

Characterization and Phenanthrene Sorption of Tea Leaf Powders

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The sorption of hydrophobic organic compounds by natural organic matter is mainly regulated by its aromatic and aliphatic fractions, but it is not clear which fraction is more dominant. In this study, six types of Chinese tea leaves (three varieties of tender and three corresponding mature leaves) and their respective brewed ones were analyzed by elemental analysis, ¹³C NMR, and Fourier transform infrared attenuated total reflectance. Their sorption of phenanthrene was examined using a batch equilibration technique. The aromatic carbon content of tea leaves reduced while the aliphatic carbon content increased with increasing maturity and brewing. Sorption isotherms by all of the 12 tea sorbents were practically linear, showing a partition type sorption. The phenanthrene *K*_{OC} (organic carbon-normalized sorption capacity) of the 12 sorbents ranged from 6960 to 32900 mL/g, which increased with increasing aliphatic carbons and decreasing aromatic carbons in the tea leaves. The dissolved organic matter was released into solution from the sorbents during the sorption process, which could bind phenanthrene in the solution, and thereafter leading to underestimation of sorption capacity of the sorbents, but this did not change the correlation trends between *K*_{OC} and functional carbon group content. Aliphatic fractions rather than aromatic moieties regulated the phenanthrene sorption of the tea leaf powders used in this study.

KEYWORDS: Sorption; tea leaves; phenanthrene; ¹³C NMR; FTIR-ATR

INTRODUCTION

Organic matter is a very important environmental component. It is ubiquitous in biosphere, pedosphere, hydrosphere, and atmosphere, which is mainly composed of fresh materials and their degradation products. Organic matter plays a key role in the environmental behavior of organic compounds, especially in sequestration of hydrophobic organic compounds (HOCs). The interaction of HOCs with organic matter and its implications have been studied for a long time (1). At the early research stage, organic matter was considered to be homogeneous when related to the sorption of HOCs, and the sorption capacities were linearly correlated to organic carbon content in sorbents such as soils and sediments (2). Later, it was reported that natural organic matter is commonly heterogeneous with varieties of functional groups (3, 4), among which aromatic and aliphatic carbons are the two key groups governing the sorption of HOCs (5, 6). Most research has focused on HOC sorption to geosorbent organic matter, such as humic substances (7–9), black carbons (10–13), and kerogen (14). Nonlinear sorption isotherms were commonly observed in these studies, due to a condensed carbon phase in the organic matter (3, 4). Several nuclear magnetic

resonance (NMR) studies concluded that HOC sorption by organic matter was strongly affected by the aromatic carbon fractions (6, 15–17), while others dealing with relatively fresh organic matter-like cuticles (18, 19), algae (5), and grasses (20) revealed that aliphatic fractions were more effective. Pristine (fresh) organic matter contains more amorphous aliphatic carbons, which may form a partition phase for HOCs and thus result in linear sorption isotherms. However, inconsistent results are reported on HOC sorption by fresh organic matter. For instance, it was pointed out that polarity and accessibility played a regulating role in HOC sorption by plant cuticular materials (21), while aromatic moieties and polarity governed HOC sorption by wood fibers after chemical alterations (22). Obviously, it is still a subject of debate if aromatic or aliphatic carbons mainly regulate the sorption of HOCs. Hence, further research is needed to clarify the mechanism of HOC sorption to organic matter, especially to fresh plant organic materials.

Plant leaves are an important component of fresh organic matter, which can increase organic carbon content in soil and water after defoliation. Leaves are widely distributed and may play a critical role in HOC sorption. However, information on HOC sorption to fresh leaves in soil or water is limited. Tea is the most widely consumed beverage in the world with a global production of about 3 million tons per year (23). After consumption, tea residues are usually discarded directly into

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the environment (24). In addition, tender and mature leaves enter the environment by defoliation and/or pruning annually. However, there are no available data on HOC sorption by tea leaves from aqueous systems. This study investigated the sorption of phenanthrene, a model HOC commonly used in sorption experiments, on fresh tender and mature tea leaves and their brewed residues. We hope to further the scientific understanding of the sorption mechanism of HOCs to fresh organic matter in general and to tea leaves in particular.

MATERIALS AND METHODS

Tea Leaves. Six types of tea leaves were collected from tea fields in different provinces of China. They were both tender and mature leaves of Longjing tea from Zhejiang province, Yunnan large-leaf tea from Yunnan province, and Huxiang tea from Hunan province. It was anticipated that leaves from various areas may have different chemical compositions, thus leading to differences in phenanthrene sorption behavior. The leaves were washed thoroughly with water to remove dust and soluble impurities and were then dried first at room temperature in shade and then overnight in an oven at 70 °C (25). Subsamples of the dried leaves were ground to pass a 1 mm sieve in a mechanical grinder and named Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2 for tender and mature leaves of Longjing tea, Yunnan large-leaf tea, and Huxiang tea, respectively. To obtain residues of the brewed tea leaves, about 1 g of each dried leaf was immersed into 40 mL of boiling distilled water, which was allowed to cool to room temperature over 2 h in a glass vial, and then, the solution was discarded. Forty milliliters of boiling distilled water was again added to the residue as above. After they were sequentially washed with distilled water three times, the residues were dried at 70 °C overnight. The dried residues were then ground into fine powders (<1 mm) and labeled as Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32 for the brewed tender and mature leaves of Longjing tea, Yunnan large-leaf tea, and Huxiang tea, respectively. All of the prepared tea leaf powders were kept in a desiccator for subsequent uses.

Characterization of Tea Leaves. Dry weight-based C, H, and N contents of all samples were determined using a Vario ELIII elemental analyzer (Elementar, Germany) with the oxygen content calculated by mass difference. Ash contents were measured by heating the tea leaf samples at 800 °C for 4 h. Solid-state cross-polarization magic angle-spinning and total sideband suppression ¹³C NMR spectra (CPMAS-TOSS) were obtained with a Bruker DSX-300 spectrometer (Karlsruhe, Germany) operated at the ¹³C frequency of 75 MHz. Except for the number of scans (3000–10000), the instrument was run under the same conditions as the one used by Chen et al. (21). Within the 0–220 ppm chemical shift range, structural carbon assignments were as follows: paraffinic carbons (0–50 ppm), methoxyl carbons (50–61 ppm), carbohydrate carbons (61–96 ppm), anomeric carbons (96–109 ppm), aromatic carbons (109–165 ppm), carboxyl carbons (163–190 ppm), and ketone carbons (190–220 ppm). Fourier transform infrared (FTIR) analysis of the samples was performed using a Perkin-Elmer Spectrum One Spectrometer with a Perkin-Elmer universal attenuated total reflectance (ATR) sampling accessory (Wellesley, MA), following the procedure of Kang and Xing (26). Tea infusions, which were supernatants obtained by the method described in the following sorbent loss section, were also analyzed by FTIR-ATR with four drops of infusions after they were air-dried onto the infrared spectrophotometer.

Sorption Experiment. ¹⁴C-labeled and unlabeled phenanthrene (>98% purity) were purchased from Sigma-Aldrich Chemical Co. and were used without further purification. For batch sorption experiments, 15 mL vials were used. The background solution (pH 7) consisted of 0.01 M CaCl₂ in double-distilled water with 200 mg/L NaN₃ as a biocide. Because of low water solubility, stock labeled and unlabeled phenanthrene solutions were prepared in methanol before adding to the aqueous background solution. Initial concentrations of phenanthrene ranged from 0.008 to 0.8 mg/L. The total amount of methanol in the solution did not exceed 0.1% by volume. The solute-containing solution was added to the vials with the tea leaves. The solid–solution ratios were adjusted to obtain 30–85% sorption of solute at apparent

equilibrium. Each isotherm had 8–10 concentration points; each point, including blanks (i.e., without tea leaves), was run in duplicate. The vials were sealed with aluminum foil-lined Teflon screw caps and were shaken for 3 days at 23 ± 1 °C. Preliminary experiments indicated that apparent equilibrium was reached before 3 days. After equilibration, the vials were centrifuged at 3000 rpm for 1 h, and approximately 0.6 mL of the supernatant was added to a ScintiVerse cocktail (5 mL) for scintillation counting (Bechman LS6500, Fullerton, CA). The solute loss, the phenanthrene concentration difference in the blank solutions before and after the sorption process, was less than 4% of the initial concentrations; therefore, sorbed solute concentrations were determined by mass balance. All sorption data were fitted to the Freundlich equation:

$$S = K_F C^N$$

where *S* is the sorbed concentration (μg/g), *C* is the liquid-phase equilibrium solution concentration (μg/mL), *K_F* is the sorption capacity coefficient [(μg/g)/(μg/mL)^{*N*}], and *N* (dimensionless) is the Freundlich exponent that describes the degree of isotherm nonlinearity.

Sorbent Loss. Similar to the sorption experiment, 100 mg of each sorbent was sealed in a 15 mL vial with 15 mL of the background solution and shaken for 3 days at 23 ± 1 °C. Thereafter, the vials were centrifuged at 3000 rpm for 1 h. Supernatants were collected and passed through 0.75 μm filters for FTIR-ATR analysis, and the residues were dried at 70 °C overnight. Each tea sample was run in duplicate. The mass difference between the original sorbent and its residue was calculated as sorbent loss as dissolved organic matter (DOM).

Phenanthrene Binding with the DOM in Tea Infusion. Five grams of the Longjing tender and mature tea leaves was immersed into 40 mL of boiling double-distilled water, which was allowed to cool to room temperature over the course of 1 day. Then, the solution was centrifuged (3000 rpm for 1 h) and filtered (0.75 μm) to obtain tea infusion. Fifteen milliliters of the tea infusions mixed with ¹⁴C-labeled and unlabeled phenanthrene (0.01 mg/L) solution was sealed into dialysis bags (3500 Da). The bags were then immersed into double-distilled water within 40 mL vials. Phenanthrene concentrations inside and outside of the bags after 3 days of equilibration were measured by scintillation counting. Phenanthrene binding capacities by the DOM (>3500 Da) in the tea infusions were obtained by calculating the concentration difference inside and outside of the bags.

Statistical Analysis. The statistical analysis of experimental data utilized Student's *t* test. Statistical significance was accepted when the probability of the result assuming the null hypothesis (*p*) was less than 0.05.

RESULTS AND DISCUSSION

Chemical Characterization of the Tea Leaves. The elemental compositions of the 12 tea sorbents are shown in **Table 1**. The nitrogen contents in the mature leaves before or after they were brewed are all about two times lower than that in the tender leaves; as a result, elemental ratios of carbon to nitrogen are significantly higher in the mature leaves. The mature leaves have higher H/C ratios than the tender ones except for Longjing tea leaves, indicating that mature leaves may contain more aliphatic carbons, consistent with the ¹³C NMR results. Carbon contents in the brewed tea leaves (Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32) are slightly higher than that in their original leaves (Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2), while the ratios of O/C and (O + N)/C in the brewed leaves are lower than their original ones, indicating that the brewing process decreased the polarity of tea leaves.

¹³C NMR results of the samples are presented in **Figure 1** and **Table 2**. The broad peak of 0–30 ppm belongs to alkyl carbon in short chain polymethylene (28 ppm) and methyl carbons in acetyl groups of hemicelluloses (21 ppm). These peaks all belong to amorphous aliphatic carbon (22). No clear

Table 1. Elemental Composition of 12 Tea Leaf Samples

sample ^a	C %	H %	N %	O % ^b	ash %	H/C	O/C	C/N	(O + N)/C
Tea1-1	44.0	6.45	5.72	37.4	6.43	1.76	0.638	8.98	0.749
Tea1-2	46.6	6.46	2.36	38.7	5.90	1.67	0.623	23.0	0.667
Tea2-1	48.8	5.66	4.66	36.2	4.64	1.39	0.556	12.2	0.638
Tea2-2	46.7	6.12	1.89	39.5	5.82	1.57	0.634	28.8	0.669
Tea3-1	45.8	6.41	5.55	37.0	5.21	1.68	0.607	9.62	0.711
Tea3-2	45.1	6.67	2.55	43.2	2.52	1.78	0.719	20.6	0.768
Tea-B11	47.1	6.35	5.18	37.5	3.83	1.62	0.597	10.6	0.691
Tea-B12	48.3	7.09	2.36	37.4	4.92	1.76	0.581	23.9	0.622
Tea-B21	50.9	6.16	5.18	35.5	2.28	1.45	0.522	11.5	0.609
Tea-B22	49.1	6.40	2.46	37.5	4.49	1.56	0.573	23.3	0.615
Tea-B31	48.2	6.77	5.86	35.9	3.31	1.69	0.558	9.60	0.662
Tea-B32	47.4	7.03	3.09	38.0	4.49	1.78	0.601	17.9	0.657

^a Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2 are tender and mature leaves of Longjing tea, Yunnang large-leaf tea, and Huxiang tea, respectively. Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32 are brewed residues of Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2, respectively. ^b The oxygen content was calculated by mass difference.

crystalline aliphatic carbon peak (31.5 ppm) was observed in the tea leaves. The peak of 56 ppm shows the presence of methoxy groups (OCH₃), which are probably the most characteristic functional group for lignin (22). The peaks between 71 and 85 are assigned to C-2, C-3, C-4, and C-5 in amorphous cellulose, whereas the strong signals around 100 ppm are associated with anomeric carbon (C-1) (22). The peak of 83 ppm belongs to C-4 in amorphous celluloses, which are more resolved in the tender leaves than in the mature leaves. The peaks in the region of 110–120 ppm are assigned to the ring carbons in which the ring is not substituted by strong electron donors such as oxygen and nitrogen (22), together with the

multiple peaks in the range from 140 to 163 ppm, which are from the carbons of phenolic components, showing the presence of catechins—the main composition of tea polyphenols (27–29). The peak at 154 ppm is due to C-3 and C-5 of the syringyl units involved in ether linkages at C-4 and C-3 and C-4 in the guaiacyl units (22). The peak at 143 ppm is from C-4 in the guaiacyl unit with free phenolic OH at C-4. The 172 ppm peak shows carbonyl carbons in acetyl groups of hemicellulose. Aliphatic carbon contents (0–109 ppm), especially nonpolar paraffinic carbon (0–50 ppm), are higher in the mature tea leaves than the tender leaves and increased after the brewing process (Table 2). On the contrary, the tender and original tea leaves contained more aromatic carbons (109–163 ppm) than the mature and brewed ones, respectively. Integration of peaks from 163 to 220 ppm, belonging to carboxylic carbon (163–190 ppm) and carbonyl carbon (190–220 ppm), was slightly lower in the mature leaves than the tender ones and decreased after brewing (Table 2).

The ¹³C NMR spectra illustrate that maturing and brewing processes caused structural modifications of tea leaves (Figure 1). Most notably, maturing and brewing reduced aromatic carbon content and increased aliphatic carbon content in the tea leaves. The brewed tea residues contained lower polar carbons than their original leaves.

The FTIR-ATR spectra between 4000 and 650 cm⁻¹ for the 12 tea leaf samples are presented in Figure 2a. The broad absorption between 3665 and 2995 cm⁻¹ indicates –OH, which may come from H₂O (3500–3200 cm⁻¹), –COOH (3400–2400 cm⁻¹), alcohols and phenols (3650–3600 cm⁻¹), or stretching N–H (26). The peak of –OH together with the strong peak at 1618 cm⁻¹ (aromatic ring) show the presence of plenty of polyphenols. The double peaks of 2916 and 2847 cm⁻¹ indicate

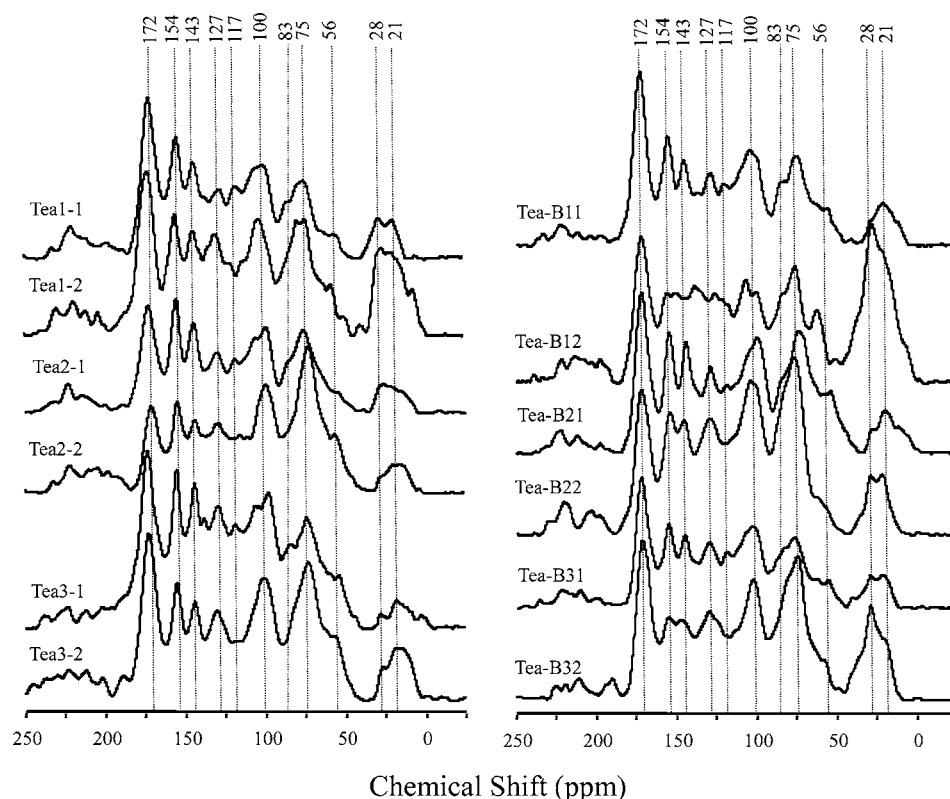


Figure 1. Solid-state ¹³C NMR spectra of tea leaves. Aliphatic C (0–109 ppm), aromatic C (109–163 ppm), and COOH/C=O (163–220 ppm). Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2 are tender and mature leaves of Longjing tea, Yunnang large-leaf tea, and Huxiang tea, respectively. Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32 are the brewed residues of Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2, respectively.

Table 2. Integration Results of Solid-State ^{13}C NMR Spectra^a

sample ^b	distribution (%) of C chemical shift, ppm								aliphatic	aromatic	polar
	0–50	50–60	60–96	96–109	109–145	145–163	163–190	190–220	C (%)	C (%)	C (%)
Tea1-1	7.5	2.0	18.3	10.9	23.6	14.6	17.9	5.1	38.8	38.2	68.9
Tea1-2	15.4	2.4	20.4	9.6	21.1	11.4	15.9	3.9	47.8	32.5	63.5
Tea2-1	7.3	2.2	21.7	11.5	22.3	15.4	15.9	3.6	42.8	37.7	70.4
Tea2-2	6.9	4.8	30.7	10.9	20.5	10.8	9.7	5.8	53.3	31.3	72.6
Tea3-1	4.4	3.3	20.7	11.1	26.3	13.7	17.0	3.5	39.5	40.0	69.3
Tea3-2	9.2	4.0	24.3	10.6	19.3	11.4	16.3	4.8	48.1	30.7	71.4
Tea-B11	8.4	3.0	20.4	10.8	21.6	13.6	19.2	2.9	42.6	35.2	70.0
Tea-B12	25.1	2.2	18.8	8.0	20.3	9.9	11.5	4.1	54.2	30.2	54.5
Tea-B21	8.8	4.7	24.6	11.3	21.8	12.3	14.2	2.3	49.4	34.0	69.4
Tea-B22	7.4	1.4	26.6	12.6	24.6	12.2	11.7	3.4	48.0	36.8	67.9
Tea-B31	8.3	2.7	20.5	11.6	23.8	13.3	16.2	3.8	42.9	37.1	68.0
Tea-B32	13.4	2.0	25.3	10.6	20.7	10.6	14.3	3.0	51.4	31.3	65.8

^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). ^b Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2 are tender and mature leaves of Longjing tea, Yunnang large-leaf tea, and Huxiang tea, respectively. Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32 are brewed residues of Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2, respectively.

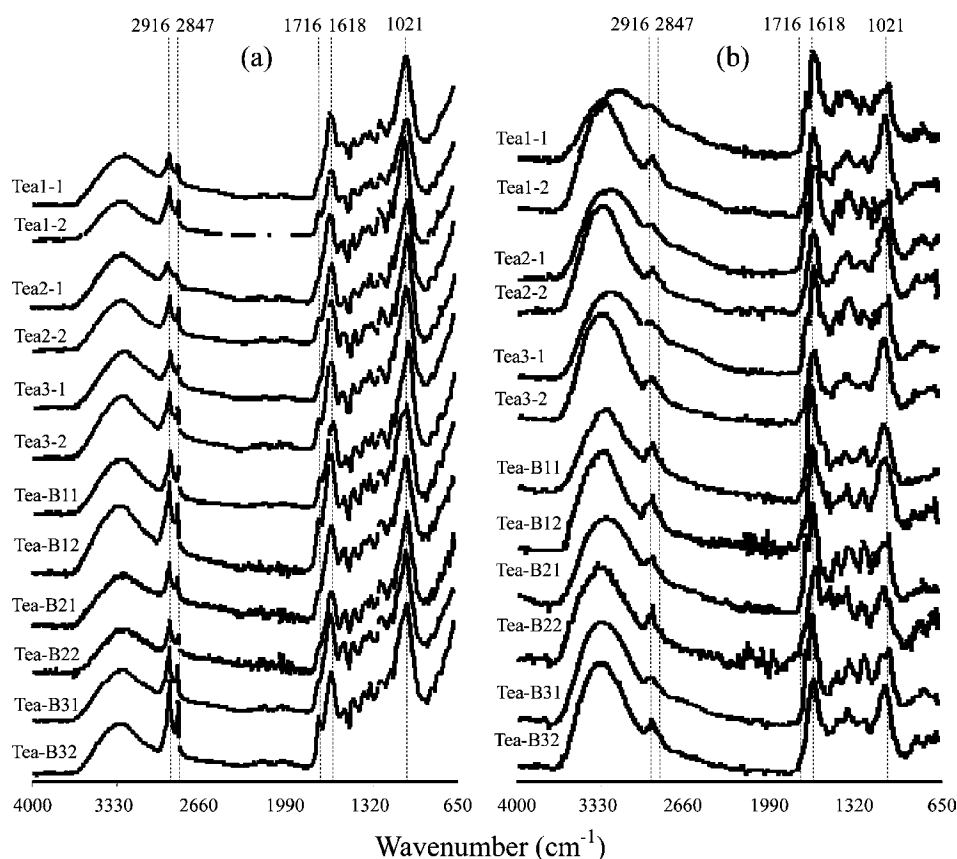


Figure 2. FTIR-ATR spectra of tea leaf powders (a) and tea infusions (b). Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2 are tender and mature leaves of Longjing tea, Yunnang large-leaf tea, and Huxiang tea, respectively. Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32 are the brewed residues of Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2, respectively.

the presence of alkanes ($-\text{R}-$) (26). The peaks of alkanes are stronger in the mature and brewed leaves than the tender and original ones, respectively, implying that the mature and brewed leaves may contain more aliphatic carbons, consistent with the ^{13}C NMR data. The strong peak at 1021 cm^{-1} belongs to $\text{C}-\text{O}$ stretching of polysaccharides, together with the peak of 1716 cm^{-1} (carbonyl stretching of $-\text{COOH}$ group), indicating that the samples contain a high amount of carboxylic acid (18).

In the FTIR-ATR spectra of tea infusions (Figure 2b), there also exists a broad and strong absorption of a $-\text{OH}$ or $\text{N}-\text{H}$ group. Peaks of aromatic ring, $\text{C}-\text{O}$, and $\text{C}=\text{O}$ groups became sharper as compared to that of the solid tea leaves. However,

the peak at 2847 cm^{-1} shows as a shoulder of 2916 cm^{-1} , which is also much weaker than the leaves, implying that the aliphatic carbon content is markedly lower in the infusions. It is obvious that the brewing process released more aromatic moieties than aliphatic groups from solid tea leaves to their infusions, resulting in a higher content of aliphatic carbons in the brewed tea residues. In fact, it is well-known that tea polyphenols are a very important component in tea leaves (up to 18–36% of tea leaves in dry weight) and can be released into infusions during brewing (29, 30).

Sorption of Phenanthrene by Tea Leaves. Sorption isotherms were fitted well to the Freundlich model (Figure 3) with

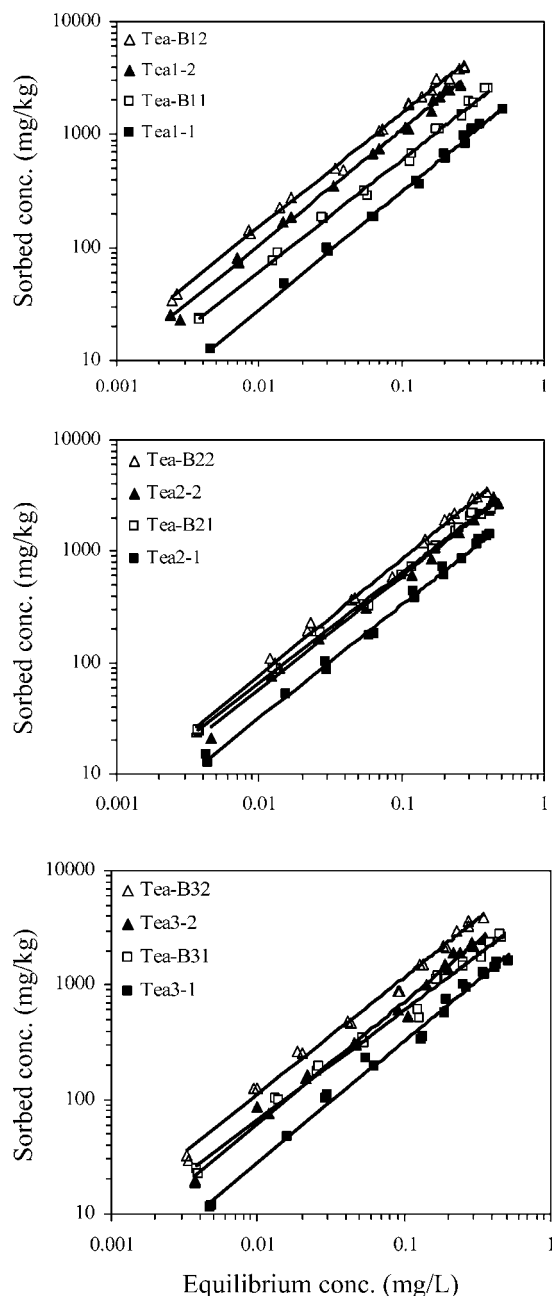


Figure 3. Sorption isotherms of phenanthrene by tea leaves. Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2 are tender and mature leaves of Longjing tea, Yunnang large-leaf tea, and Huxiang tea, respectively. Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32 are the brewed residues of Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2, respectively.

the Freundlich exponent N ranging from 0.964 to 1.059 (Table 3). All isotherms were practically linear, showing a predominant partition type sorption, similar to other types of fresh organic matter (5, 18–20). Organic carbon-normalized sorption capacity (K_{OC}) was calculated from organic carbon contents of the tea leaves and K_d values (apparent sorption coefficient, mL/g, from linear fitting: $S = K_d C$). The K_{OC} values are in a range of 6960–32900 mL/g (Table 3), which are comparable to and even a bit higher than reported K_{OC} values of phenanthrene in soils (7200–25300 mL/g) (31) and also much higher than that of unmodified Aspen wood fiber (3940–4660 mL/g) (22). The mature leaves have higher phenanthrene K_{OC} values, and brewing increased the K_{OC} values as can be seen for the tea residues.

Table 3. Sorption Coefficients and Freundlich Model Parameters of Phenanthrene by Tea Leaf Samples

sample ^a	K_f^b	N	Freundlich r^2	K_d (mL/g)	linear r^2	K_{OC} (mL/g)	K_{OC}^c (mL/g)
Tea1-1	3400	1.038 ± 0.014	0.998	3290	0.989	7480	10200
Tea1-2	11800	1.027 ± 0.013	0.998	11200	0.989	24000	31800
Tea2-1	3390	1.016 ± 0.013	0.997	3400	0.993	6960	10600
Tea2-2	6000	1.012 ± 0.016	0.996	5880	0.991	12600	16400
Tea3-1	3720	1.059 ± 0.023	0.992	3450	0.985	7530	11200
Tea3-2	8070	1.054 ± 0.022	0.993	7560	0.986	16800	23100
Tea-B11	5860	0.993 ± 0.014	0.997	6120	0.990	13000	13900
Tea-B12	15500	1.006 ± 0.013	0.997	15900	0.990	32900	35500
Tea-B21	6150	0.985 ± 0.013	0.997	6270	0.985	12300	13500
Tea-B22	9330	1.042 ± 0.021	0.993	8950	0.990	18200	19100
Tea-B31	5540	0.964 ± 0.022	0.991	5820	0.984	12100	13500
Tea-B32	12100	1.018 ± 0.021	0.993	11200	0.987	25200	27200

^a Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2 are tender and mature leaves of Longjing tea, Yunnang large-leaf tea, and Huxiang tea, respectively. Tea-B11 and Tea-B12, Tea-B21 and Tea-B22, and Tea-B31 and Tea-B32 are brewed residues of Tea1-1 and Tea1-2, Tea2-1 and Tea2-2, and Tea3-1 and Tea3-2, respectively. ^b K_f unit = (mg/kg) (mg/L)^{-N}. ^c K_{OC} values are the recalculated K_{OC} values according to the sorbent loss.

The relationships between phenanthrene K_{OC} and selected carbon functional groups are shown in Figure 4. It can be seen that the K_{OC} value generally increased with increasing aliphatic carbon content and decreasing aromatic carbon content (Figure 4a,b). Thus, aliphatic carbon rather than aromatic carbon dominated the sorption of phenanthrene, which can be further demonstrated by the positive relationship between K_{OC} and aliphaticity (Figure 4c), a ratio of aliphatic carbon to aromatic carbon content. As a main part of nonpolar aliphatic carbon, paraffinic carbon (0–50 ppm in NMR spectra) contributed greatly to the sorption of phenanthrene with a strong positive relationship with K_{OC} , in agreement with the reported results of phenanthrene sorption by other aliphatic-rich organic matter (5, 7, 21). In addition to aliphaticity, polarity (polar carbon content) of the sorbent was reported, affecting the sorption capacity of organic contaminants (21, 22). In this study, the K_{OC} values are inversely related to the polar carbon contents (Figure 4f).

Aromatic carbon was usually observed to increase the HOC's K_{OC} values of geosorbent organic matter (6, 15–17), and aliphatic carbon contributed to the increase of the K_{OC} values of fresh organic matter (18–20). However, few studies reported a negative relationship between K_{OC} values and aromatic carbons as observed in this study. Figure 4e shows an inverse relationship ($r^2 = 0.697$) between K_{OC} values and phenolic carbon contents. The released DOM during brewing might bind phenanthrene in the infusions and thus inhibit the phenanthrene sorption by solid tea leaf, just as other DOMs did on HOCs (32–34). To prove this hypothesis, we designed a phenanthrene binding experiment using the tender and mature Longjing tea leaves as representative sorbents. The phenanthrene concentrations in the infusions of the tender and the mature Longjing tea leaves inside the dialysis bags were 20 and 15% higher than that in the solutions outside the dialysis bags, respectively. Fresh tea leaves can release DOM into the infusion during brewing; thus, the released DOM can bind phenanthrene, leading to reduction in phenanthrene sorption by the solid leaf powders.

Fresh organic matter may contain more soluble components than humic substances. As determined by the sorbent loss experiment, the average mass losses of the six original tea leaves and their brewed ones during sorption equilibration were 31.6 ± 4.4 and $8.5 \pm 2.0\%$, respectively. The brewed residues could

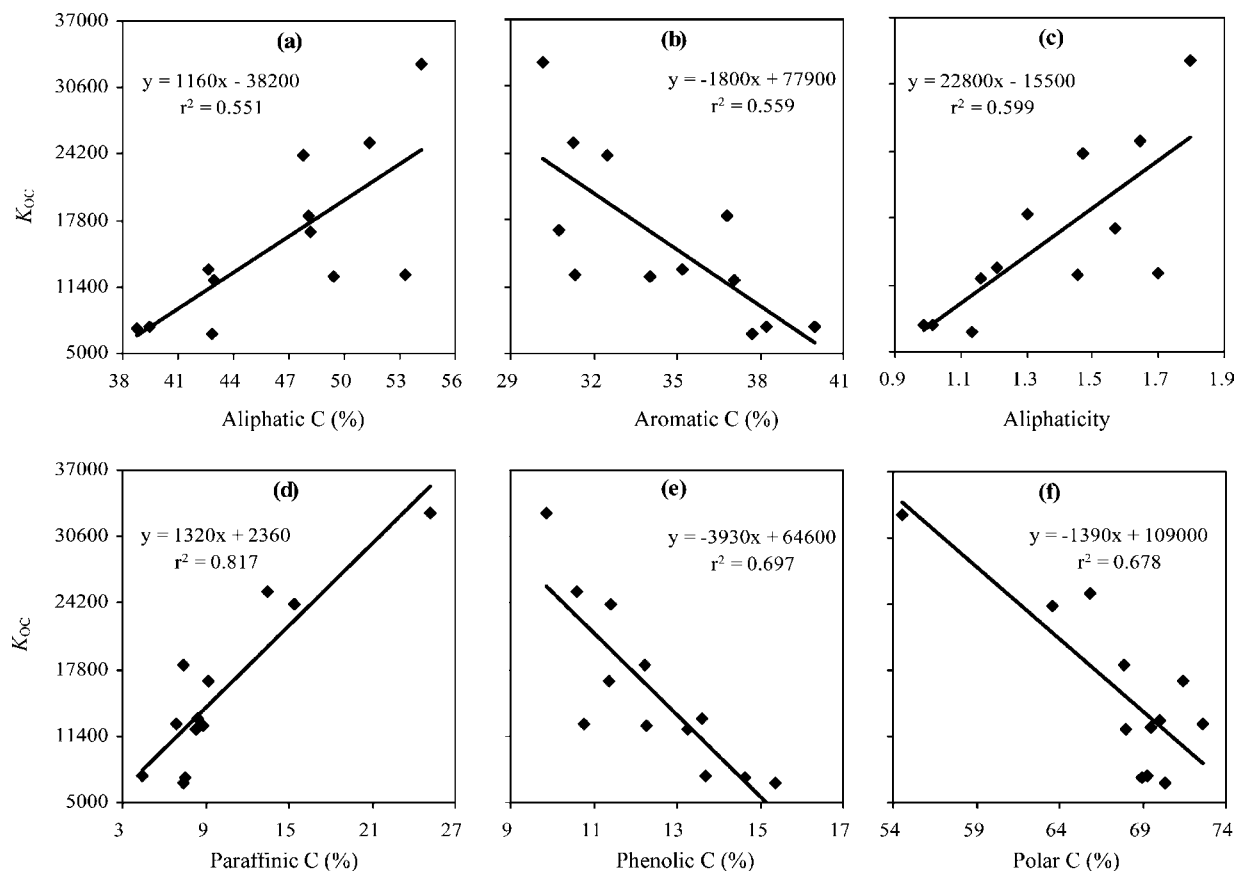


Figure 4. Relationship between K_{OC} and aliphatic carbon content (a), aromatic carbon content (b), aliphaticity (c), paraffinic carbon content (d), phenolic carbon content (e), and polar carbon content (f).

still release small fractions into infusions but much lower than their original leaves did. The K_d values could increase to a degree of 31.6 ± 4.4 and $8.5 \pm 2.0\%$ for the pristine tea leaves and their brewed residues, respectively, when sorbent loss was considered. However, the K_{OC} values (K_d/f_{oc}) would increase to a lesser extent because organic carbon content (f_{oc}) of the sorbents might increase after the sorption process, as f_{oc} of the six tea leaves could increase by up to $2.2 \pm 0.5\%$ (the average f_{oc} difference between the brewed tea residues and original tea leaves determined by the elemental analysis). We recalculated the K_{OC} values based on the sorbent loss and the two assumptions: (i) that the average f_{oc} increase of the six original leaf sorbents after sorption process is the same as that of tea leaves after brewing (i.e., 2.2%) and (ii) that the average f_{oc} increase of the six brewed tea residue sorbents after sorption process is proportional to that of the original leaf sorbents according to the sorbent loss ($2.2/31.6\% \times 8.5\% = 0.6\%$). The recalculated K_{OC} values increased from 6960–32900 to 10200–35500 mL/g (Table 3), and the mean phenanthrene K_{OC} ratios of the six brewed residues to their original tea leaves significantly reduced from 1.56 ± 0.16 to 1.22 ± 0.09 , while the K_{OC} ratios of the six mature leaves (including original and brewed mature leaves) to their corresponding tender ones showed no significant difference (from 2.23 ± 0.60 to 2.12 ± 0.63). Mass loss can also change the sorbent chemical composition. From Table 2, it can be seen that the aliphatic carbon content in the brewed residues increased up to 6.6%, while the aromatic carbon content reduced up to 3.7% (Tea2-1) as compared to their original tea leaves. The chemical composition of the brewed residues would not change much during the sorption process due to their lower sorbent loss. It is difficult to make an accurate adjustment of the correlation coefficients between the K_{OC} values and carbon

functional group contents because of the unavailability of exact chemical composition changes, but the correlation trend (showed by r^2 in Figure 4) did not vary significantly when the adjusted K_{OC} values were used without considering the slight changes of the chemical composition. Furthermore, the correlation trends were similar when only the six brewed tea residues or the six original tea leaves, in which the sorbent loss and chemical composition changes were similar, were considered, indicating that slight chemical composition changes of the sorbents during the sorption process did not alter the correlation trends between the K_{OC} values and the carbon functional group contents. Hence, the conclusions based on the sorption experiment are reasonable and appropriate even when sorbent loss is considered.

In summary, we analyzed the chemical characteristics of six types of tea leaves and their respective brewed residues and performed the sorption experiments of phenanthrene on these sorbents. Mature tea leaves contain more aliphatic carbons than the corresponding tender ones, and the brewing process released more aromatic than aliphatic carbons into infusions from the leaves. Aliphatic fractions other than aromatic moieties played a major role in regulating the phenanthrene sorption potential of the solid tea leaves used in this study, and the sorption isotherms were linear. DOM in the tea infusions could bind phenanthrene and thus can inhibit (reduce) phenanthrene sorption by the solid leaves. However, the K_{OC} values of the tested tea leaf powders could be up to 32900 mL/g, higher than that of the recorded soils and wood fiber, suggesting that tea leaves, especially tea residues, after entering our environment, may strongly sorb HOCs and influence their environmental behavior. In addition, tea residues can be a potential sorbent for HOCs, which may be used to clean up HOC-contaminated water if properly managed.

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