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Sorption of Polar and Nonpolar Aromatic Organic Contaminants by Plant Cuticular Materials: Role of Polarity and Accessibility

BAOLIANG CHEN,[†,‡]
ELIZABETH J. JOHNSON,[†]
BENNY CHEFETZ,[§] LIZHONG ZHU,[‡] AND
BAOSHAN XING*,[†]

Department of Plant, Soil and Insect Sciences, University of Massachusetts, Amherst, Massachusetts 01003, USA, Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310028, China, and Department of Soil and Water Sciences, The Hebrew University of Jerusalem, Rehovot 76100, Israel

In both forest and agricultural soils, plant derived cuticular materials can constitute a significant part of soil organic matter. In this study, the sorption of nonpolar (naphthalene and phenanthrene) and polar (phenol and 1-naphthol) aromatic organic pollutants to aliphatic-rich cuticular fractions of green pepper (*Capsicum annuum*) (i.e., bulk (PC1), dewaxed (PC2), nonsaponifiable (PC3), nonsaponifiable−nonhydrolyzable (PC4), and dewaxed−hydrolyzed residue (PC5)) were examined to better understand the influence of polarity and accessibility on their sorption behavior. The polarity and structures of cuticular fractions were characterized by elemental analysis, Fourier transform infrared spectroscopy, and solid-state ^{13}C NMR. The sorption isotherms fit well to the Freundlich equation. Sorption of the tested organic compounds to PC4, which had more condensed domains, was nonlinear (Freundlich N_s values of 0.766−0.966). For naphthalene and phenanthrene, the largest sorption capacity (K_{oc}) occurred in PC5, which contained the highest paraffinic carbons (63%) and the lowest polarity: ∼2 and ∼3 times higher than the respective carbon-normalized octanol−water partition coefficient (K_{owc}), indicating that PC5 was a powerful sorption medium. For phenol and 1-naphthol, the largest K_{oc} values occurred in PC4 with polar aromatic cores: ∼17 and ∼7 times higher than the respective K_{owc}, suggesting that PC4 was much more accessible and compatible to polar aromatic pollutants than nonpolar aromatic pollutants. There was little or no correlation of K_{oc} with either aliphatic or aromatic components of the tested aliphatic-rich sorbents because the polarity and accessibility apparently played a regulating role in the sorption of organic contaminants.

Introduction

Sorption and desorption are the major processes influencing the fate (uptake; bio-, chemical-, and photodegradation; and mobility) of hydrophobic organic contaminants (HOCs) (e.g., polycyclic aromatic hydrocarbons (PAHs)) in the soil environment. Sorption is of growing concern due to the strong affinity of HOCs to solid matrix and the potential risks associated with their long-term persistence in the environment. Hence, understanding sorption behavior is vital to accurate fate prediction of HOCs and remediation of contaminated areas (*1*−*2*).

The predominant sorbent of HOCs is the soil or sedimentary organic matter (SOM) (*3*, *4*). The content and chemical natures of SOM have been suggested as major factors controlling its sorption mechanism and affinity (*5*−*8*). Most of these studies suggested a positive correlation between the amount of HOC sorption and the aromatic carbon content of the samples. It was concluded that the aromatic content of SOM is a good predictor of the soil's ability to sorb HOCs. However, this theory failed to predict high sorption to soil samples characterized by highly aliphatic SOM (*9*−*13*).

SOM is derived from plants, animals, and microbes via decomposition processes. As decomposition proceeds, aliphatic components tend to accumulate in soils (*14*−*17*). In both forest and agricultural soils, leaf derived plant litter constitutes a significant portion of SOM (*14*, *16*, *18*). This litter mainly contributes aliphatic components to SOM, many of which are derived from the plant cuticle (*19*, *20*). The plant cuticle is a thin layer of predominantly lipid material, which is synthesized by the epidermal cells and deposited on the outer walls of leaves. Modeled as a bilayer, the outer region of the plant cuticle is composed mainly of aliphatic lipids, while the inner layer contains large amounts of various cell wall polysaccharides. The principal lipid component of the cuticle is the polyester cutin (*21*, *22*). Cutin is an insoluble polyester of cross-linked hydroxyl-fatty acids and hydroxyepoxy-fatty acids (*21*, *22*). Some plant cuticles have been shown to additionally contain an acid and base hydrolysis-resistant biopolymer known as cutan (*20*). Cutan is made up of polyethylene-like chains attached to aromatic cores (*23*−*25*). Both of these biopolymers are thought to be difficult to degrade microbiologically, and several studies have shown that the aliphatic biopolymers could be selectively preserved in soils with little or no alteration (*17*, *19*). Therefore, it was suggested that aliphatic components of SOM could be dominant sorption domains in forest and agricultural soils (*11*, *13*, *17*).

Although it is well-documented that SOM predominantly controls sorption of HOCs in soils and sediments, the role of its composition, nature, and physical conformation in determining the sorption coefficient requires further investigation (*26*). Recently, Kang and Xing (*10*) proposed that the polarity of SOM is the predominant regulator for the magnitude of phenanthrene sorption rather than structure (e.g., aromaticity or aliphaticity); high sorption capacity (K_{oc}) of both aromatic-rich SOM and aliphatic-rich SOM was thought to be due to their low polarity. The accessibility, depending mainly on conformation, is another important parameter of SOM influencing sorption of organic pollutants. The aromatic and carbohydrate components were reported to play an important role in the conformation of the condensed and expanded domains of SOM (*7*, *9*, *27*, *28*). Thus, SOM polarity and accessibility appear to be important factors in organic contaminant sorption, but more research is needed to confirm this.

The objective of this study was to examine sorption of nonpolar (naphthalene and phenanthrene) and polar (phenol and 1-naphthol) aromatic organic compounds to aliphatic-

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* Corresponding author phone: (413)545-5212; fax: (413)545-3958; e-mail: bx@pssci.umass.edu.

[†] Department of Plant, Soil and Insect Sciences, University of Massachusetts, Amherst, Massachusetts 01003, USA.

[‡] Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310028.

[§] Department of Soil and Water Sciences, The Hebrew University of Jerusalem, Rehovot 76100, Israel.

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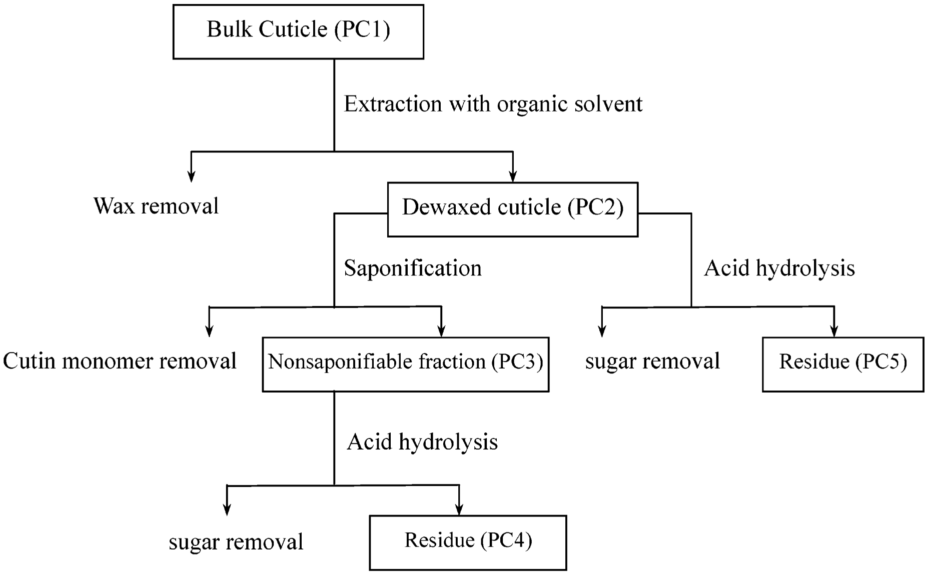


FIGURE 1. Flowchart of the isolation process of cuticular fractions.

rich isolated plant cuticular fractions (mineral and black-carbon free) with a wide range of polarity to better understand the influence of polarity and accessibility on HOCs sorption. All samples were analyzed for carbon, nitrogen, and hydrogen content to calculate the polarity index (i.e., (O + N)/C atomic ratio) and were examined by solid-state ^{13}C NMR and infrared spectroscopy (DRIFT) for the presence and/or relative differences in structural and polar carbons, from which the accessibility was evaluated.

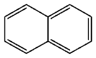
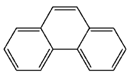
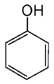
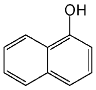
Materials and Methods

Isolation of Plant Cuticlar Fractions. Cuticle sheets were isolated from the fruits of green pepper (*Capsicum annuum*) using a modified version of the method reported by Kogel-Knabner et al. (*29*). In brief (Figure 1), skins were manually peeled from fresh green pepper fruits. The skins were boiled in water for 1 h, and the pulp was removed manually as much as possible. Then, the skins were incubated in a solution of oxalic acid (4 g/L) and ammonium oxalate (16 g/L) at 90 °C for 24 h and washed with deionized distilled water to remove any residual fruit pulp material. This procedure yielded the bulk cuticle fraction (PC1). Waxy materials were removed from PC1 fraction by Soxhlet extraction with chloroform/methanol (1:1) at 70 °C for 6 h to yield a dewaxed cuticle fraction (PC2). To remove the cutin monomer, the materials (PC2) were saponified with 1% potassium hydroxide in methanol for 3 h at 70 °C under refluxing and stirrer-spinning conditions, producing the nonsaponifiable fraction (PC3). Carbohydrates were further removed from the PC3 fraction by acid hydrolysis in 6 mol/L HCl solution with refluxing for 6 h at 100 °C, resulting in the nonsaponifiable−nonhydrolyzable residue (PC4). Dewaxed cuticles (PC2) underwent exhaustive acid hydrolysis in 6 mol/L HCl to yield a dewaxed−hydrolyzed residue (PC5) containing the non-saponibiable−nonhydrolyzable PC4 fraction. The resulting fractions of PC3, PC4, and PC5 were separated from the basic or acidic solution by filtration, and then the residues were washed with a mixed solution of methanol and deionized distilled water (V/V = 1:1) 5 times to adjust these fractions to neutral conditions at the end and to remove dissolved organic matter (e.g., cutin monomer and carbonhydrates) sorbed by these residues. All samples were freeze-dried, ground, and sieved (<0.18 mm) before analysis and sorption experiments.

Characterization of the Cuticular Fractions. The C, H, and N contents of the cuticular fractions were determined using a Carlo Erba 1110 CHN Elemental Analyzer. The oxygen content was calculated by the mass difference. The H/C, O/C, C/N, and (O + N)/C atomic ratios were calculated. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) was performed using a Midac series M2010 infrared spectrophotometer (Irvine, CA) with a DRIFT accessory (Spectros Instruments, Whitinsville, MA), following the procedure of Kang and Xing (*10*). Solid-state cross-polarization magic angle-spinning and total-sideband-suppression ^{13}C NMR spectra (CPMAS-TOSS) were obtained with a Bruker DSX-300 spectrometer (Karlsruhe, Germany) operated at the ^{13}C frequency of 75 MHz. The instrument was run under the following conditions: contact time, 1 ms; spinning speed, 5 kHz; 90° ^{1}H pulse, 5 μs; acquisition delay, 4 s; line broadening, 50 Hz; and number of scans, 2000−5000. Within the 0−220 ppm chemical shift range, C atoms were assigned (*30*) to paraffinic carbons (0−50 ppm); substituted aliphatic carbons including alcohol, amines, carbohydrates, ethers, and methoxyl and acetal carbon (50−109 ppm); aromatic carbons (109−163 ppm); carboxyl carbons (163−190 ppm); and carbonyl carbons (190−220 ppm).

Sorption Isotherms. Nonpolar (i.e., naphthalene and phenanthrene) and polar (i.e., phenol and 1-naphthol) aromatic organic compounds were chosen as sorbates. Their selected properties are listed in Table 1. Ring-UL-^{14}C and unlabeled organic compounds were purchased from Sigma-Aldrich Chemical Co. and used without further purification. These organic compounds are common organic contaminants in soil and sediment and have often been used in environmental research. All sorption isotherms were obtained using a batch equilibration technique (*9*) at room temperature (23 ± 1 °C) in screw cap vials with aluminum foil liners: 15 mL vials for phenanthrene and 8 mL vials for naphthalene, 1-naphthol, and phenol. The background solution was comprised of 0.01 mol/L $CaCl_2$ in deionized distilled water with 200 mg/L NaN_3 as a biocide. To have the tested organic compounds at a neutral state, the pH value of the background solution was controlled at 7. Initial concentrations ranged from 0.006 to 0.8 mg/L for phenanthrene, 0.009−14 mg/L for naphthalene, 10−2000 mg/L for phenol, and 0.02−600 mg/L for 1-naphthol. Because of the low water solubility, stock naphthalene and phenanthrene solutions were made at high concentrations in MeOH before being added to the background solution, while the nonradioactive stock solution of phenol and 1-naphthol was prepared directly in aqueous solution. The ^{14}C-labeled organic compound and its non-

TABLE 1. Selected Properties of Organic Pollutants[a]

Organic pollutants	Formula	M	S	K_{ow}	K_{owc}	BP	MP	MR	pK_a
Naphthalene		128.2	31.02	1950	2640	474	261	42.45	-
Phenanthrene		178.2	1.15	28000	37900	589	351	59.62	-
Phenol		94.11	89100	30	41	439	282	27.09	9.92
1-naphthol		144.2	866	501	678	555	328	44.26	9.34

[a] M: molecular weight, g/mol. S: aqueous solubility, μg/mL. K_{ow}: octanol–water partition coefficient. K_{owc}: carbon-normalized K_{ow} (K_{owc} = K_{ow}/f_{oc}), where f_{oc} is the percentage of carbon contents of octanol (73.8%). MP and BP are melting and boiling point temperature (unit is K), respectively. MR: molar refractivity, cm^3/mol. pK_a: acid dissociation constant.

radioactive stock solutions were mixed with plant cuticular fractions at different solid-to-solution ratios. The ratios were adjusted to achieve 30–80% sorption of organic compounds at apparent equilibrium. MeOH concentrations were always less than 0.1% of the total solution volume to avoid cosolvent effects. Isotherms consisted of eight to ten concentration points; each point, including the blank, was run in duplicate. The vials were sealed with aluminum foil-lined Teflon screw caps and then placed on a shaker for 3 days at room temperature (23 ± 1 °C) (preliminary tests indicated that apparent equilibrium was reached before 2 days). The vials were then centrifuged at 1000g for 30 min, followed by 0.5 mL removal of supernatant, which was added to a Scintiverse cocktail (8 mL), purchased from Fisher Scientific (Pittsburgh, PA), for scintillation counting (Bechman [Fullerton, CA] LS6500). The final pH of the supernatant after sorption experiment was measured, showing that the pH values of solution during sorption process were practically unchanged. Because of little sorption by vials and no biodegradation, sorbed sorbate by the sorbents was calculated by mass difference. The other experimental details were reported elsewhere (*2*, *9*).

All sorption data were fitted to the logarithmic form of the Freundlich equation

$$\log S = \log K_f + N \log C_e \qquad (1)$$

where S is the solid-phase concentration (mg/kg) and C_e is the liquid-phase equilibrium concentration (mg/L). The parameters K_f for the sorption capacity coefficient [(mg/kg)/(mg/L)^N] and N (dimensionless) indicating isotherm nonlinearity were determined by linear regression of log-transformed data. Slopes of sorption isotherms (K_d) were calculated from the linear fitting of whole isotherms for phenanthrene, naphthalene, and phenol except for PC4 because of its nonlinear isotherms. The K_d values were calculated from the linear part of isotherms at low concentration ranges for the four tested organic compounds by the PC4 sample. For 1-naphthol by all cuticular fractions, the K_d values were also calculated from the linear part of isotherms at low concentration ranges. Values of K_{oc} were calculated from normalizing K_d to the carbon level of each cuticular fraction.

TABLE 2. Relative Yields of the Different Pepper Cuticle Fractions and Their Elemental Analysis and Atomic Ratios

sample[a]	yield[b] (%)	C (%)	H (%)	N (%)	H/C	O/C[c]	C/N	(O + N)/C
PC1	100	64.2	9.29	1.06	1.72	0.30	70.5	0.31
PC2	93.8	63.0	9.22	1.05	1.74	0.32	69.9	0.33
PC3	29.0	42.4	6.06	3.50	1.70	0.85	14.2	0.92
PC4	7.9	48.8	6.25	0.60	1.53	0.68	95.0	0.69
PC5	71.8	67.8	9.86	0.24	1.73	0.25	326	0.25

[a] PC1: bulk cuticle; removal of waxy material from PC1 yielded dewaxed cuticle (PC2); saponification of PC2 produced nonsaponifiable fraction (PC3); the PC2 and PC3 samples were hydrolyzed to yield a dewaxed–hydrolyzed residue (PC5) and a nonsaponifiable–nonhydrolyzable residue (PC4), respectively. [b] The yields of PC2, PC3, PC4, and PC5 were calculated to the percentage contents of PC1. [c] Oxygen content was calculated by the mass difference.

Results and Discussion

Characterization of Cuticular Fractions. The yields and elemental compositions of isolated plant cuticular fractions are presented in Table 2. The amount of external lipids, which were removed by Soxhlet extraction, was 6.2 wt %, whereas the fraction removed by saponification was the major part of the cuticle (i.e., cutin monomer), corresponding to 65 wt %. Similar loss of the total mass occurred when the PC2 and PC3 were acid-hydrolyzed (i.e., 22 and 21% for PC2 and PC3, respectively). The final residue (nonsaponifiable–nonhydrolyzable, PC4) corresponded to less than 8% of the total bulk cuticle mass, whereas the dewaxed–hydrolyzed residue (PC5) was approximately 72% of the total bulk cuticle mass (there was about 11% PC4 in PC5). These data were consistent with the literature results (*24*). The major structural component of the cuticle is cutin, a biopolyester mainly composed of interesterified hydroxyl and epoxy-hydroxy fatty acids with a chain length of 16 and/or 18 carbons (C_{16} and C_{18} class) (*22*). Cutan, the nonsaponifiable–nonhydrolyzable component, is made up of polyethylene-like chains attached to aromatic cores (*23*, *25*). The organic carbon content of PC5 was the highest (68%), while C% of PC3 was the lowest (42%). The H/C ratios for PC1, PC2, PC3, and PC5 samples were ~1.72, higher than that of PC4 (1.53). The polarity index ((O + N)/C) was highest with PC3, with an order of PC3 (0.92) > PC4 (0.69) > PC2 (0.33) > PC1 (0.31) > PC5 (0.25). These elemental composition data indicate that the cuticular fractions were mainly aliphatic components with a wide range

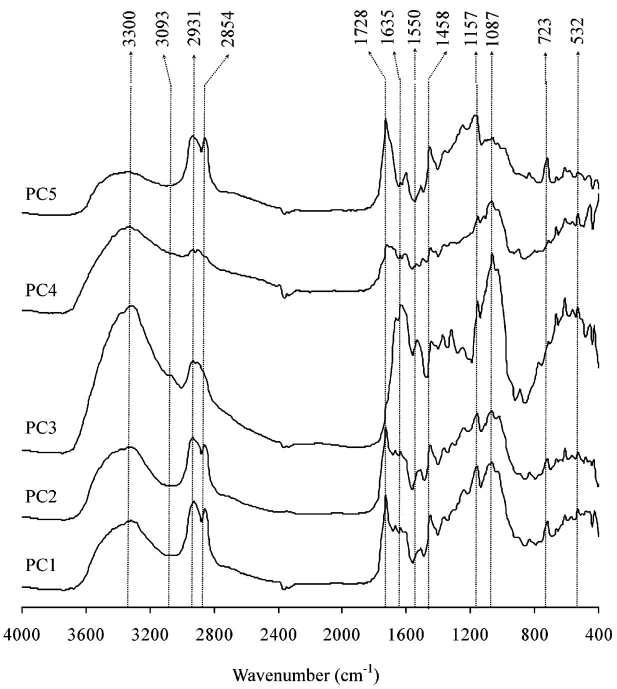


FIGURE 2. DRIFT spectra of bulk cuticle (PC1), dewaxed cuticle (PC2), nonsaponifiable fraction (PC3), nonsaponifiable−nonhydrolyzable residue (PC4), and dewaxed−hydrolyzed residue (PC5).

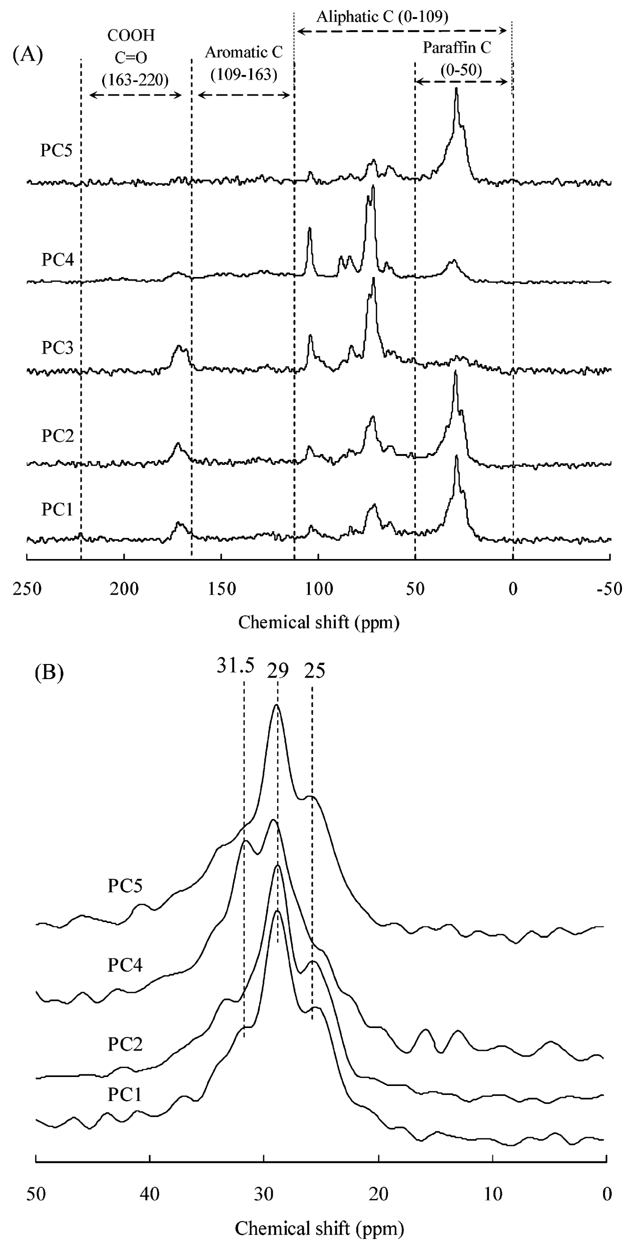


FIGURE 3. Solid-state ^{13}C NMR spectra of bulk cuticle (PC1), dewaxed cuticle (PC2), nonsaponifiable fraction (PC3), nonsaponifiable−nonhydrolyzable residue (PC4), and dewaxed−hydrolyzed residue (PC5). (A) 0−220 ppm and (B) 0−50 ppm, the spectra normalized by the maximal intensity of this range (0−50 ppm).

of polarities, which is in agreement with the following spectroscopic data.

The DRIFT spectra between 4000 and 400 cm^{-1} for the five cuticle fractions are shown in Figure 2. The broad band observed at about 3300 cm^{-1} was assigned to the stretching vibration of hydroxyl functional groups. The broad band is indicative of hydroxyl group stretching vibrations when the hydroxyl group is hydrogen bonded. Further, the frequency is in the range of intermolecular hydrogen bonds that give rise to polymeric association (*31*). On the other hand, the absence of IR absorption near 3600 cm^{-1} indicates that there were no appreciable free hydroxyl groups in the cuticular materials. The spectra of PC1 and PC2 samples were similar. The bands at 2931, 2854, 1458, 1380, 1319, and 723 cm^{-1} are assigned mainly to CH$_2$ units in cutan and cutin polymers. The bands at 1728 with a shoulder at 1700 cm^{-1} are assigned to C=O stretching vibrations of ester groups. The presence of the shoulder indicates that some of these functional groups are involved in hydrogen bonding. The bands at 1164 and 1100 cm^{-1} are assigned to the asymmetric and symmetric C−O−C stretching vibrations of the ester groups. The peaks at 1249, 1157, 1087, and 1049 cm^{-1} are assigned to C−O stretching of polysaccharides. The bands at 3093, 1627, 1604, 1550, 1500, 1450, 840, and 532 cm^{-1} are assigned to aromatic components.

During the saponification treatment, ester bonds were broken, corresponding to removal of hydroxyl-fatty acids. The PC3 sample was dominated primarily by cuticular polysaccharides (e.g., 1087 cm^{-1}) and ionized carboxyl groups -COO$^-$ (e.g., 1635 cm^{-1}). The PC3 sample exhibited a significant increase in the O/C ratio (Table 2). When the PC3 sample was further treated by hydrolysis (PC4), polysaccharides were removed, the peaks at 2931 and 2854 cm^{-1} were decreased further, and a resultant spectrum was dominated by peaks at 1728 (carbonyl stretch of -COOH group), 1627, 1604, 1550, and 1500 cm^{-1} (C=C stretching vibration in the aromatic ring). A strong band at 1450 cm^{-1} (C−C stretching vibration in the aromatic ring) only appears when the aromatic ring is conjugated with unsaturated groups (e.g., -COOH), suggesting that phenolic acids or analogous compounds are present in the matrix in the PC4 sample (*31*). The presence of two distinct bands at 840 and 532 cm^{-1}, corresponding to C−H and C−C out-of-plane bending vibration in the aromatic ring, are typical for infrared absorption by 1,4-disubstituted benzene molecules (*31*). These observations indicate that PC4 contained more aromatic cores than other fractions and that these aromatic cores were substituted by polar functional groups (e.g., -COOH and -OH), which was further supported by our NMR data. After hydrolyzing the PC2 sample, the resultant PC5 sample was dominated by CH$_2$ bands (e.g., 2931 and 2854 cm^{-1}, ascribed to aliphatic CH$_2$ asymmetric and symmetric stretching, respectively).

The NMR spectra of different cuticle fractions and C-containing functional group contents are presented in Figure 3 and Table 3. The ^{13}C NMR spectra of the bulk cuticle (PC1) and the dewaxed cuticle (PC2) were similar. The total percentage of paraffinic carbons (0−50 ppm) was 46% for

TABLE 3. Integration Results of Solid-State ^{13}C NMR Spectra[a]

	distribution of C chemical shift, ppm (%)											
sample[b]	0−50	50−61	61−96	96−109	109−145	145−163	163−190	190−220	aliphatic C (%)	aromatic C (%)	polar C (%)	aliphatic polar C (%)
PC1	45.7	5.0	26.6	5.3	7.0	1.5	8.2	0.6	82.6	8.5	47.3	36.9
PC2	40.7	5.4	30.3	6.2	5.7	2.2	9.2	0.4	82.5	7.9	53.7	41.8
PC3	17.4	7.7	48.1	9.8	3.1	2.0	12.4	0.0	82.9	5.1	79.9	65.5
PC4	13.6	3.1	43.9	10.8	14.1	5.8	5.8	2.8	71.5	20.0	72.2	57.8
PC5	63.3	4.6	21.0	2.7	6.3	2.2	0.7	0.0	91.6	8.5	31.2	28.3

[a] Aliphatic C: total aliphatic carbon region (0−109 ppm). Aromatic C: total aromatic carbon region (109−163 ppm). Polar C: total polar C region (50−109 and 145−220 ppm). Aliphatic polar C: polar C in aliphatic region (50−109 ppm). [b] PC1: bulk cuticle; removal of waxy material from PC1 yielded dewaxed cuticle (PC2); saponification of PC2 produced nonsaponifiable fraction (PC3); the PC2 and PC3 samples were hydrolyzed to yield dewaxed−hydrolyzed residue (PC5) and nonsaponifiable−nonhydrolyzable residue (PC4), respectively.

PC1 and 41% for PC2, and the total calculated aliphatic carbon of the two samples was >82%. The level of aromatic carbon (109−163 ppm) was 8.5% for PC1 and 7.9% for PC2. The spectrum of PC3 was dominated by carbohydrate-type carbons, and the total level of polysaccharide was 66% in this sample. The significant reduction of the methylene C peaks from 41% in the PC2 sample to 17% in PC3 was due to saponification. After hydrolysis of PC3, the aromatic carbons increased from 5.1% in PC3 to 20% in PC4, while the paraffinic carbon was further reduced to 14%. This indicates that the aromatic core in the cuticle was exposed after the removal of cutin monomer and polysaccharide. Phenolic carbon content in the aromatic core of PC4 (5.8%) was 2 times more than that of other sorbents, suggesting that the aromatic core in PC4 was substituted (e.g., by -OH groups) and polar, which is consistent with the reported result (*22*, *23*, *25*). The saponification process broke ester linkages and yielded -OH terminals, thus the increase in phenolic carbon content seen for PC4. Hence, the high phenolic carbons found in PC4 were most likely not present in the starting raw cuticular material. After exhaustive acid hydrolysis of PC2, the paraffinic carbon substantially increased to 63% for PC5, and the level of total aliphatic carbons was 92%. Thus, all the cuticular fraction samples were aliphatic-rich organic matter (71−91%), while the polar carbon contents (50−109 and 145−220 ppm) of the samples varied greatly among the cuticular fractions: PC3 (80%) > PC4 (72%) > PC2 (54%) > PC1 (47%) > PC5 (31%). This observation was consistent with the result of elemental composition (Table 2).

In the paraffinic carbon region (0−50 ppm), signals with chemical shift values in the vicinity of 29−35 ppm are ascribed to alkyl C in long chain polymethylene, -$(CH_2)_n$-type structures (e.g., fatty acids, waxes, and resins). Two peaks that are assigned to amorphous aliphatic carbons (29 ppm) and crystalline aliphatic carbons (31.5 ppm) (*25*) were observed for the cuticular fractions (Figure 3B). The peak at 31.5 ppm was very weak for PC1, PC2, and PC5 in comparison with the 29 ppm peak but was strong for PC4, indicating that along with the low H/C and high aromatic content, the PC4 sample contained more condensed domains than the PC1, PC2, and PC5 samples (*32*). In comparison to the PC1, PC2, and PC5 samples, a decrease in the chemical shift of the signal toward 25 ppm in the PC4 sample suggests a reduction in the amount of long chain polymethylene materials and an increase in short chain materials (*33*), which is in line with the isolation processes.

The elemental composition and structural characteristics of sorbents play an important role in their sorption behavior for organic pollutants. The relationship between polarity index (i.e., (O + N)/C) and percentage of paraffinic carbon (equal to paraffinic carbon content × C% of sorbent) in organic sorbents in this study and in the literature was plotted in Figure 4. An overall negative correlation was observed. This observation suggests that polarity and paraffinic carbons could be interactive parameters to regulate the sorption activity of organic pollutants.

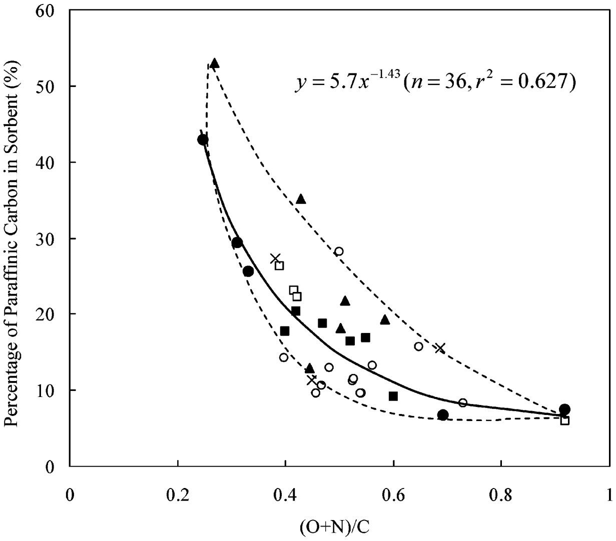


FIGURE 4. Relationship between polarity index ((O + N)/C) and percentage of paraffinic carbon in organic sorbents in this study (●) and in the literature [■ (*11*), ○ (*34*), × (*11*), ▲ (*13*), and □ (*24*)]. The percentage of paraffinic carbon was calculated as the product of paraffinic carbon content from NMR distribution and percentage of carbon contents from elemental analysis. The solid curve is a fit to our data plus all the literature values between percentage of paraffinic carbon (*y*) and (O + N)/C (*x*). The insert equation is the regression equation of the solid curve; the parameters of *n* and r^2 are the data point number and correlation coefficient, respectively. The dotted lines are the data range of paraffinic carbon percentage and (O + N)/C.

Sorption of Organic Pollutants with Cuticle Fractions. Sorption isotherms of nonpolar (naphthalene and phenanthrene) and polar (phenol and 1-naphthol) aromatic organic pollutants by the cuticular materials are presented in Figure 5. The sorption isotherms fit well to the Freundlich equation; the Freundlich model parameters are listed in Table 4. However, precise comparison cannot be made between K_f values because of their different units as a result of nonlinearity. Therefore, the sorption coefficients (K_{oc}) were calculated (see Materials and Methods) (Table 4). The whole sorption isotherms of naphthalene, phenanthrene, and phenol to PC1, PC2, PC3, and PC5 were practically linear, whereas isotherms of the tested organic compounds to the PC4 sample were nonlinear (Freundlich N_s values of 0.860, 0.836, and 0.966 for naphthalene, phenanthrene, and phenol, respectively). The nonlinearity of PC4 may be a result of relatively condensed domains in this sample (higher content of aromatic moieties and crystalline aliphatic carbons) as compared to the other fractions. In contrast to the other sorbates, isotherms of 1-naphthol to all five cuticular fractions were nonlinear (N_s = 0.727 to ∼0.929).

To explain the nonlinearity of SOM, dual-mode sorption (DMSM) or dual-reactive domain models (DRDM) were

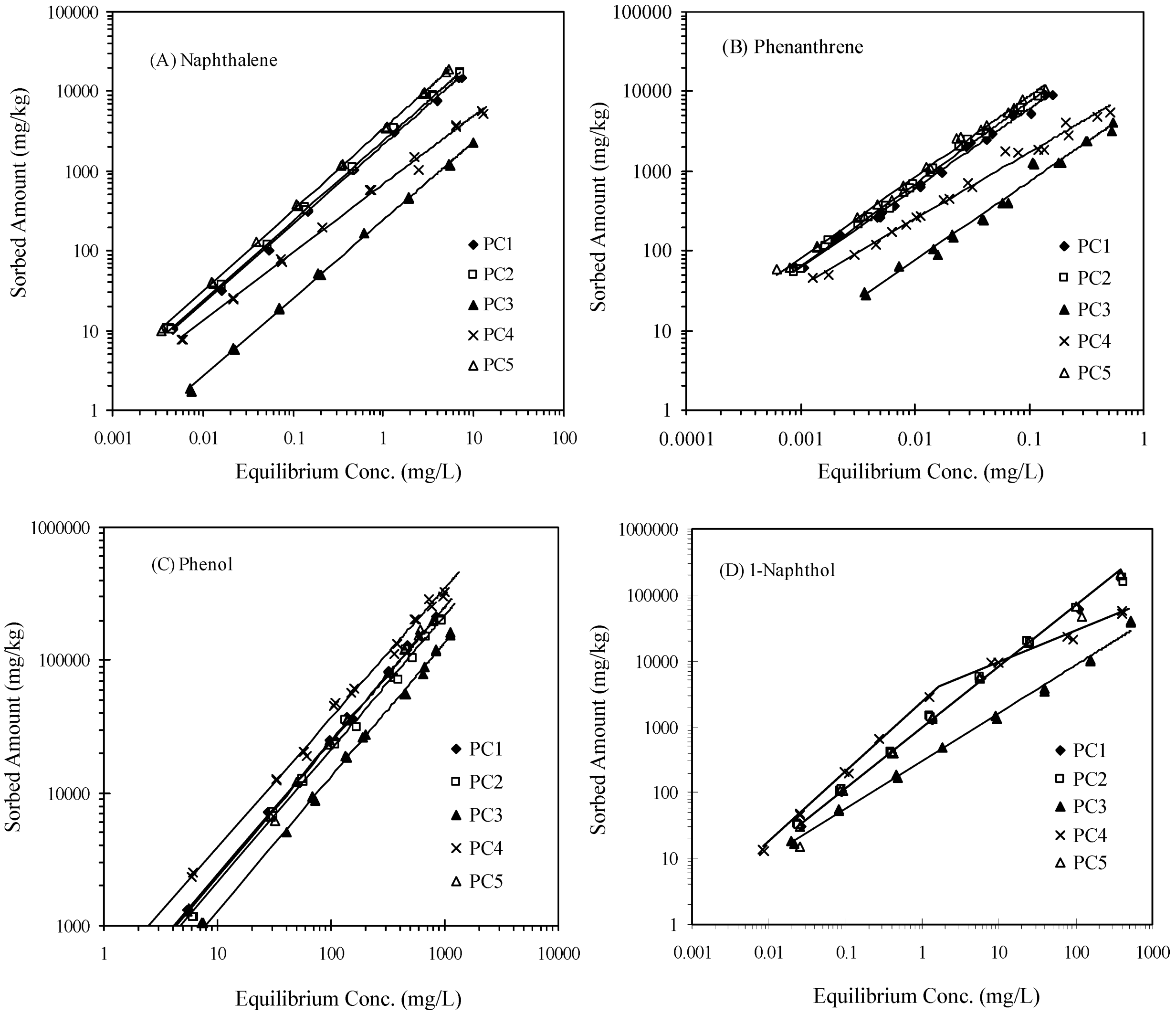


FIGURE 5. Sorption isotherms of organic pollutants by cuticular fractions.

suggested. According to these models, SOM was considered to be a heterogeneous substance, which consists of two types of amorphous domains. The domains are characterized as expanded and condensed, analogous to rubbery and glassy synthetic polymers, respectively. Sorption of HOCs to the expanded rubbery-like domain generates linear isotherms due to partitioning, while nonlinear isotherms are observed for the condensed glassy-like domain due to adsorption in Langmuir-type sorption sites. Recent sorption and spectroscopic studies have indicated that the condensed domain is mainly attributed to aromatic moieties, producing isotherm nonlinearity (*9*); thus, nonlinear isotherms of PC4 are consistent with the conclusion in the literature (*7*, *9*, *27*, *28*). Nonlinear isotherms of 1-naphthol might be due to specific sorption involved with the -OH group of this compound. An inflection point in the sorption isotherm of 1-naphthol to PC4 occurred at the solution concentration of ~1.7 mg/L, but the cause is unclear. Linear isotherms of phenol might be due to the narrow concentration range used in this study (*4*).

From Table 4, the K_{oc} values were quite dependent on sorbent structural characteristics and sorbate properties. For naphthalene and phenanthrene (nonpolar), the largest K_{oc} values (i.e., 5130 (naphthalene) and 122 800 mL/g (phenanthrene)) were obtained in the PC5 sample. These values were ~2 and ~3 times higher than their corresponding carbon-normalized octanol–water partition coefficients (K_{owc}) (Table 4). This observation together with the linear isotherm indicated that the PC5 sample was a powerful partition medium probably due to both the lowest polarity (0.25) and the highest paraffinic carbons (63%) consisting of C_{16} or C_{18} long-alkyl moieties (*22*) (Tables 2 and 3). For phenol and 1-naphthol (polar), the largest K_{oc} values (i.e., 697 (phenol) and 4660 mL/g (1-naphthol)) occurred in the PC4 sample: ~17 and ~7 times higher than their respective K_{owc} values (Table 4). The high ratios of K_{oc}/K_{owc} for the tested polar aromatic compounds in PC4, along with nonlinear sorption isotherms, suggest that a specific interaction (e.g., polar interaction, H-bonding, $\pi-\pi$ electron interaction) was a dominant sorption mechanism (*35*, *36*). Relatively lower sorption of the four tested organic pollutants by PC3 (Figure 5) may be attributed to the large content of pectin polysaccharides in the samples with high polarity (0.92) (Table 2 and Figure 3).

The controversy on whether aromatic or aliphatic groups are dominantly responsible for sorption of HOCs is ongoing (*10*, *11*). High sorption of HOCs by both aliphatic-rich (*10*, *11*, *13*, *24*) and aromatic-rich SOM (*5*, *7*, *27*) has been observed. Kang and Xing recently observed that aliphatic- and aromatic-rich SOM, each with a relatively high sorption capacity (K_{oc}), is often associated with low polar functional group content or low polarity (*10*). In our present study, the sorption capacities (K_{oc}) of sorbates were not correlated with aromatic components of sorbents (data not shown), which may be contributed to the low aromatic contents and/or less accessibility to the aromatic core masked by a large quantity

TABLE 4. Sorption Coefficients and Freundlich Model Parameters of Organic Pollutants with Cuticular Fractions

organic pollutants	sorbents[a]	K_d (mL/g)	linear r^2	K_{oc} (mL/g)	K_{oc}/K_{owc}[b]	K_f[c]	N_S	Freundlich r^2
naphthalene	PC1	2100	0.998	3270	1.24	2160	1.001 ± 0.007	0.999
	PC2	2430	1.000	3860	1.46	2400	1.009 ± 0.004	1.000
	PC3	228	0.999	537	0.20	243	0.982 ± 0.007	0.999
	PC4	463	0.966	949	0.36	683	0.860 ± 0.013	0.997
	PC5	3480	0.999	5130	1.94	3390	1.018 ± 0.004	1.000
phenanthrene	PC1	66100	0.995	103000	2.72	59800	0.998 ± 0.017	0.995
	PC2	72200	0.998	114600	3.02	79800	1.032 ± 0.018	0.997
	PC3	7090	0.969	16700	0.44	7190	0.990 ± 0.028	0.986
	PC4	12560	0.911	25700	0.68	11800	0.836 ± 0.020	0.990
	PC5	83230	0.991	122800	3.24	90600	1.016 ± 0.017	0.995
phenol	PC1	252	0.998	393	9.59	232	1.013 ± 0.003	0.999
	PC2	216	0.990	343	8.37	197	1.016 ± 0.006	0.996
	PC3	138	0.994	325	7.93	134	0.999 ± 0.004	0.998
	PC4	340	0.987	697	17.0	432	0.966 ± 0.005	0.997
	PC5	285	0.996	381	9.29	196	1.041 ± 0.009	0.992
1-naphthol	PC1	923	1.000	1440	2.12	926	0.898 ± 0.011	0.998
	PC2	1020	0.999	1620	2.39	1000	0.892 ± 0.012	0.998
	PC3	264	0.969	621	0.92	300	0.727 ± 0.013	0.996
	PC4	2280	0.986	4660	6.87	1040	0.761 ± 0.039	0.969
	PC5	984	0.998	1450	2.14	883	0.929 ± 0.020	0.994

[a] PC1: bulk cuticle; removal of waxy material from PC1 yielded dewaxed cuticle (PC2); saponification of PC2 produced nonsaponifiable fraction (PC3); the PC2 and PC3 samples were hydrolyzed to yield dewaxed−hydrolyzed residue (PC5) and nonsaponifiable−nonhydrolyzable residue (PC4), respectively. [b] K_{owc} is carbon-normalized K_{ow} ($K_{owc} = K_{ow}/f_{oc}$), and f_{oc} is the percentage of carbon content of octanol (73.8%). [c] K_f is the sorption capacity coefficient [(mg/kg)/(mg/L)^N].

of aliphatic components. However, poor correlations of the aliphatic-rich plant cuticular fraction K_{oc} values with their percent aliphaticity were also found (data not shown), which may result from high contents of polar aliphatic components in these samples, regulating sorption behavior. Thus, we believe that polarity (e.g., (O + N)/C) and accessibility play a critical role in the sorption of polar and nonpolar organic pollutants by regulating the compatibility of sorbate with sorbent.

Since SOM contains both polar and nonpolar functional groups, significant differences in sorption of various (polar and nonpolar) organic compounds in SOM may result from differences in their combined interactions with SOM via dispersion forces (London forces), polar interaction, and H-bonding (*35*). The relationships of the K_{oc} values with the polarity index (i.e., (O + N)/C) of the sorbents were plotted in Figure 6A. The K_{oc} values decreased with increasing polarity of sorbents, which is consistent with previous reports (*10*, *37*, *38*). However, our current study demonstrates that the effect of sorbent polarities on K_{oc} values was also dependent on organic pollutant properties (e.g., polarity and K_{ow}) and molecular structures (e.g., functional group). As illustrated in Figure 6A, the sorption capacities (K_{oc}) of naphthalene and phenanthrene were more sensitive to the polarity change of sorbents (i.e., large negative slope), whereas the K_{oc} of phenol was much less sensitive; the sensitivity of 1-naphthol K_{oc} to the sorbent polarities was intermediate (except for phenol and 1-naphthol in PC4). A simple plot of polarity (i.e., (O + N)/C (Table 2)) versus the area under the 61−96 ppm region of the NMR spectra (percentage of polysaccharide carbons, Table 3) yielded a linear fit with an r^2 of 0.943 (the linear plot not shown). Hence, a very similar plot to Figure 6A is yielded if (O + N)/C is replaced by the area under the 61−96 ppm region (polar components of sorbents), which further supports the effect of polarity on sorption properties of HOCs.

The varying sensitivities of K_{oc} of sorbates to sorbent polarities may be due to their different sorption mechanisms. Sorption of phenanthrene and naphthalene was dominated by partition (dissolution) processes (see the practically linear isotherms, Table 4), so their compatibilities with cuticle fractions would be reduced significantly with an increase in sorbent polarities. This is apparent in the ratios of K_{oc}/K_{owc}, which decreased from 3.2 to 0.4 for phenanthrene (i.e., ~8 times),and from 1.9 to 0.2 for naphthalene (i.e., ~9.5 times) (Table 4). The high K_{oc}/K_{owc} ratios of phenol (i.e., 9.6−8) and the small decrease in this ratio with an increase in polarity (i.e., ~1.2 times) (except for phenol in PC4) were attributed to polar interaction and H-bonding (specific interaction) in addition to partitioning. In comparison with naphthalene, the high K_{oc}/K_{owc} ratios of 1-naphthol (~2.4−0.9) and the small decrease in this ratio with an increase in polarity (~2.6 times) (except for 1-naphthol in PC4) suggest that sorption of 1-naphthol was also controlled by specific interaction (e.g., polar interaction and H-bonding).

The K_{oc} values of phenol and 1-naphthol for PC4 were much higher than their respective predicted values from the relationship between log K_{oc} and (O + N)/C (Figure 6A). The K_{oc} value of phenol with PC4 nearly approached the predicted K_{oc} values for 1-naphthol and naphthalene, while the K_{oc} of 1-naphthol with PC4 was comparable to the highest K_{oc} value of naphthalene by PC5. The extremely high K_{oc}/K_{owc} ratios of phenol (~17) and 1-naphthol (~7) by the PC4 sample (Table 4) might be attributed to, in addition to polar interaction and H-bonding, strong $\pi-\pi$ electron interaction, corresponding to π-donor (e.g., 1-naphthol) and π-acceptor structures (e.g., aromatic rings with electron-withdrawing groups such as −O−R). The polarity and structure of phenol and 1-naphthol (polar aromatic compounds) may fit much better with the newly exposed polar aromatic cores in PC4 than that of phenanthrene and naphthalene (*35*, *36*), thus increasing the compatibility between polar aromatic compounds and polar aromatic cores of PC4. The effective $\pi-\pi$ electron interaction would be limited in the PC1, PC2, PC3, and PC5 samples because the aromatic cores were inaccessible due to the surrounding nonpolar paraffinic carbons and polar polysaccharide components.

A comparison between sorbate K_{oc} values and sorbent paraffinic carbon contents (Figure 6B) reveals a generally positive trend between these two variables. Recently, phenanthrene sorption by SOM has been correlated to polymethylene-rich domains in the sorbents (*11*, *12*). In the current study, the K_{oc} values increased sharply with paraffinic carbon at contents less than 40%, then increased slowly or nearly leveled off. The magnitude of increasing K_{oc} values for the four tested organic pollutants decreased in the following

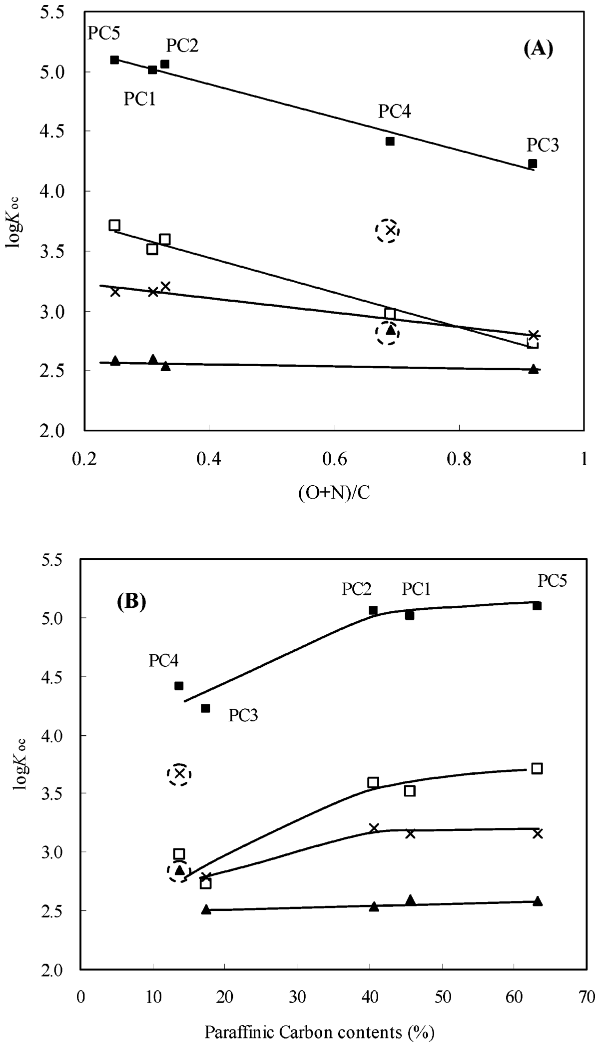


FIGURE 6. Relationships between log K_{oc} for organic pollutants and polarity of cuticular fractions (A) and between log K_{oc} and paraffinic carbon contents (i.e., 0−50 ppm) (B). Phenanthrene (■), naphthalene (□), 1-naphthol (×), and phenol (▲). The points in the dashed circle were not used in the correlation analysis due to the strong interactions between sorbent and sorbates, causing abnormally high K_{oc}.

order: phenanthrene ≈ naphthalene > 1-naphthol > phenol, except for the PC4 sample, which was consistent with the order of organic pollutant's polarity.

The negative relationship between paraffinic carbon contents and (O + N)/C (Figure 4) suggest that high paraffinic carbon contents would often be associated with low polarity in a sorbent. The two variables, polarity and paraffinic carbon contents, were intercorrelated parameters influencing the K_{oc} values. As mentioned earlier in this study, PC2 contained both paraffinic carbons and polar components, and PC3 is the fraction after removal of paraffinic carbons from PC2. The polysaccharide was further removed from PC2 and PC3 samples to produce the PC5 and PC4 samples, respectively. The K_{oc} ratios of different isolated cuticular fractions were calculated, as shown in Table 5, to analyze the interactive effect of paraffinic carbon and polarity on sorption. The K_{oc} ratios of both PC4/PC3 and PC5/PC2 were greater than 1 (except for PC5/PC2 of 1-naphthol), and the ratio of PC4/PC3 was larger than PC5/PC2, indicating that the sorption capability increased after removing polysaccharide polar components. The increased magnitude was larger for a relatively low-paraffinic-carbon sorbent (PC4/PC3) than high-paraffinic-carbon sorbent (PC5/PC2). For naphthalene and phenanthrene, the observed K_{oc} ratio of PC2/PC3 (i.e., ~7) greater than that of PC5/PC4 (i.e., ~5) suggests that the sorption capability decreased sharply after removing paraffinic components and that the decreased magnitude was larger for relatively high polysaccharide sorbents (PC2/PC3) than low polysaccharide sorbent (PC5/ PC4). The K_{oc} ratios of PC5/PC4 for phenol and 1-naphthol were 0.55 and 0.31, respectively, indicating that the sorption capability of polar organic pollutants increased after removing polysaccharide and paraffinic carbon components from PC1 because newly exposed condensed aromatic cores substituted by −COOH (1728 cm^{-1}) and −OH (NMR data) groups were more accessible and/or compatible to phenol and 1-naphthol than to naphthalene and phenanthrene.

TABLE 5. K_{oc} Ratio between Different Cuticular Fraction Sorbents

K_{oc} ratios[a]	naphthalene	phenanthrene	phenol	1-naphthol
PC5/PC2	1.33	1.07	1.11	0.90
PC4/PC3	1.77	1.54	2.14	7.50
PC2/PC3	7.18	6.86	1.05	2.60
PC5/PC4	5.41	4.78	0.55	0.31

[a] PC1: bulk cuticle; removal of waxy material from PC1 yielded dewaxed cuticle (PC2); saponification of PC2 produced nonsaponifiable fraction (PC3); the PC2 and PC3 samples were hydrolyzed to yield dewaxed−hydrolyzed residue (PC5) and nonsaponifiable−nonhydrolyzable residue (PC4), respectively.

In summary, this study demonstrates the markedly high sorption capacity of various plant cuticular fractions, including the dewaxed−hydrolyzed residue, for nonpolar and polar organic pollutants. However, for the aliphatic-rich sorbents, there are little or no correlations of K_{oc} with either aromatic or aliphatic components. The data reported in this study highlight the significance of polarity and accessibility of organic matter in the uptake of nonpolar and polar organic pollutants by regulating the compatibility of sorbate to sorbent. The K_{oc} values decreased with increasing sorbent polarities, and the decreasing rates were dependent on organic pollutants' properties and their corresponding sorption mechanisms (partition or specific interaction). The negative relationship between polarity and paraffinic carbon contents of organic matter again signifies the role of polarity in sorption of HOCs. The highest sorption of nonpolar organic pollutants occurred with the highest paraffinic carbon contents and the lowest polarity (PC5), while that of polar organic pollutants appeared with the sorbent containing accessible, polar aromatic cores (PC4) due to more compatibility as a result of similar structures between polar aromatic pollutants and polar aromatic cores. Therefore, compatibility between HOCs and SOM needs to be considered in HOCs predictive and risk assessment models.

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