5.0	38.3	<0.1	1.12	0.53	0.58	0.53	0.35
HA Fluka	0.6	48.4	4.7	46.3	<0.1	1.16	0.72	0.73	0.71	0.22

[a] Atomic ratio.

[b] Aliphatic C: chemical shift of 0–108 ppm from solid C-13 NMR spectra.

[c] Aromatic C: chemical shift of 108–162 ppm from solid C-13 NMR spectra.

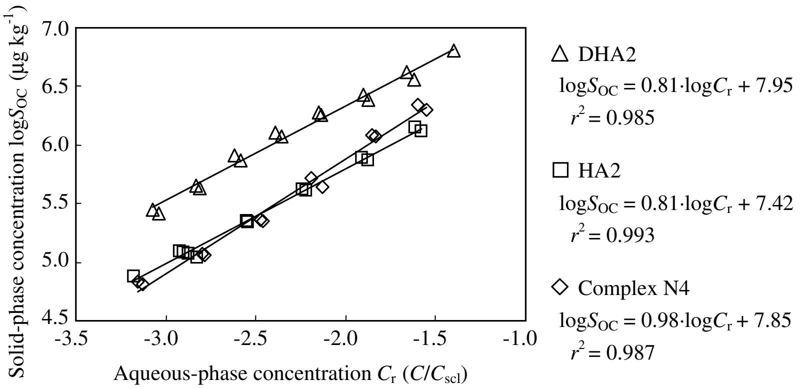

Fig. 1. Typical sorption curves of PHE on SHA, DHA, and the complexes (HA2, DHA2 and complex N4 were chosen as examples).

Table 3
Sorption fitting results of SHA, DHA and organo-mineral complexes

Sample	Fitting results using Freundlich equation[a]					Single point K_{OC} (l kg C^{-1})	
	n[b]	Std.	$\log K_{FOC}$ (μg kg C^{-1})	Std.	r^2	$C_e = 0.1C_S$[c]	$C_e = 0.01C_S$
SHA 1	0.80*	0.02	7.35	0.05	0.994	8230	13200
SHA 2	0.81*	0.02	7.42	0.05	0.993	9050	14000
SHA 3	0.81*	0.02	7.36	0.04	0.995	7980	12300
SHA Fluka	0.82*	0.02	7.49	0.06	0.988	10300	15700
DHA1	0.92*	0.03	7.94	0.07	0.985	20200	24500
DHA2	0.81*	0.03	7.95	0.06	0.985	31200	48400
DHA3	0.87*	0.03	7.84	0.07	0.985	18900	25400
DHA Fluka	0.82*	0.02	7.53	0.05	0.991	11400	17300
Complexes[d]							
A0	0.68*	0.05	7.40	0.11	0.935	13800	30000
A1	0.81*	0.02	7.68	0.04	0.995	16700	26200
A2	0.83*	0.02	7.61	0.05	0.993	12900	19100
A3	0.94	0.02	7.73	0.04	0.996	11300	13000
A4	0.93*	0.02	7.72	0.05	0.996	11300	13100
N0	0.67*	0.04	7.41	0.09	0.952	15000	32500
N1	0.85*	0.03	7.72	0.06	0.988	15700	21900
N2	0.96	0.04	7.95	0.10	0.979	17400	19200
N3	0.93	0.04	7.75	0.10	0.979	12100	13900
N4	0.98	0.04	7.85	0.09	0.987	12500	13000
N6	0.92*	0.03	7.72	0.07	0.989	11700	14000
B0	0.69*	0.06	7.38	0.13	0.907	12500	26300
B1	0.98	0.06	8.05	0.15	0.959	20700	21700
B2	1.04	0.07	8.08	0.15	0.962	17400	15800
B3	1.03	0.05	7.87	0.10	0.980	11200	10400
B4	0.99	0.05	7.84	0.12	0.973	12200	12500

[a] Each isotherm contained 6–8 concentration points and each concentration was run in duplicate.
[b] * Means the value is significantly different from 1 ($P < 0.01$).
[c] C_S is water solubility of PHE at 20 °C, 1290 μg l^{-1}.
[d] Samples A are the organo-mineral complex formed at pH 4 (acidic), samples N at pH 7 (neutral), and samples B at pH 10 (basic).

0.92. This differs from many previous studies in which the interaction between HOCs and DOM was considered linear (i.e., dissolution). Laor and Rebhun (2002) also reported the nonlinear binding between DOM and polyaromatic hydrocarbons. They suggested that site specificity at limited molecular surfaces could be used to explain the nonlinearity. Some other nonideal phenomena have been reported, such as saturation of DOM binding sites (Borisover et al., 2006), and desorption resistance of DOM-bound HOCs (Schlebaum et al., 1998). More research is needed to clarify the mechanism of HOCs binding with DOM.

The K_{DHA} values for four DHAs varied between 11400 l kg C^{-1} to 31200 l kg C^{-1} at $C = 0.1C_S$ and 17300 l kg C^{-1} to 48400 l kg C^{-1} at $C = 0.01C_S$, with much greater variation than those of SHAs. A negative trend between K_{DHA} and polarity ((N + O)/C) could be seen (Fig. 2b).

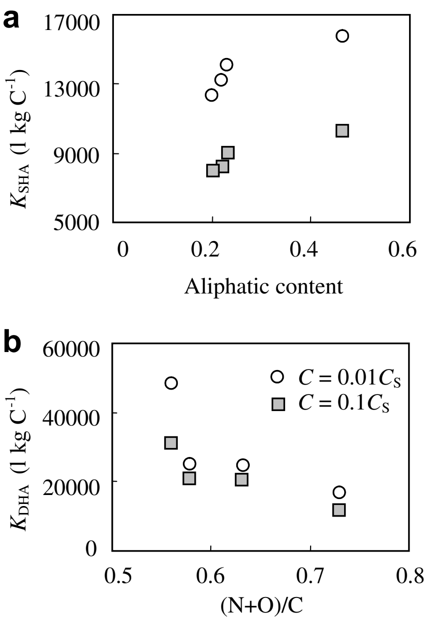

Fig. 2. The relationship between K_{SHA} or K_{DHA} and chemical properties of organic matter. K_{SHA} is positively related with aliphatic carbon content, whereas K_{DHA} is negatively related with (N + O)/C. C_S is water solubility of PHE at 20 °C, 1290 μg l^{-1}. Open circles are for $C = 0.01C_S$ and solid squares are for $C = 0.1\ C_S$.

3.4. Sorption of PHE on DHA-mineral complexes

The complexes were synthesized at pH = 4, 7 and 10, followed by washing with distilled water. The pH values of all sorption experiments were approximately 7. Therefore, pH affected only the formation of the complexes. A typical isotherm is also given in Fig. 1, and the overall results are in Table 3.

All the complexes showed significantly higher *n* values than the H_2O_2-treated soil particles which had *n* values lower than 0.7. All *n* values were not significantly different from 1 for the complexes formed at pH 10 with $f_{OC} > 0.08\%$, and the complexes formed at pH 7 with $f_{OC} > 0.18\%$. Although not significantly different, the complexes formed at pH 4 showed lower *n* values than other ones. The K_{OC}s were not significantly different for complexes formed at different pHs (Table 3).

4. Discussion

4.1. Nonlinear sorption of PHE by H_2O_2-treated soil particles

Sorption of PHE to the H_2O_2-treated particles showed strong nonlinearity. The *n* values were 0.67–0.69 for A0, B0 and N0 (Table 3). As indicated by many studies, mineral particles usually have linear sorption isotherms for nonpolar HOCs (Huang et al., 1996; Wang and Xing, 2005a). The strong nonlinear sorption of PHE could not be attributed to the inorganic components of the particles. Numerous studies suggested that organic matter can form stable complexes with clay minerals. The organic matter would thus be preserved because the organic-mineral complexes are highly resistant to degradation and oxidation (Rice, 2001; Kalbitz et al., 2005; Tharayil et al., 2006). The H_2O_2 treatment lasted for 40 d in this study, however, 0.08% organic carbon remained, which is most likely the condensed carbon fraction of SOM. According to dual mode model (Xing and Pignatello, 1997), condensed (hard) carbons exhibit strong nonlinear isotherms. Our results indicate that the residual condensed carbon of the H_2O_2-treated soil particles played a major role on the apparent nonlinear sorption, consistent with the results by Wang and Xing (2005b).

4.2. Linear sorption by coated humic acid

Sorption by organo-mineral complexes includes the sum contributed by both H_2O_2-treated soil particles and coated humic acid. Researchers proposed a method to deduct the maximum contribution of H_2O_2-treated soil particles using the following equation (Zhou et al., 1995):

$$S = S_t - S_p = S_t - K_{Fp}\left(\frac{C}{C_{scl}}\right)^{n_p} \tag{5}$$

where S_t is the overall solid-phase concentration (μg kg^{-1}). S (μg kg^{-1}) and S_p (μg kg^{-1}) are the solid-phase concentration contributed by organic matter and H_2O_2-treated soil particles, respectively. K_{Fp} (μg kg^{-1}) and n_p are the sorption parameters of H_2O_2-treated soil particles.

All the *n* values increased after subtracting the contribution of H_2O_2-treated soil particles (Fig. 3). The contribution of the treated soil particles may be overestimated in the subtraction procedure, as could be seen for the two points with *n* values significantly higher than 1 ($P < 0.01$, for B2 and B3, Fig. 3b). However, the trend indicated that the apparent sorption of the organo-complex is the combination of two fractions with different sorption properties.

The complexes formed at pH 4 had lower *n* values than the other complexes at lower TOC content (< 0.5%, Fig. 3a), and the correction for the sorption of H_2O_2-treated soil particles did not result in any significant change of those low *n* values (Fig. 3b). Thus, sorption of PHE on the coated humic acid at pH 4 with lower f_{OC} was relatively nonlinear.

The SHAs in this study, from the precipitation of DHA at pH < 1, had nonlinear isotherms. Although DHAs did not precipitate at pH 4, the proton (H^+) would be concentrated during the drying process, which could subsequently cause the DHA precipitation on the surface of soil particles. Since larger volumes of DHA solution were used for the complexes with higher f_{OC}, the proton concentration during drying should be higher than the lower f_{OC} ones. Then, if the H^+-induced HA precipitation play any role in nonlinear sorption, the nonlinearity should be stronger for the complexes with higher f_{OC}. However, nearly linear isotherms were observed for the complexes with higher f_{OC} formed at pH 4. Thus, proton concentration change during drying should not be the reason of nonlinear sorption.

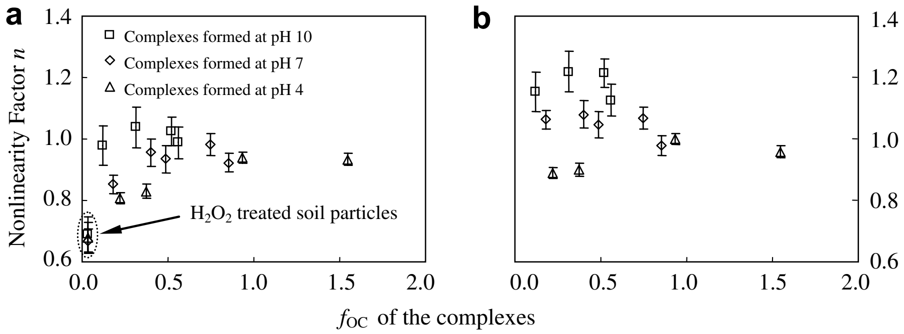

Fig. 3. Nonlinearity factor n for the organo-mineral complexes (a) and humic acid coating (b). The sorption by coated humic acid was calculated by deducting the maximum contribution of H_2O_2-treated soil particles (Eq. (5)). All the n values increased after subtracting the contribution of H_2O_2-treated soil particles.

Previous studies have shown that the sorption of natural organic matter on minerals is accompanied with fractionation of SOM, and the n value increased as f_{OC} increased on the minerals (Wang and Xing, 2005a). Also, the acidic condition was reported to enhance the sorption of organic matter on mineral particles (Schlautman, 1992; Laor et al., 1998). Therefore, the complexes formed at pH 4 might be different from those formed at pH 7 and 10 at lower f_{OC}. As the f_{OC} increased, a more physical-like coating process became dominated. In other words, physical coating resulted in an expanded conformation showing linear sorption (Fig. 3b), supported by a previous study (Wang and Xing, 2005a).

4.3. Different sorption characteristics of SHAs and DHAs

According to the preparation procedure of SHAs, the solution was filtered through a 0.45 μm filter followed by acid precipitation. Chemical structure and composition of the corresponding DHAs and SHAs should be identical. However, sorption coefficients, K_{DHA}s were significantly higher than the corresponding K_{SHA}s. Moreover, K_{DHA} and K_{SHA} were found to be related to different properties of SOM. A positive trend was noticed between K_{SHA} and aliphatic carbon content, whereas a negative relationship was observed between K_{DHA} and (N + O)/C. Different regulating factors between SHAs and DHAs may result from different self-organization patterns of humic molecules. For DHAs, molecular assembly would be relatively open and nonpolar molecules such as PHE can have access to and associate with hydrophobic regions of DHAs. Therefore, a negative relationship was observed for polarity and K_{DHA} (Fig. 2b), as reported by Tanaka et al. (2005). However, for SHAs, the humic acid molecules may be self-coiled to a form in which the aliphatic regions (nonpolar) are physically more available for PHE, and have stronger effect on K_{SHA} (Fig. 2a). Clearly, further investigations are required to elucidate why DHAs and SHAs had different correlating parameters with PHE sorption.

Different chemical characteristics (aliphatic content, aromatic content or polarity) of SOM had been reported to affect sorption properties. It is most likely that chemical characteristics are not the only factor controlling the sorption properties of SOM. Physical organization of SOM has been proposed to affect HOC sorption. For example, by comparing the sorption characteristics of separated SOM fractions and whole soil, Salloum et al. (2001) reported that fractionation procedure reorganized the organic matter in such a way that more favorable sorption sites became available. Their observation was supported by the results reported by Xing (2001). Laor et al. (1998), and Jones and Tiller (1999) reported that DHA showed significantly higher sorption capacity for HOCs than HA solid particles. Our current work also showed different sorption characteristics of SHA, DHA and physically coated DHA. All the results indicate that sorption characteristics of HOCs by SOM vary with the conformations of SOM.

Wang et al. (2003) observed different proton spin–lattice relaxation times (T_1) of humic acids in NaOD/D_2O and d_6-DMSO using NMR. They suggested that humic acids might have different conformations in the two solvents. Simpson et al. (2001) also reported that aromatic content of SOM was not detectable in the solvent of D_2O, indicating that the aromatic content was protected in hydrophobic regions. These studies confirmed the existence of different physical conformations of SOM.

K_{OW}, water solubility (S) or atomic ratio of O/C were used to predict K_{OC} (Chiou et al., 1979; Karickhoff et al., 1979; Huang and Weber, 1997). This line of research facilitated modeling the behavior of HOCs in the environment. However, physical conformation is seldom addressed in K_{OC} prediction. As discussed in this study, plenty of evidence could be found both from the literature and this work that the sorption characteristics are different among different physical forms of a same organic sorbent. Future research should be directed on SOM physical conformation in order to better understand its environmental impact on the fate and bioavailability of HOCs.

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