

Novel Phenanthrene Sorption Mechanism by Two Pollens and Their Fractions

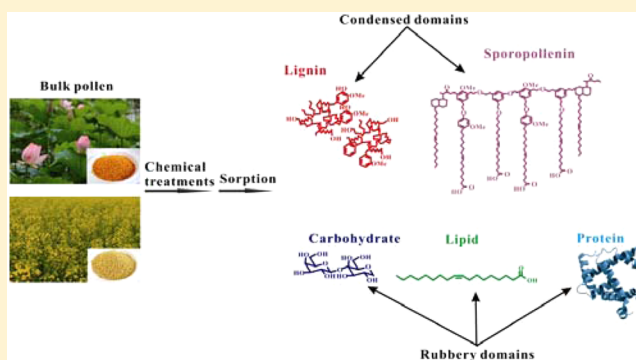
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S Supporting Information

ABSTRACT: A pair of pollens (*Nelumbo nucifera* and *Brassica campestris* L.) and their fractions were characterized by elemental analysis and advanced solid-state ¹³C NMR techniques and used as biosorbents for phenanthrene (Phen). Their constituents were largely aliphatic components (including sporopollenin), carbohydrates, protein, and lignin as estimated by ¹³C NMR spectra of the investigated samples and the four listed biochemical classes. The structure of each nonhydrolyzable carbon (NHC) fraction is similar to that of sporopollenin. The sorption capacities are highly negatively related to polar groups largely derived from carbohydrates and protein but highly positively related to alkyl carbon, poly(methylene) carbon, and aromatic carbon largely derived from sporopollenin and lignin. The sorption capacities of the NHC fractions are much higher than previously reported values, suggesting that they are good sorbents for Phen. The Freundlich *n* values significantly decrease with increasing concentrations of poly(methylene) carbon, alkyl C, aromatic moieties, aliphatic components, and the lignin of the pollen sorbents, suggesting that aliphatic and aromatic structures and constituents jointly contribute to the increasing nonlinearity. To our knowledge, this is the first investigation of the combined roles of alkyl and aromatic moiety domains, composition, and accessibility on the sorption of Phen by pollen samples.



INTRODUCTION

Pollens are the physiological containers that produce the male gametes of seed plants and travel through the air from flower to flower for pollination purposes. Just like soot, pollen may act as cloud condensation nuclear (CCN) in the atmosphere, influencing the climate.^{1,2} The soot contents in the atmosphere range from several hundreds of ng/m³ in unpolluted areas to several μg/m³ in urban regions.¹ In anemophilous pollen regions of the southeastern United States, maximum pollen counts reach up to 15 000 grains per m³ in the winter, followed by 5000–10 000 grains per m³ in early spring.² Because pollens can be produced in large quantities and transported for long distances (up to 100–1000 km),^{3–7} they are important to the global transport of air pollutants. Pollens have also been widely used for the biomonitoring of heavy metal⁸ and organic pollutants including polycyclic aromatic hydrocarbons (PAHs).⁹ Because pollen lipid contents vary depending on their species, the concentrations of PAHs change with lipid contents in lipid-rich pollens.^{9,10} The outer layer (exine) of the grain is made of an extremely stable and complex biopolymer known as sporopollenin, which is highly resistant to chemical attack and can survive in geological strata over millions of years with full retention of its morphology.¹¹ Because it is one of the most abundant biopolymers, sporopollenin has been proposed

as a potential biomaterial for the removal of various toxic pollutants from aqueous solutions. Most of the available sorption studies on pollen and sporopollenin address heavy metals in contaminated wastewaters.^{12–14} However, only one study on the sorption of hydrophobic organic contaminants (HOCs) by pollen has been reported.¹⁵

Previous investigations have reported that compositional and structural components of natural organic matter (NOM) affect the sorption of HOCs.^{16–21} Whether the aliphatic or aromatic groups of NOM are correlated with HOC sorption is still a matter of debate.²² In previous studies, high-sorption-affinity domains in aromatic-rich²³ or aliphatic-rich^{17,24,25} organic matter have been observed. Wang et al. showed that the polarity, structure, and domain spatial arrangements of biopolymers collectively influenced the magnitude of HOC sorption.¹⁹ However, Chen et al. suggested that the polarity and accessibility of biopolymers, rather than their structure (aliphatic or aromatic moieties), played a regulating role in the sorption of HOCs.¹⁶ Therefore, the exact roles of the

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composition, structure, and physical conformation of NOM including pollen in determining the sorption process requires further investigation.

Sporopollenin, carbohydrates, proteins, and lignin have been identified as key components of pollen biomass compositions.^{2,26} Plant residues (such as pollens) are transformed via chemical, biological, and physical processes into more stable forms during humification processes.²⁷ During humification, the number of aromatic and paraffinic carbons increases, whereas the level of alkyl C–O carbons decreases. It is well-established that refractory biomacromolecules (such as lignin and sporopollenin biopolymers) are a recalcitrant and important constituent of NOM.²⁸ Prior studies have elucidated the structure and chemical composition of sporopollenin.^{29–32}

In this study, lotus pollen and rape pollen were chosen as representatives to demonstrate the sorption mechanism of pollen for HOCs in aqueous media, given the wide occurrence of two pollens. Lotus pollen and rape pollen are commercially produced and widely consumed for their nutritional and medicinal values in China. It is likely that other types of pollen may have similar sorption mechanisms and could be used to meet future demand for environmental remediation. However, to our knowledge, the role of domain spatial arrangements in pollen biopolymers in relation to HOC sorption has not been examined. The “domain spatial arrangement” is defined here as the spatial positions and relative abundances of hydrophilic versus hydrophobic moieties in biopolymers. Moreover, chemical treatments have been used to selectively remove carbohydrates and proteins from biomass,³³ allowing for the investigation of the domain-arrangement role toward HOC sorption.

In this study, two pollens were selected and also sequentially fractionated into free-lipid (LP), lipid-free residue (LF), residue obtained after successive TFA hydrolyses (TFAR), residue obtained after saponification (SR), and nonhydrolyzable carbon (NHC) fractions. Phenanthrene (Phen) was chosen as a model HOC. The objectives of this study are the following: (i) to quantify and compare the sorption affinities for Phen of bulk pollen samples (OS) and their isolated organic-matter fractions; (ii) to examine correlations between Phen sorption affinity and structural composition (i.e., poly(methylene) carbon and aromatic moieties) as determined by advanced solid-state NMR; and (iii) to assess the role of composition and domain arrangements on the sorption of Phen.

MATERIALS AND METHODS

Pollen Samples and Isolation of Organic Fractions. A pair of commercial pollen samples, lotus pollen (*Nelumbo nucifera*) and rape pollen (*Brassica campestris* L.), were purchased from a supermarket in Guangzhou. The two pollens were sequentially fractionated into the mentioned five fractions. The flowchart of this process is presented in Figure S1, which summarizes the major steps for isolation of the organic fractions, as described elsewhere.³³ All of the inorganic chemicals are reagent grade or better, and all of the organic solvents are HPLC grade. In brief, the lyophilized bulk samples (OS) were extracted to separate lipids via Soxhlet extraction with CH₂Cl₂/CH₃OH (2:1, v/v) (CNW Technologies, Shanghai, China) for 24 h. The LP fractions were dried at 60 °C. Subsamples of the LF fractions were hydrolyzed twice with 2 N trifluoroacetic acid (TFA, CNW Technologies GmbH, Germany) at 100 °C for 3 h. Subsequently, samples were hydrolyzed in 4 and 6 N TFA at 100 °C for 18 h. The TFAR

fractions were saponified by refluxing for 1 h in 5% KOH in 2-methoxy ethanol/H₂O (88:12, v/v) (Fuyu Chemical Reagent, Tianjin, China). The SR fractions were treated by 6 N HCl at 110 °C for 24 h. The remaining residues made up the final NHC fractions.

Characterization of Pollens and Their Fractions.

Elemental (C, H, N) analyses were conducted using an Elementar Vario EL CUBE elemental analyzer (Elementar, Germany), and oxygen content was analyzed with a Vario ELIII elemental analyzer (Elementar, Germany). Solid-state NMR experiments were performed on a Bruker AVANCE III 400 spectrometer (Bruker, Germany) operating at 400 MHz ¹H and 100 MHz ¹³C frequencies. The ¹³C chemical shifts were referenced to tetramethylsilane, using the COO resonance of glycine α -modification at 176.46 ppm as a secondary reference. The cross-polarization (CP) experiments included ¹³C cross-polarization–total sideband suppression (CP–TOSS), CP–TOSS plus dipolar dephasing (CP–TOSS–DD), and a ¹³C chemical-shift-anisotropy (CSA) filter. The spectra were measured at a spinning speed of 5 kHz. The number of scans for CP–TOSS and CP–TOSS–DD experiments for each of the samples was 4096. The number of scans for ¹³C CSA filter experiments for each of the samples was also 4096. The assignments are as follows: 0–45 ppm, alkyl C; 45–60 ppm, O–CH₃ and NCH; 60–95 ppm, alkyl C–O; 95–110 ppm, O–C–O anomeric C; 110–145 ppm, aromatic C; 145–165 ppm, aromatic C–O; 165–190 ppm, COO and N–C=O; and 190–210 ppm, ketone and aldehyde.

Batch Sorption Experiments. Phen was obtained from Aldrich Chemical Co. (purity >98%). The physicochemical properties of Phen are as follows: molecular weight (MW) of 178.2 g/mol; water solubility (S_w) of 1.12 mg/L; octanol–water partition coefficient ($\log K_{ow}$) of 4.57; and supercooled liquid-state solubility (S_{sc}) of 5.18 mg/L. Batch Phen sorption by pollens and their isolated fractions was performed as described elsewhere^{20,34} and was described in the Supporting Information. Our preliminary test indicated that because the TFAR, SR, and NHC fractions were nonhydrolyzable organic matter by using a series of the acid and alkali treatments, no apparent organic matter was detectable in the supernatants. For the OS and LF sorbents, as concentrations of the sorbent organic matter reached 70.7–326 mg/L, 6.54–8.13% of the sorbent organic matters were dissolved in the supernatants. Previous study showed that the presence of inherent DOM in sediments impeded the sorption.³⁵ If it is assumed that the sorption isotherms of the DOC fractions would be similar to those of the sorbent organic matters, it is estimated that the sorption contents of Phen by the DOC fractions would account for 7.03–8.85% of the sorption contents by the sorbents. The intrinsic K_{OC} values would be 1.20, 1.16, 1.34, and 1.16 times those of the apparent K_{OC} values for the OS and LF fractions of lotus and rape pollens, respectively, if the sorption of Phen by the DOC fractions is taken into account. Moreover, Phen concentrations were measured by using a high-performance liquid chromatograph (HPLC) (LC-20A, Shimadzu, Japan) fitted with a fluorescence detector and Inertsil ODS-SP reverse-phase column (150 cm \times 4.6 mm \times 5 μ m). The injection volume was 10 μ L. A mixture of 90% acetonitrile and 10% water (acetonitrile: Merck KGaA, Germany) was used as the mobile phase at a flow rate of 1.0 mL/min, and excitation and emission wavelengths for the detector were 250 and 364 nm, respectively.

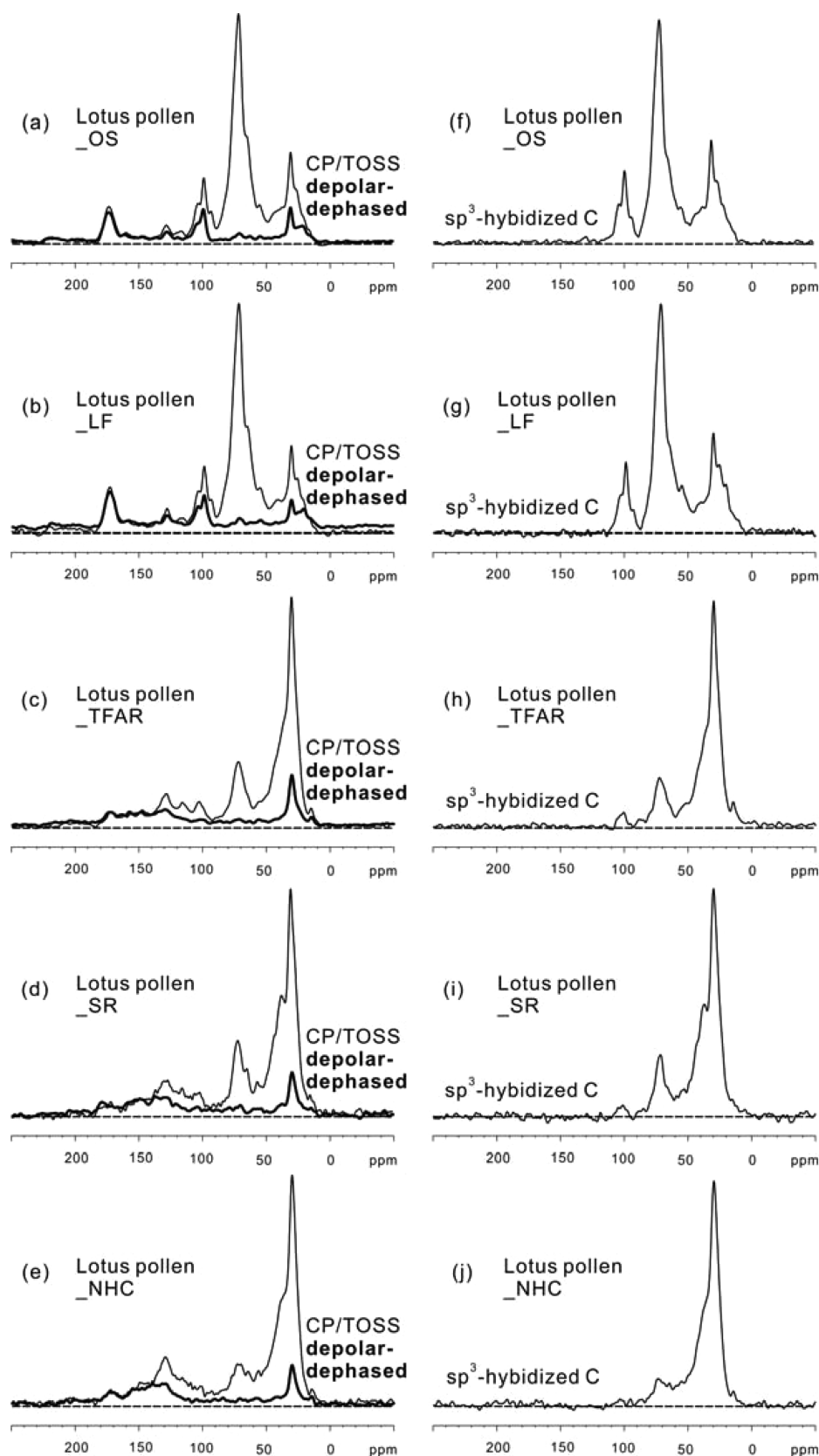


Figure 1. Advanced ^{13}C NMR spectra for the identification of functional groups in the lotus-pollen sample and their fractions: (a–e) thin lines indicate unselective CP–TOSS spectra; and thick lines indicate corresponding dipolar-dephased CP–TOSS spectra; (f–j) selection of sp^3 -hybridized C signals by a ^{13}C CSA filter.

Isotherm Modeling. The modified Freundlich model has been widely employed to describe sorption of HOCs and used

to fit our data. The modified Freundlich model is described in the reference³⁶ and in the [Supporting Information](#).

Table 1. Functional Group Percentages of Lotus Pollen, Rape Pollen, and Their Fractions from the ^{13}C CP–TOSS NMR Spectra

samples	alkyl (%)	OCH ₃ and NCH (%)	O-alkyl (%)	O-alkyl-O (%)	aromatic C–C (%)	aromatic C–H (%)	aromatic C–O (%)	COO and NC=O (%)	ketone and aldehyde (%)	(CH ₂) _n	F _{aro}	polar C
	0–45 ppm	45–60 ppm	60–95 ppm	95–110 ppm	110–145 ppm		145–165 ppm	165–190 ppm	190–210 ppm	27.5–33.5 ppm	(%) ^a	(%) ^b
	OS											
lotus	17.6	7.27	53.9	9.54	2.27	2.46	1.61	5.36	0.00	7.28	6.34	68.1
rape	18.3	9.50	47.7	8.51	3.49	3.53	2.23	6.81	0.00	6.71	9.25	66.2
	LF											
lotus	13.6	6.89	52.4	10.1	2.89	4.13	2.34	7.17	0.59	6.21	9.34	68.8
rape	18.1	10.4	44.7	8.00	3.81	3.68	2.80	8.32	0.30	6.24	10.3	66.1
	TFAR											
lotus	51.3	8.03	17.3	4.45	7.11	5.24	3.87	2.17	0.48	21.5	16.2	31.4
rape	44.5	9.59	13.9	5.53	10.2	7.53	5.76	2.6	0.3	16.0	23.5	31.9
	SR											
lotus	44.9	9.68	19.1	4.21	7.17	7.18	4.29	2.97	0.51	18.2	18.6	36.0
rape	46.4	9.94	14.1	5.05	11.5	5.75	4.60	2.53	0.18	16.1	21.8	31.1
	NHC											
lotus	53.2	8.82	12.6	3.24	11.1	5.36	4.02	1.56	0.22	21.0	20.4	27.0
rape	44.1	10.4	11.6	4.53	11.0	8.91	5.89	2.88	0.79	16.2	25.8	30.7

^aNote: F_{aro} = aromatic C–C (110–145 ppm) + aromatic C–H (110–145 ppm) + aromatic C–O (145–165 ppm). ^bPolar C = polar aliphatic (45–95 ppm) + polar aromatic and C=O (145–210 ppm) (%).

RESULTS AND DISCUSSION

Composition and Elemental Ratios of Bulk Pollen and Isolated Fractions. The yields and elemental compositions of the bulk pollens and their fractions are presented in Table S1 and Table S2. Each of the yields was estimated at a percentage accounting for the bulk pollen. The chemical compositions and elemental characteristics of the bulk pollen and their fractions vary for the two species. As listed in Table S1, the percentage of LP content accounting for total organic carbon (TOC) in the bulk lotus pollen is 11.8%, lower than that in the bulk rape pollen (23.2%). The LF, TFAR, SR, and NHC fractions of lotus pollen account for 84.4%, 20.0%, 15.4%, and 13.6% of TOC, respectively, higher than those of rape pollen do. It is noted that these NHC contents are higher than those observed in algae (4.07–5.93% of TOC).²¹ The TFAR contents decrease dramatically relative to those of LF, and the contents of SR and NHC vary slightly in comparison with those of TFAR.

The different chemical composition of the two pollens is reflected in the different elemental characteristics of the bulk pollens and their fractions (Table S2). The C and O contents are, respectively, 43.2% and 43.2% in bulk lotus pollen, which are lower than the values of 47.3% and 37.3% in bulk rape pollen. In addition, the successive TFA hydrolyses led to significant changes in C and O content. Moreover, the H-to-C and O-to-C atomic ratios were calculated to evaluate the aliphatic nature and polarity of the isolated pollen fractions. H-to-C and O-to-C atomic ratios of TFAR greatly decreased after the successive TFA treatments. The saponification increased the H-to-C and O-to-C atomic ratios for SR, and the H-to-C and O-to-C ratios of NHC greatly decreased after 6 N HCl treatment. The H-to-C ratio is lowest for the NHC fractions, excluding the LP fractions. The O-to-C and (O+N)-to-C ratios reveal that successive TFA and 6 N HCl treatments decreased the levels of O-containing groups. The O-to-C ratios in the NHC fractions are 0.16–0.21, which are much lower than 0.59–0.75 in their bulk samples. The H-to-C and O-to-C atomic ratios of NHC (e.g., sporopollenin) are lower in this

study than those reported previously.³⁷ It seems that there are significant correlations among H-to-C and O-to-C atomic ratios and the sorption affinity of Phen by the pollens and their fractions, as observed previously for other biosorbents.²⁰

Structure of Bulk Pollen and Isolated Fractions. The ^{13}C solid NMR spectra of the investigated bulk pollens and their fraction samples (thin lines, Figure 1 and Figure S2) represent ^{13}C CP–TOSS NMR spectra of all C. The corresponding integration results are summarized in Table 1. A pair of spectral editing techniques, dipolar dephasing and ^{13}C chemical shift anisotropy filter, were employed to study the structures of the bulk pollens and their fractions in more detail. The corresponding ^{13}C CP–TOSS spectra after dipolar dephasing (thick lines, Figure 1 and Figure S2) exhibit solely signals of nonprotonated carbon and mobile groups, including rotating CH₃ groups, which have reduced C–H dipolar coupling due to their fast motion. After dipolar dephasing, all the spectra (thick lines) contain the signals derived from C–CH₃ at 0–24 ppm and from mobile (CH₂)_n at approximately 30 ppm. The dipolar dephasing spectra for the NHC fractions demonstrate that the aromatic region (110–165 ppm) almost matches that in the corresponding unselective CP–TOSS spectra, suggesting that most of the aromatic moieties in NHC are nonprotonated. Aromatic C–C, aromatic C–H, and aromatic C–O (aromatic moieties, F_{aro}) are obtained using a combination of the CP–TOSS technique with CP–TOSS–DD³⁸ and listed in Table 1.

The ^{13}C CSA-filtered spectra exhibit signals attributed primarily to saturated carbon moieties. In particular, this technique separates overlapping anomeric C from aromatic C between 90 and 120 ppm. The anomeric carbon seen in the ^{13}C CSA-filtered spectra for the SR fractions is the same as that seen in the corresponding unselective CP–TOSS spectra. A clear O–C–O band, characteristic of sugar rings, is displayed in the ^{13}C CSA-filtered spectrum of SR (Figure 1i and Figure S2i), but no anomeric carbon is observed in any spectrum of the NHC fractions.

The bulk lotus and rape pollen samples contain the largest amounts of alkyl C–O (53.9% and 47.7%, respectively). Integration values of the alkyl C–O region for TFAR, SR, and NHC fractions (10.7–18.2%) decrease compared to those for LF fractions (41.9–49.3%). The removal of alkyl C–O from LF fractions using TFA hydrolysis results in a redistribution of the total ^{13}C NMR signal among the other regions of the NMR spectrum. The relative proportions of alkyl carbon (0–45 ppm) and aromatic groups (110–165 ppm) increase after successive TFA and 6 N HCl treatments. After these treatments, aromatic C–C increases to a greater extent than does aromatic C–H or aromatic C–O. The TFAR, SR, and NHC fractions display the highest relative amount of alkyl carbon (44.4–53.3%), which includes polymethylene-based functionalities. The alkyl carbon content of lotus pollen fractions is in the order SR < TFAR < NHC, and that of rape pollen fractions is in the order NHC < TFAR < SR. The lower relative integration values for the alkyl carbon of NHC in the rape pollen may have resulted from the hydrolysis of amino acids with alkyl side-chains. The residual alkyl C–O signal of NHC is attributed to the methoxy group resonance of lignin (56 ppm). The polar C content is in the order NHC < TFAR < SR, in agreement with their polarity index [O/C or (N+O)/C]. The saponification caused a clear increase in the number of polar aliphatic moieties. After successive TFA hydrolysis and 6 N HCl treatments, the NHC fractions are enriched in alkyl C and aromatic C (especially aromatic C–C) due to the removal of carbohydrates.

The CP–TOSS spectra of the NHC fractions reveal the aliphatic nature as a signal with a chemical shift maximized at 30 ppm (CH_2 in poly(methylene) C) is present. The poly(methylene) $((\text{CH}_2)_n\text{C})$ content is estimated by integrating the chemical shift region from 27.5–31.8 ppm.^{24,39} The NHC fractions have the highest poly(methylene) carbon percent among all OS samples and their fractions, up to 16.2–21.0%. The NHC fractions mainly consist of alkyl carbon (44.1–53.2%), aromatic moieties (110–165 ppm) (20.4–25.8%), alkyl C–O (11.6–12.6%) and O– CH_3 and NCH (8.82–10.4%). The low contents of carbon in the forms of anomeric C, ketones, quinones, and aldehydes in NHC fractions are also observed. The structure of the NHC fractions in pollen samples is similar to that reported for sporopollenin, which principally contains aliphatic, aromatic, ether, and carbonyl and carboxylic groups in varying degrees.^{29,30,32,40} NMR spectroscopy therefore indicates that the investigated NHC fractions are the same as sporopollenin. All of these observed structures will significantly affect their affinities to HOC, which will be discussed later.

Furthermore, previous study has indicated that composition and accessibility is crucial to the sorption of HOCs by NOM.⁴¹ A high lignin or low carbohydrate content is likely to result in an increase of sorption affinity to HOCs.⁴¹ The major structural groups identified for pollen originate from the four biomacromolecule classes, namely lignin, protein, carbohydrates, and aliphatic components.^{2,26} Based on the ^{13}C NMR spectra of these classes reported by Nelson and Baldock,⁴² we estimated the contribution of these four biomacromolecule classes to the original pollen samples and their fractions (Table 2). Carbohydrate and aliphatic components accounted for 63.3–68.0% and 12.5–15.4% of the total organic carbon in the bulk pollen samples, respectively, followed by protein ranging from 9.34% to 14.9% of the OC content. The calculated lignin contents are in the ranges of 5.83–8.67% of the OC, which are close to the values of cinnamyl phenols (6.41–8.90 mg per 100

Table 2. Relative Contributions of Four Model Components to Pollens and Their Fractions

samples	protein (%)	aliphatic component (%)	lignin (%)	carbohydrate (%)
		OS		
lotus pollen	9.34	15.4	5.83	68.0
rape pollen	14.9	12.5	8.67	63.3
		LF		
lotus pollen	6.89	11.7	8.16	66.7
rape pollen	17.3	10.8	9.25	61.0
		TFAR		
lotus pollen	6.32	59.0	15.2	19.5
rape pollen	6.95	55.5	22.7	14.9
		SR		
lotus pollen	10.5	48.9	18.5	22.2
rape pollen	8.57	54.3	21.7	15.4
		NHC		
lotus pollen	7.96	58.2	20.5	13.4
rape pollen	10.4	52.1	25.9	11.5

mg of OC) reported for *P. glauca* and *P. mariana*.²⁶ After organic-solvent extraction, the aliphatic components range from 10.8% to 11.7%, which are lower than in their OS samples. The data in Table 2 show that NHC fractions are composed of aliphatic components (52.1–58.2%), lignin (20.5–25.9%), carbohydrate (11.5–13.4%), and protein (7.96–10.4%), the same as reported for sporopollenin. Previous studies have also indicated that sporopollenin is not a uniform macromolecule but rather a series of closely related biopolymers with different chemical groups occurring in varying amounts.^{29,40}

Sorption Isotherms. All of the Freundlich sorption isotherms for Phen are well fitted by the Freundlich eq (Table 3 and Figure S3). The sorption isotherms are linear for the bulk samples (OS), slightly nonlinear for the LF fractions, and highly nonlinear for the TFAR, SR, and NHC fractions. The Freundlich n values generally increase in the order of NHC < TFAR < SR < LF < OS. The n values for the NHC, TFAR, SR, LF, and OS fractions in the lotus pollen are 0.737, 0.750, 0.814, 0.932, and 0.990, respectively. The n values for the NHC, TFAR, and SR fractions in the rape pollen are 0.644, 0.727, and 0.766, respectively, lower than those for the corresponding fractions in the lotus pollen. The nonlinearity factor n for Phen by the NHC fractions in this study is close to that of NHC fractions from sediments ($n = 0.652$ – 0.751).¹⁷ The NHC fractions exhibit the highest nonlinearity due to their glassier or more-condensed NOM domains in comparison with other fractions. The nonlinearity factor n is related to sorption-site energy distribution and has been related to glassy or condensed NOM domains (such as aromatic structure).^{41,43} The nonlinearity factors (n) will be related to the structure and compositions of the pollen sorbents in the later sections.

The modified Freundlich coefficients ($\log K'_{\text{FOC}}$) for Phen increase in the following order: LF < OS < SR < TFAR < NHC. High $\log K'_{\text{FOC}}$ values indicate high sorption capacity for Phen of the pollen organic fractions. After the removal of protein and carbohydrates, the sorption affinity becomes highest for the NHC fraction. The K_{OC} value measured for Phen decreases as a function of C_e because of isotherm nonlinearity. Regardless of C_e levels, the OS and LF fractions exhibit much lower sorption affinity than their TFAR, SR, and NHC fractions (Table 3). Moreover, the sorption capacity parameters ($\log K'_{\text{FOC}}$ and K_{OC}) for the bulk lotus pollen, and

Table 3. Freundlich Isotherm Parameters and Concentration-Dependent Distribution Coefficients (K_{OC}) for the Lotus and Rape Pollens and Their Fractions

samples	K_F^a	n	N^b	R^2	OC (%)	K_{FOC}^c	$\log K_{FOC}$	$K'_F{}^d$	$K'_{FOC}{}^e$	$\log K'_{FOC}$	K_{OC} , mL/g		
											$C_e = 5.6$ $\mu\text{g/mL}$	$C_e = 56$ $\mu\text{g/mL}$	$C_e = 560$ $\mu\text{g/mL}$
OS													
lotus	9.30 ± 0.09	0.990 ± 0.001	19	0.996	43.2	21.5	1.33	47.4	110	2.04	21 000	21 000	20 000
rape	14.3 ± 0.09	0.999 ± 0.001	19	0.995	47.3	30.2	1.48	73.8	156	2.19	30 000	30 000	30 000
LF													
lotus	6.31 ± 0.11	0.932 ± 0.004	20	0.993	43.0	14.7	1.17	29.2	67.9	1.83	13 000	11 000	9 500
rape	6.77 ± 0.08	0.988 ± 0.001	19	0.994	45.7	14.8	1.17	34.4	75.2	1.88	15 000	14 000	14 000
TFAR													
lotus	360 ± 1.4	0.750 ± 0.002	20	0.997	70.8	508	2.71	1235	1745	3.24	330 000	190 000	100 000
rape	507.6 ± 3.3	0.727 ± 0.005	20	0.996	69.5	730	2.86	1678	2415	3.38	460 000	240 000	130 000
SR													
lotus	148 ± 0.7	0.814 ± 0.005	20	0.994	64.3	231	2.36	565.3	879.5	2.94	170 000	110 000	71 000
rape	398 ± 1.2	0.766 ± 0.005	20	0.994	62.95	633	2.80	1404	2230	3.35	420 000	250 000	140 000
NHC													
lotus	569 ± 4.4	0.737 ± 0.007	19	0.990	75.0	758	2.88	1911	2547	3.41	480 000	260 000	140 000
rape	887 ± 9.3	0.644 ± 0.006	20	0.991	72.1	1230	3.09	2557	3549	3.55	670 000	290 000	130 000

^a K_F is the sorption capacity coefficient with unit of $(\mu\text{g/g})/(\mu\text{g/L})^n$. ^bNumber of data. ^c K_{FOC} is the OC-normalized sorption capacity coefficient with units of $(\mu\text{g/g})/(\mu\text{g/L})^n$. ^d K'_F is the modified Freundlich sorption capacity coefficient with unit of $(\mu\text{g/g})$. ^e K'_{FOC} is the OC-normalized modified Freundlich sorption capacity coefficient with units of $(\mu\text{g/g})$.

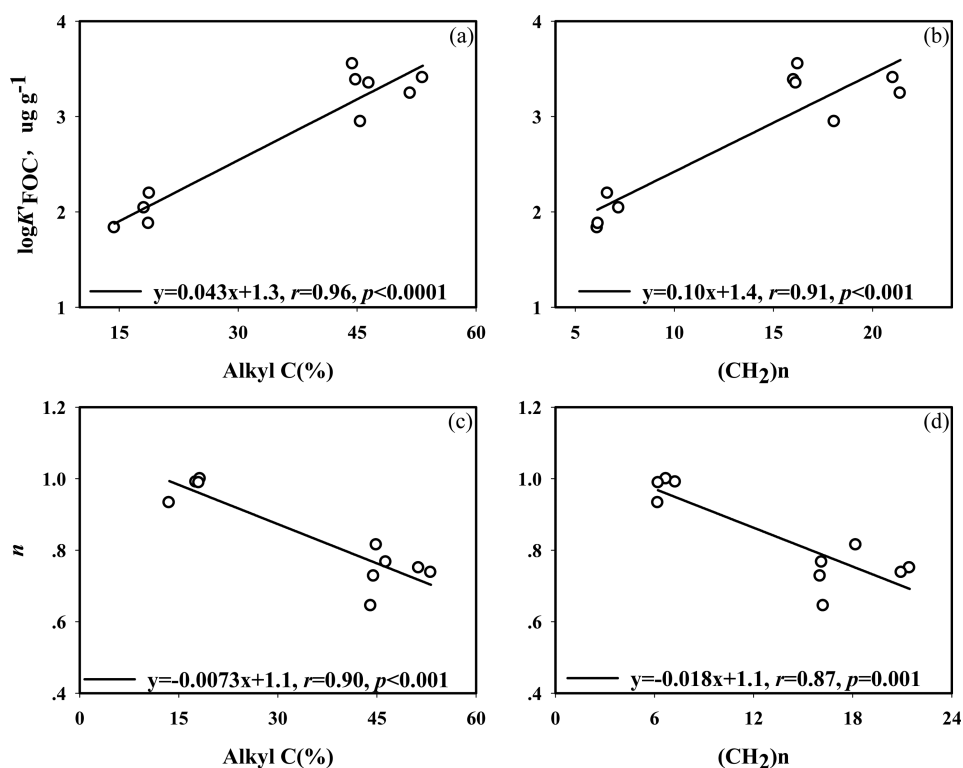


Figure 2. Correlations among $\log K'_{FOC}$ ($\mu\text{g g}^{-1} \text{OC}^{-1}$) values and concentrations of alkyl C, $(\text{CH}_2)_n$, aromatic C, and aromatic C–O from CP–TOSS ^{13}C NMR for the pollens and their fractions (a–d).

its LF, TFAR, SR, and NHC fractions are significantly lower than those of the bulk rape pollen and its LF, TFAR, SR, and NHC fractions, respectively. It is obvious that lotus pollen has a stronger sorption capacity for Phen than rape pollen whether or not the polar organic matter and functional groups are removed.

The average K_{OC} value for Phen at $C_e = 0.005S_w$ ($5.6 \mu\text{g/mL}$) for two bulk pollens is $26\,000 \pm 5000$ mL/g. The average K_{OC} value ($570\,000 \pm 90\,000$ mL/g) at $C_e = 0.005S_w$ ($5.6 \mu\text{g/}$

mL) estimated for the isolated NHC in the pollens is 2.6 and 4.6 times higher than those for the six NHC in soils and three NHC in sediments, respectively.¹⁷ The average K_{OC} values at $C_e = 0.005S_w$ ($5.6 \mu\text{g/mL}$) measured for the bulk pollens, and the corresponding NHC fractions (sporopollenin) in this study are 2.4 and 6.0 times higher for Phen than for bulk algae and NHC fractions (algaenan), respectively.²⁰ At $C_e = 0.005S_w$, the K_{OC} values for NHC fractions of pollens for Phen fall into a range of 480 000–670 000 mL/g, which are higher than for

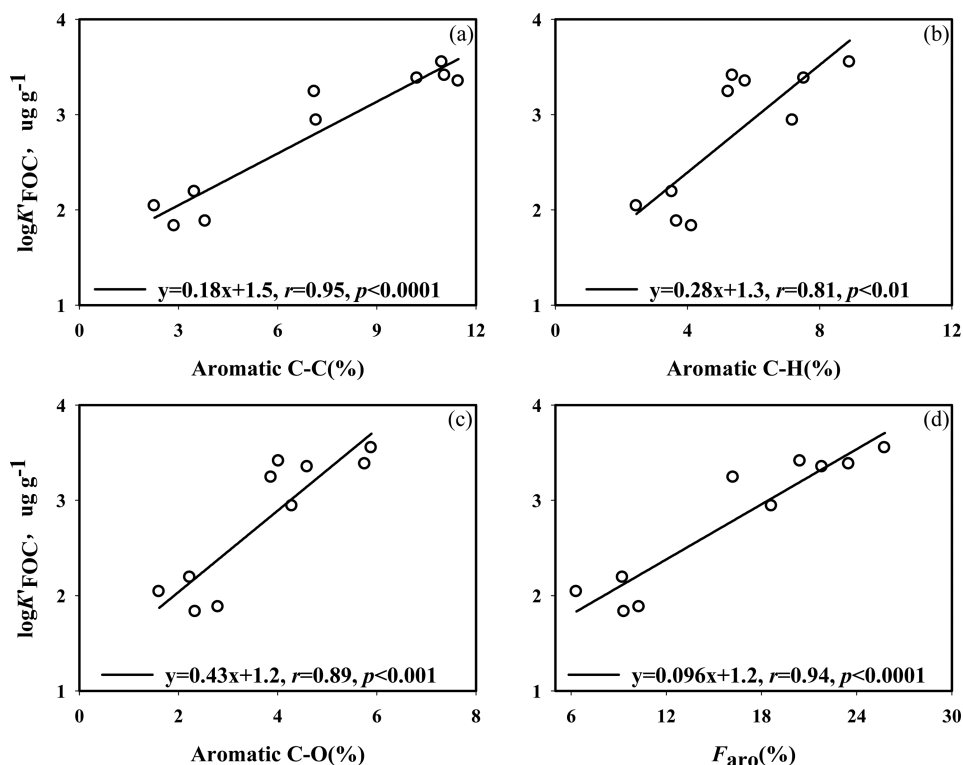


Figure 3. Correlations among sorption nonlinearity factors (n) values and concentrations of alkyl C, $(\text{CH}_2)_n$, aromatic C, and aromatic C–O from CP–TOSS ^{13}C NMR for the pollens and their fractions (a–d).

isolated kerogen (350 000 mL/g) from the Borden sand⁴⁴ and almost comparable to those for black carbon (350 000–1 600 000 mL/g) in three contaminant soils.¹⁷ The Phen sorption capacities of the NHC fractions of pollens are much higher than previously reported values for other NHC fractions and isolated kerogen, suggesting that they could be used as good sorbents for the remediation of Phen and similar hydrophobic organic contaminants.

Effects of Alkyl and Aromatic Structure on Phenanthrene Sorption by Pollen. Whether aliphatic groups or aromatic groups of NOM are correlated with HOC sorption is still a matter of debate.²² In previous studies, high-sorption-affinity domains in aromatic-rich²³ or aliphatic-rich^{17,24,25} organic matter were observed. In this study, the $\log K'_{\text{FOC}}$ values are positively related to the $(\text{CH}_2)_n$ and alkyl C concentrations for the OS and their fractions (Figure 2a,b). Positive relationships among $\log K'_{\text{FOC}}$ values and aromatic C–C, aromatic C–H, aromatic C–O, and aromatic moieties (F_{aro}) concentrations for the OS and their fractions are observed (Figure 3a–d). Moreover, the nonlinearity factors (n) are negatively related to concentrations of $(\text{CH}_2)_n$, alkyl C, aromatic moieties, and aliphatic component and lignin component for the pollen sorbents (Figures 2c,d, S5a–d, and S8a,b), suggesting that both aliphatic and aromatic structures (or compositions) serve as the condensed NOM domains and jointly contribute to the increasing nonlinearity. This behavior could be explained by assuming that NOM consists of at least two types of sorption domains: a “rubbery” domain and a “glassy” domain.^{43,45,46} The sorption of the “rubbery” domain is governed by a partitioning process, resulting in noncompetitive sorption and linear sorption isotherms. However, the sorption of the “glassy” (condensed) domain of NOM is generally nonlinear. The condensed domains have a higher sorption

affinity and nonlinearity for Phen than do rubbery ones in sediments and soils.¹⁷ The rigid and condensed domains of pollens in this investigation are highly aliphatic or moderately aromatic, with low contents of polar functional groups.

Furthermore, based on the sorption of two bulk pollens and their fractions, multivariate correlation analysis finds that the following regression equations hold: (1) $\log K'_{\text{FOC}} = 0.576x_1 + 0.443x_2$ ($r = 0.98$, $p < 0.0001$; x_1 is alkyl C, x_2 is F_{aro}); (2) $n = -0.325x_1 - 0.671x_2$ ($r = 0.96$, $p < 0.0001$; x_1 is alkyl C, x_2 is F_{aro}). According to the above equations, alkyl carbon moieties exhibit a greater effect on $\log K'_{\text{FOC}}$ than do aromatic moieties (F_{aro}), and aromatic moieties show a greater effect on n than do alkyl carbon moieties. In addition, the multivariate correlations among $\log K'_{\text{FOC}}$, n , and aromatic moieties have relationships as follows: (1) $\log K'_{\text{FOC}} = 0.822x_1 + 0.110x_2 + 0.045x_3$ ($r = 0.95$, $p < 0.01$; x_1 is aromatic C–C, x_2 is aromatic C–H, x_3 is aromatic C–O); (2) $n = -0.596x_1 - 0.403x_2 - 0.003x_3$ ($r = 0.95$, $p < 0.01$; x_1 is aromatic C–C, x_2 is aromatic C–H, x_3 is aromatic C–O). These correlations demonstrate that aromatic C–C exhibits higher sorption affinity and nonlinearity than other aromatic moieties (aromatic C–H and aromatic C–O) do. It is concluded that $(\text{CH}_2)_n$, alkyl C, and aromatic moieties are the main factors leading to the increasing sorption affinity and nonlinearity (due to van der Waals interactions and π – π interactions).

Effects of Composition and Accessibility on Phenanthrene Sorption by Pollen. Negative correlations among $\log K'_{\text{FOC}}$ values and the O-to-C atomic ratios, alkyl C–O, O-alkyl-O, COO and N–C=O, and polar C on the OS samples and their fractions are highly significant ($p < 0.001$, Figures S4b and S6a–d). Moreover, the sorption nonlinearity factors (n) are positively related to the O-to-C atomic ratios, alkyl C–O, O-alkyl-O, COO and N–C=O, and polar C for the OS and their

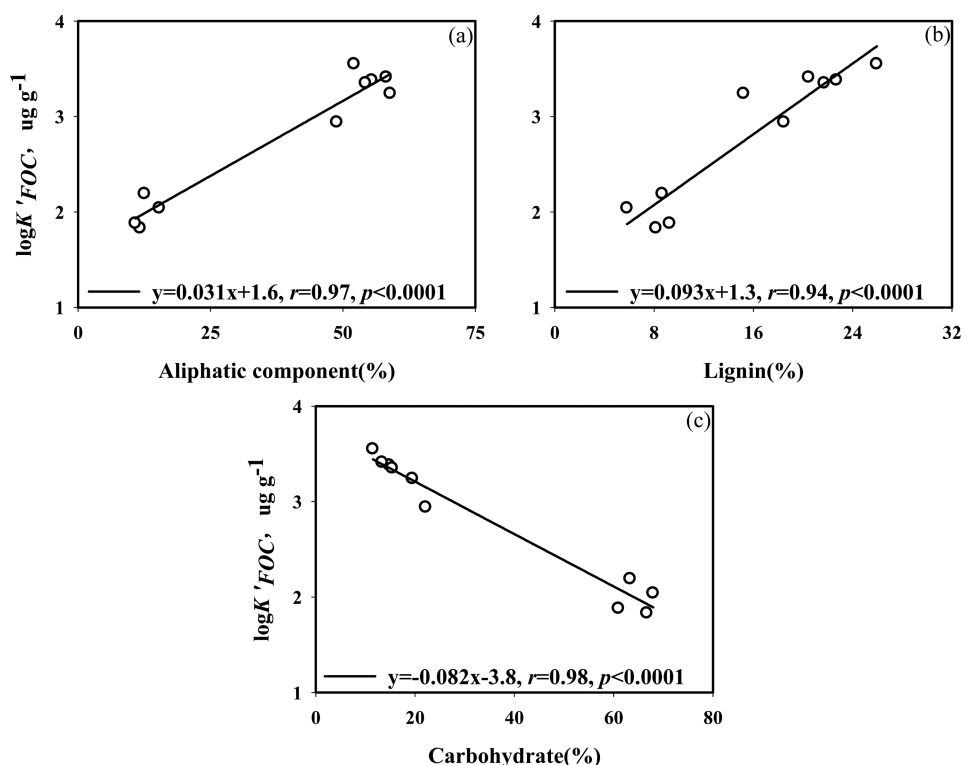


Figure 4. Correlations among $\log K'_{FOC}$ ($\mu\text{g g}^{-1} \text{OC}^{-1}$) values and concentrations of aliphatic components, lignin, and carbohydrate from CP-TOSS ^{13}C NMR for the pollens and their fractions (a–c).

fractions ($p < 0.001$, Figures S4d and S7a–d). These correlations strongly suggest that polarity affects the sorption affinity for Phen. The same trend is also observed for the sorption of Phen in other plant biomass.^{16,19} These correlations could be explained by the fact that competition between HOCs and water molecules for hydrogen bonding through heteroatoms such as oxygen sites may reduce the sorption affinity for HOCs.⁴⁷

The $\log K'_{FOC}$ values are negatively related to the carbohydrate contents of the OS, LF, and NHC fractions (Figure 4c). The n values are positively related to the carbohydrate content for the OS, LF, and NHC fractions (Figure S8c). Furthermore, the multivariate correlations among the $\log K'_{FOC}$ and n , as well as carbohydrates and proteins for the bulk pollens and their fractions, have the forms of $\log K'_{FOC} = -0.964x_1 - 0.040x_2$ ($r = 0.98, p < 0.0001$; x_1 is carbohydrates, x_2 is proteins) and $n = 0.889x_1 + 0.144x_2$ ($r = 0.97, p < 0.0001$; x_1 is carbohydrates, x_2 is proteins). This observation indicates that the potential sorption affinity of LF is restricted by the coexistence of carbohydrates and proteins. Previous studies have suggested that oxygen-containing components such as carbohydrates, amino acids, and peptides may reduce the accessibility of high-affinity sorption sites and thus limit HOC binding.^{47,48} After the removal of carbohydrates and proteins, the sorption affinity for Phen by the NHC fractions increases greatly. Once the alkyl and aromatic domains of pollen are masked by surrounding polar groups, the sorption affinity for Phen decreases, indicating the significance of composition and accessibility of pollen in the sorption of Phen.

The $\log K'_{FOC}$ values are positively related to the aliphatic component and lignin concentrations for the OS and their fractions (Figure 4a,b). The n values are negatively related to

the aliphatic component and lignin contents for the OS and their fractions (Figure S8a,b). Moreover, the multivariate correlations have the forms: $\log K'_{FOC} = 0.646x_1 + 0.368x_2$ ($r = 0.99, p < 0.0001$; x_1 is aliphatic component, x_2 is lignin), and $n = -0.444x_1 - 0.554x_2$ ($r = 0.97, p < 0.0001$; x_1 is aliphatic component, x_2 is lignin). The multivariate analysis data suggest that aliphatic component exhibits a greater effect on $\log K'_{FOC}$ than lignin does, and lignin shows a greater effect on n than the aliphatic component does. A previous study found that the K_{OC} value for Phen on lignin is 2 orders of magnitude higher than those for chitin and cellulose, respectively.⁴¹ An increase in Phen sorption affinity and nonlinearity by lignin-coated biopolymers as compared to chitin and cellulose was contributed to the newly created high-energy sites in condensed domains and coated lignin, very likely due to π - π interactions.^{19,41}

Sporopollenins are composed of alkyl carbon and poly(methylene) carbon^{40,49} and tend to exhibit a high sorption affinity for Phen, as demonstrated in this study. The results of this study suggest that poly(methylene) carbon, alkyl, and aromatic domains, as well as the composition and accessibility of NOM, require more attention when the uptake, sequestration, and bioavailability of organic contaminants are considered in the examination of sorption processes in the natural environment. However, this study with only one compound (Phen) has its limitations on extrapolating to other HOCs and further investigations on other HOCs are required.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00046.

Additional details of the modified Freundlich model and the sorption experiment procedure. Figures showing the flow diagrams for the separation of each organic fraction; NMR spectra for the identification of functional groups of the pollens and their fractions; the Freundlich sorption isotherms of Phen; and correlations among sorption parameters, H-to-C and O-to-C ratios, concentrations of aromatic moiety, polar functional groups, and contents of aliphatic component, lignin and carbohydrate. Tables listing weight and OC contents in the OS, LP, LF, TFAR, SR, and NHC samples and the elemental compositions of the pollens and their fractions. (PDF)

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Notes

The authors declare no competing financial interest.

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