

**Supporting Information for**  
**“LFERs for Soil Organic Carbon–Water Distribution Coefficients ( $K_{OC}$ )**  
**at Environmentally Relevant Sorbate Concentrations”**  
**in *Environmental Science & Technology***

Satoshi Endo<sup>\*1,3</sup>, Peter Grathwohl<sup>1</sup>, Stefan B. Haderlein<sup>1</sup>, and Torsten C. Schmidt<sup>1,2</sup>

<sup>1</sup> *Center for Applied Geoscience, Eberhard-Karls-University of Tübingen  
Sigwartstrasse 10, D-72076 Tübingen, Germany*

<sup>2</sup> *Instrumental Analytical Chemistry, University of Duisburg-Essen,  
Lotharstrasse 1, D-47048 Duisburg, Germany*

<sup>3</sup> Current address: Department of Analytical Environmental Chemistry, Helmholtz Centre for Environmental Research UFZ, Permoserstrasse 15, D-04318 Leipzig, Germany

\*Corresponding author phone: +49 341 235 1434, fax: +49 341 235 1443;  
e-mail: satoshi.endo@ufz.de

- SI-1. Probe sorbates used in this study and their LSER descriptors
  - SI-2. Testing mass conservation of sorbates during sorption experiments by solvent extraction
  - SI-3. Measured and calculated log  $K_{OC}$  values
  - SI-4. Correlation between log  $K_{OC}$  and log  $K_{OW}$
  - SI-5. Re-calculation of PP-LFER equations for log  $K_{OC}$  reported by Nguyen et al. (2005) and by Poole and Poole (1999)
  - SI-6. Comparison between lignite and peat
  - SI-7. Comparison of log  $K_{OC}$  for lignite to the literature PP-LFERs
  - SI-8. Comparison of PP-LFERs from this study for peat and from Poole & Poole (1999)
  - SI-9. Agreement between the log  $K_{OC, High}$  estimated for peat and the log  $K_{OC, High}$  predicted by the literature PP-LFER in relation to the sorbed concentration ( $C_s$ )
  - SI-10. List of sorbates analyzed individually and sorbates mixed and analyzed together
  - SI-11. Comparison with PP-LFERs from Niederer et al. (2007)
- Containing 8 tables and 11 figures; 31 pages.

# SI-1. Probe sorbates used in this study and their LSER descriptors.

Table S1. List of probe sorbates used in this study and their LSER descriptors.

	<i>E</i>	<i>S</i>	<i>A</i>	<i>B</i>	<i>V</i>	<i>L</i>	ref
<b>alkanes</b>							
<i>n</i> -pentane	0.000	0.00	0.00	0.00	0.813	2.162	(1)
<i>n</i> -hexane	0.000	0.00	0.00	0.00	0.954	2.668	(1)
<i>n</i> -heptane	0.000	0.00	0.00	0.00	1.095	3.173	(1)
<i>n</i> -octane	0.000	0.00	0.00	0.00	1.236	3.677	(1)
<i>n</i> -nonane	0.000	0.00	0.00	0.00	1.377	4.182	(1)
<i>n</i> -decane	0.000	0.00	0.00	0.00	1.518	4.686	(1)
isohexane	0.000	0.00	0.00	0.00	0.954	2.503	(1)
cyclopentane	0.263	0.10	0.00	0.00	0.705	2.477	(1)
cyclohexane	0.305	0.10	0.00	0.00	0.845	2.964	(1)
cyclooctane	0.413	0.10	0.00	0.00	1.127	4.329	(2, 3)
<i>cis</i> -decaline	0.544	0.25	0.00	0.00	1.300	5.156	(3)
<i>trans</i> -decaline	0.467	0.23	0.00	0.00	1.300	4.984	(3)
<b>halo-aliphatic compounds</b>							
dichloromethane	0.387	0.57	0.10	0.05	0.494	2.019	(1)
trichloromethane	0.425	0.49	0.15	0.02	0.617	2.480	(1)
tetrachloromethane	0.458	0.38	0.00	0.00	0.739	2.823	(1)
pentachloroethane	0.648	0.66	0.17	0.06	1.002	4.267	(1)
$\gamma$ -hexachlorocyclohexane	1.450	0.91	0.00	0.68	1.580	7.467	(4)
<i>cis</i> -dichloroethene	0.436	0.61	0.11	0.05	0.592	2.439	(1)
trichloroethene	0.524	0.37	0.08	0.03	0.715	2.997	(1)
tetrachloroethene	0.639	0.44	0.00	0.00	0.837	3.584	(1)
tribromomethane	0.974	0.68	0.15	0.09	0.775	3.784	(1)
1,2-dibromoethane	0.747	0.76	0.10	0.17	0.740	3.382	(1)
<b>monopolar aliphatic compounds</b>							
di- <i>n</i> -propyl ether	0.008	0.22	0.00	0.45	1.013	2.803	(5)
di- <i>n</i> -butyl ether	−0.008	0.24	0.00	0.45	1.295	3.924	(5)
di- <i>n</i> -pentyl ether	−0.017	0.27	0.00	0.45	1.576	4.845	(5, 6)
octan-2-one	0.108	0.68	0.00	0.51	1.252	4.257	(1)
<i>n</i> -butyl acetate	0.071	0.60	0.00	0.45	1.028	3.353	(1)
hexanenitrile	0.166	0.90	0.00	0.36	0.968	3.513	(2, 6)
1-nitrohexane	0.203	0.95	0.00	0.29	1.129	4.441 <sup>a</sup>	(2)
<b>bipolar aliphatic compounds</b>							
2-octanol	0.158	0.36	0.33	0.56	1.295	4.343	(2, 7)
3-ethyl-3-hexanol	0.203	0.30	0.31	0.60	1.295	4.189 <sup>b</sup>	(7)
2,6-dimethyl-2-heptanol	0.131	0.27	0.31	0.60	1.435	4.469 <sup>b</sup>	(7)
4-methyl-4-nonanol	0.167	0.30	0.31	0.60	1.576	5.219 <sup>b</sup>	(7)
<b>nonpolar aromatic compounds</b>							
benzene	0.610	0.52	0.00	0.14	0.716	2.786	(1)
toluene	0.601	0.52	0.00	0.14	0.857	3.325	(1)
<i>n</i> -propylbenzene	0.604	0.50	0.00	0.15	1.139	4.230	(1)
chlorobenzene	0.718	0.65	0.00	0.07	0.839	3.657	(1)
1,2-dichlorobenzene	0.872	0.78	0.00	0.04	0.961	4.518	(1)
naphthalene	1.340	0.92	0.00	0.20	1.085	5.161	(1)
phenanthrene	2.055	1.29	0.00	0.26	1.454	7.632	(1)
fluoranthene	2.377	1.55	0.00	0.24	1.585	8.827	(8)
thiophene	0.687	0.56	0.00	0.15	0.641	2.819	(1)
benzofuran	0.888	0.83	0.00	0.15	0.905	4.355	(2, 3)
dibenzofuran	1.407	1.02	0.00	0.17	1.274	6.716	(2, 3)
<b>monopolar aromatic compounds</b>							
benzothiazole	1.330	1.10	0.00	0.40	0.969	5.739 <sup>b</sup>	(2, 3)
quinoline	1.268	0.97	0.00	0.54	1.044	5.457	(1)
anisole	0.708	0.74	0.00	0.29	0.916	3.890	(1)
acetophenone	0.818	1.01	0.00	0.49	1.014	4.501	(1)
ethylbenzoate	0.689	0.85	0.00	0.46	1.214	5.075	(1)
benzonitrile	0.742	1.11	0.00	0.33	0.871	4.039	(1)
4-nitrotoluene	0.870	1.11	0.00	0.28	1.032	5.154	(2, 3)
1-nitronaphthalene	1.600	1.59	0.00	0.29	1.260	7.056	(9)
<b>bipolar aromatic compounds</b>							
phenol	0.805	0.89	0.60	0.31	0.775	3.766	(1)
4-ethylphenol	0.800	0.90	0.55	0.36	1.057	4.737	(1)
2,6-dimethylphenol	0.860	0.79	0.39	0.39	1.057	4.680	(1)
2,4,6-trimethylphenol	0.860	0.79	0.37	0.44	1.198	5.133	(2, 3)

2-naphthol	1.520	1.08	0.61	0.40	1.144	6.200	(1)
2-chlorophenol	0.853	0.88	0.32	0.31	0.898	4.178	(1)
4-chlorophenol	0.915	1.08	0.67	0.21	0.898	4.775	(1)
2,4,5-trichlorophenol	1.070	0.92	0.73	0.10	1.142	5.725	(10)
indole	1.200	1.12	0.44	0.22	0.946	5.505	(2, 3)

<sup>a</sup>Extrapolated from data for nitromethane to 1-nitropentane. <sup>b</sup>Estimated by SPARC, May 2008 release w4.2.1405-s4.2.1408 (<http://ibmlc2.chem.uga.edu/sparc/>; accessed July 2008) (11, 12).

---

## SI-2. Testing mass conservation of sorbates during sorption experiments by solvent extraction.

Conservation of the mass of sorbates during the equilibration periods was tested by solvent extraction. Some sorbates were not subjected to this test, assuming that compounds within the same class (e.g., *n*-alkanes, alkyl ethers) behave similarly. For discussions about the mass conservation of 2-octanone and 1-nitrohexane, see ref 13.

One or two extra batches containing sorbent suspension were prepared for each sorbate and sorbent. After the equilibration periods, 2 or 5 mL of organic solvent was added to these batches. Ethyl acetate was used as extractant for bipolar sorbates (i.e., alcohols, phenols), whereas *n*-pentane, isohexane, or cyclohexane was used for the other sorbates. For volatile compounds (alkanes, halogenated compounds, ethers, alkyl benzenes) of which a significant mass fraction is expected to be present in the gas phase, 1 mL of solvent was introduced into the vials through the septum sealing. Then, the vials, kept closed, were gently shaken by hand for several minutes so that the fraction of sorbate in the gas phase can partition into the solvent. The vials were then opened, and 4 mL of solvent was added. For the other nonvolatile sorbates, the vials were simply opened and 2 or 5 mL solvent was added. After adding solvent, the vials for all sorbates were closed with new septa and shaken for one to two days for extraction. The organic phase was withdrawn and analyzed by GC/MS. Experimental sorbate concentrations had to be relatively high for the recovery experiments (around the highest concentrations adopted in the experiments to determine  $K_{OC}$ ) in order to obtain quantifiable concentrations in the extracts.

The results are shown in Table S2. Most of the compounds showed >90% recovery. Dichloromethane, *cis*-dichloroethene, benzothiazole, acetophenone, and benzonitrile exhibited a relatively low recovery (47–83%), but this is expected from the relatively low solvent–water partitioning coefficients

(estimated by LSERs, ref 14) of these sorbates. Thus, these compounds are regarded as conservative in the batches. The recovery rates achievable by the incomplete solvent extraction were estimated using the LSER-estimated solvent–water partitioning coefficients and are shown in Table S2 for comparison.

Ethylbenzoate and *n*-butyl acetate in peat were not detected, likely because of degradation of the sorbates. In addition, recovery for 2-octanol in peat and 2,4,6-trimethylphenol in lignite was relatively low, which could cause significant ( $>0.30$ ) errors in  $\log K_{OC}$ . Hence, the corresponding  $K_{OC}$  data were removed from the data list.

Recovery rates for *n*-heptane, *n*-decane,  $\gamma$ -hexachlorocyclohexane, phenanthrene, and fluoranthene were relatively low by the solvent extraction with an extraction period of one to two days. For some of these compounds, extension of the extraction period considerably increased the recovery (Table S2), which indicates that these sorbates undergo slow desorption from the sorbents. To circumvent the kinetic problem, a separate experiment was conducted in which the sorption batches after equilibration were centrifuged, the supernatant was removed, and the remaining sorbent with a reduced volume of water (ca. 1 mL) was extracted with 3 mL methanol and 5 mL isohexane under sonication (1 h). The isohexane phase was then analyzed by GC/MS. The results (Table S2) show that the amounts of the sorbates extracted from the lignite phase agree well with the sorbed amounts determined by the mass balance calculations, which confirms the mass conservation in the lignite suspensions. On the other hand, moderate losses of some sorbates are suggested for the peat suspensions. These losses would lead to 0.05–0.25 errors in  $\log K_{OC}$ . These levels of errors, however, can neither significantly affect the LFER coefficients (see comparison in Table S3) nor influence the discussions on comparison with the literature PP-LFERs (no data shown). Therefore, the  $K_{OC}$  data for the corresponding sorbates were used in the following discussions without any correction.

Table S2. Recovery test by solvent extraction after sorption equilibration periods<sup>a</sup>.

	recovery obtained by solvent extraction		estimated achievable recovery		recovery for sorbed fraction <sup>d</sup>	
	lignite	peat	lignite	peat	lignite	peat
<i>n</i> -heptane	77%/98% <sup>b</sup>	53%/96% <sup>b</sup>	100%	100%	104%	104%
<i>n</i> -octane	90%	87%	100%	100%		
<i>n</i> -decane	63%/93% <sup>b</sup>	61%/91% <sup>b</sup>	100%	100%	109%	127%
<i>cis</i> -decaline	92%	95%	100%	100%		
<i>trans</i> -decaline	86%	117%	100%	100%		
dichloromethane	81%	76%	80%	82%		
trichloromethane	90%	88%	92%	92%		
tetrachloromethane	88%	86%	99%	99%		
$\gamma$ -hexachlorocyclohexane	75%/90% <sup>b</sup>	94%	100%	100%	93%	
<i>cis</i> -dichloroethene	78%	83%	83%	82%		
trichloroethene	86%	90%	99%	99%		
tribromomethane	92%	93%	96%	97%		
1,2-dibromoethane	98%	97%	86%	90%		
di- <i>n</i> -butyl ether	96%	92%	99%	100%		
di- <i>n</i> -pentyl ether	91%	94%	100%	100%		
<i>n</i> -butyl acetate	93%	0%	91%			
2-octanol	92%	71%	98%	99%		
3-ethyl-3-hexanol	99%	102%	99%	99%		
2,6-dimethyl-2-heptanol	100%	92%	100%	100%		
4-methyl-4-nonanol	101%	97%	100%	100%		
benzene	95%	84%	96%	95%		
chlorobenzene	93%	86%	99%	98%		
1,2-dichlorobenzene	99%	84%	100%	100%		
phenanthrene	75%	48%	100%	100%	99%	72%
fluoranthene	61% <sup>c</sup>	42% <sup>c</sup>	100%	100%	94%	73%
thiophene	85%	83%	91%	92%		
benzofuran	77%	92%	97%	98%		
dibenzofuran	94% <sup>c</sup>	77% <sup>c</sup>	100%	100%	96%	66%
benzothiazole	67%	74%	76%	84%		
anisole	91%	86%	98%	97%		
acetophenone	47%	54%	44%	60%		
ethylbenzoate	105%	0%	94%			
benzonitrile	50%	56%	48%	61%		
4-nitrotoluene	97%	88%	89%	92%		
1-nitronaphthalene	90%	73%	96%	98%	108%	56%
phenol	83%	96%	92%	90%		
2,4,6-trimethylphenol	39%	76%	97%	99%		
2-naphthol	76%	108%	99%	99%		
2-chlorophenol	90%	89%	94%	96%		
4-chlorophenol	93%	89%	94%	95%		
2,4,5-trichlorophenol	110%	119%	100%	100%		

<sup>a</sup>Extraction periods were one to two days, unless otherwise noted. <sup>b</sup>Seven days. <sup>c</sup>Five days. <sup>d</sup>Sorbate mass recovered from the sorbent phase (determined by methanol-isohehexane extraction, SI-2) divided by the sorbed sorbate mass determined by the regular sorptin experiment (based on the mass conservatin assumption, see the main manuscript). Underlined values could lead to >0.3 log-unit errors in log  $K_{OC}$ , and thus the corresponding log  $K_{OC}$  data were not used in the later discussions. Note that errors in log  $K_{OC}$  depend also on the sorbed mass fraction of the sorbate at equilibrium.

Table S3. Comparison of PP-LFER coefficients based on uncorrected and recovery-corrected data for log  $K_{OC, Low}$  of peat.

	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>v</i>	$R^2$	SD	<i>N</i>
Uncorrected log $K_{OC, Low}$ for peat	-1.04	0.31	1.27	-0.10	-3.94	3.71	0.91	0.34	51
SE	0.24	0.20	0.29	0.25	0.35	0.22			
Recovery-corrected log $K_{OC, Low}$ for peat	-0.96	0.29	1.21	-0.04	-3.87	3.65	0.90	0.35	51
SE	0.24	0.20	0.29	0.26	0.36	0.22			

### SI-3. Measured and calculated log $K_{OC}$ values.

Table S4. List of measured and calculated log  $K_{OC}$  by PP-LFERs for peat and lignite<sup>a</sup>.

	lignite		peat			
	log $K_{OC, Low}$		log $K_{OC, Low}$		log $K_{OC, High}$	
	measured	calculated	measured	calculated	measured <sup>b</sup>	calculated
<i>n</i> -pentane	3.03	2.75	n.a.		n.a.	
<i>n</i> -hexane	3.55	3.28	2.92	2.50	2.85	2.53
<i>n</i> -heptane	4.19	3.81	3.42	3.02	3.36	3.02
<i>n</i> -octane	4.66	4.33	3.88	3.55	3.81	3.52
<i>n</i> -nonane	5.28	4.86	4.45	4.07	4.39	4.01
<i>n</i> -decane	5.71	5.39	5.01	4.59	4.95	4.51
isohexane	3.33	3.28	n.a.		n.a.	
cyclopentane	2.61	2.51	n.a.		n.a.	
cyclohexane	2.94	3.05	2.27	2.32	2.15	2.30
cyclooctane	3.72	4.15	3.26	3.40	3.14	3.33
<i>cis</i> -decaline	4.60	4.93	4.12	4.28	3.90	4.03
<i>trans</i> -decaline	4.44	4.89	3.94	4.23	3.74	3.99
dichloromethane	1.59	1.79	0.96	1.44	0.51	1.00
trichloromethane	2.09	2.32	1.57	1.91	1.18	1.55
tetrachloromethane	2.74	2.85	2.11	2.33	1.80	2.04
pentachloroethane	3.30	3.80	2.62	3.47	2.10	2.88
$\gamma$ -hexachlorocyclohexane	4.16	4.34	3.58	3.76	2.82	2.91
<i>cis</i> -dichloroethene	2.22	2.20	1.75	1.86	1.27	1.37
trichloroethene	2.75	2.66	2.35	2.12	2.05	1.87
tetrachloroethene	3.27	3.32	2.73	2.83	2.38	2.47
tribromomethane	2.75	3.00	2.24	2.64	1.70	2.10
1,2-dibromoethane	2.41	2.55	1.98	2.23	1.36	1.59
di- <i>n</i> -propyl ether	2.17	2.06	n.a.		n.a.	
di- <i>n</i> -butyl ether	3.18	3.11	2.24	2.29	2.03	2.04
di- <i>n</i> -pentylether	4.10	4.18	3.14	3.37	2.92	3.04
octan-2-one	3.23	3.00	3.00	2.49	2.45	1.80
<i>n</i> -butyl acetate	2.14	2.32	n.a.		n.a.	
hexanenitrile	2.46	2.58	n.a.		n.a.	
1-nitrohexane	3.35	3.46	2.95	3.28	2.15	2.30
octan-2-ol	3.03	2.78	n.a.		n.a.	
3-ethyl-3-hexanol	2.31	2.64	1.50	1.82	1.25	1.58
2,6-dimethyl-2-heptanol	2.84	3.12	1.92	2.28	1.69	2.03
4-methyl-4-nonanol	3.35	3.68	2.40	2.85	2.15	2.55
benzene	2.34	2.42	1.86	1.92	1.45	1.52
toluene	2.86	2.94	2.47	2.44	2.06	2.01
<i>n</i> -propylbenzene	3.78	3.95	3.21	3.42	2.82	2.96
chlorobenzene	3.15	3.22	2.90	2.85	2.38	2.29
1,2-dichlorobenzene	3.81	3.91	3.55	3.64	2.91	2.92
naphthalene	4.07	4.09	4.00	3.79	3.23	2.97
phenanthrene	5.77	5.75	5.58	5.62	4.36	4.41
fluoranthene	6.50	6.56	6.09	6.62	4.46	5.14
thiophene	2.32	2.15	1.75	1.68	1.30	1.25
benzofuran	3.50	3.35	3.45	3.06	2.77	2.32
dibenzofuran	5.16	4.97	5.20	4.76	4.32	3.80
benzothiazole	3.50	3.05	3.24	2.80	2.27	1.83
anisole	2.79	2.79	2.54	2.38	1.95	1.73
acetophenone	2.89	2.64	2.80	2.33	1.93	1.40
ethylbenzoate	3.54	3.36	n.a.		n.a.	
benzonitrile	2.73	2.67	2.52	2.54	1.54	1.50
4-nitrotoluene	3.60	3.50	3.69	3.37	2.71	2.31
1-nitronaphthalene	4.70	4.85	4.76	5.02	3.06	3.48
phenol	2.08	2.15	1.86	1.94	1.12	1.24
4-ethylphenol	3.02	3.05	3.00	2.81	2.25	2.04
2,6-dimethylphenol	2.92	2.96	2.55	2.58	1.90	1.92
2,4,6-trimethylphenol	n.a.		2.94	2.91	2.30	2.23
2-naphthol	4.24	3.62	4.19	3.42	3.25	2.53
2-chlorophenol	2.79	2.70	2.72	2.43	1.99	1.68
4-chlorophenol	3.00	3.07	3.07	3.06	2.12	2.14
2,4,5-trichlorophenol	4.48	4.34	4.32	4.24	3.55	3.46

<sup>a</sup>Measured values include those from ref 13. Log  $K_{OC, Low}$  values for lignite and peat correspond to log  $K_{OC}$  at sorbed sorbate concentrations of 19 and 4.3 mg/kg-organic-carbon, respectively. <sup>b</sup>Log  $K_{OC, High}$  is estimated for a sorbed sorbate concentration of 430 mg/kg-organic-carbon, using measured log  $K_{OC, Low}$  and the  $1/n-S$  relationship. See the main manuscript for details. n.a., not available.

#### SI-4. Correlation between $\log K_{OC}$ and $\log K_{OW}$ .

For comparison to the PP-LFER approaches,  $\log K_{OC}$  values were plotted with literature  $\log K_{OW}$  (Figure S1). Figure S1 clearly shows that the correlations with  $\log K_{OW}$  were poorer than those obtained with PP-LFERs. The correlation between  $\log K_{OW}$  and  $\log K_{OC, Low}$  measured for peat was in particular weak:  $\log K_{OC, Low}$  varies over 3 log-units for sorbates of similar  $\log K_{OW}$ . For both sorbents, there would be better correlations between  $\log K_{OC, Low}$  and  $\log K_{OW}$  if sorbates were sorted by their H-bonding properties and the presence of aromatic structures. This class-specificity follows the common agreement that prediction using a simple regression with  $\log K_{OW}$  works only within a group of compounds that possess similar interaction properties. Note, however, that grouping of compounds is not always trivial, but rather requires quantitative indicators for interaction properties of each compound, such as the LSER descriptors anyway.

A literature  $\log K_{OC}$ – $\log K_{OW}$  relationship by Karickhoff (15), which is frequently used for environmental modeling, is also shown in Figure S1. Although this relationship was established for PAHs, it underestimates  $\log K_{OC, Low}$  values for naphthalene, phenanthrene, and fluoranthene, too, by more than one log unit. In contrast, the  $\log K_{OC, High}$  values of these PAHs for peat agree well with the relationship from ref 15 (for determination of  $\log K_{OC, High}$ , see the main manuscript). This agreement suggests that nonlinear sorption can explain the deviations between  $\log K_{OC, Low}$  and the literature regression line, which is in accord to the conclusions from PP-LFER calculations in the article. The overall correlation with  $\log K_{OW}$  is also better for  $\log K_{OC, High}$  than for  $\log K_{OC, Low}$ , which shows that relationships between  $\log K_{OW}$  and  $\log K_{OC}$  at environmental concentrations could be even less linear than those reported previously using  $\log K_{OC}$  at near solubility concentrations (16, 17).



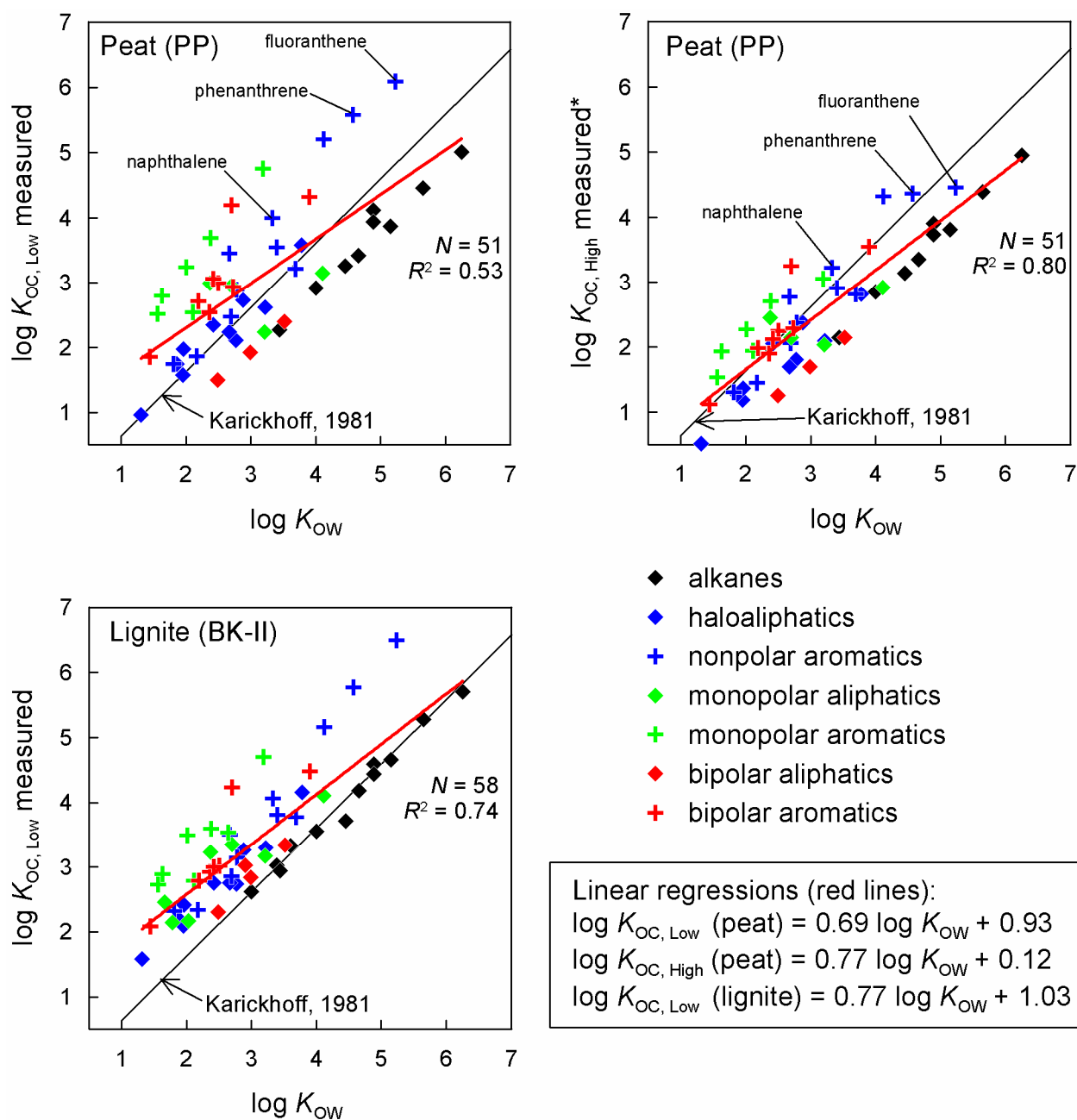


Figure S1. Correlations between  $\log K_{OC}$  and  $\log K_{OW}$ . Red lines are the linear regressions using all sorbates. Black lines indicate the relationship " $\log K_{OC} = 0.989 \log K_{OW} - 0.346$ " reported by Karickhoff (15).  $N$  = number of data points. \*Estimated values based on experimental data, see the main manuscript for details.

#### **SI-5. Re-calculation of PP-LFER equations for log $K_{OC}$ reported by Nguyen et al. (2005) and by Poole and Poole (1999).**

The PP-LFER equations reported by Nguyen et al. (16) and Poole and Poole (17) were re-calculated in this study using the log  $K_{OC}$  compilations by these authors. This re-calculation was done for two reasons. First, updated descriptors are now available for some of the sorbates used in the literature. These sorbates include polychlorinated biphenyls (PCBs) (18) and diuron (19). These updated descriptors are more rigorously calibrated on various experimental partitioning coefficients, and thus are considered to be more accurate. Second, this study and Nguyen et al. used “ $B$ ” descriptor for the solute hydrogen bond basicity, whereas Poole and Poole used “ $B^0$ ” descriptor instead of “ $B$ ”. These two descriptors are numerically identical for most compounds, but slightly different for some compounds such as anilines (for details about these descriptors, see ref 20). Accordingly, the regression coefficients of the PP-LFERs might become slightly different depending on using whether  $B$  or  $B^0$ . Therefore, we analyzed all log  $K_{OC}$  data sets consistently using the  $B$  descriptor.

All sorbates considered and the descriptors used for the re-calculations are listed in Tables S5 and S6 below. Monolinuron was removed from Nguyen’s data set, because only estimated descriptor values were available for this sorbate. For 4-bromoaniline and carbazole,  $B^0$  had to be used nevertheless, as  $B$  values for these sorbates were not available. Poole and Poole excluded seven outliers (urea, 2,3,5-trimethylphenol, 1-aminonaphthalene, diethylacetamide, butylamine, 4-methylphenol) from their analysis. These sorbates, except for diethylacetamide, showed large discrepancies (experimental log  $K_{OC}$  – calculated log  $K_{OC}$  = 0.74–2.21) in our first calculation, too. Therefore, these six compounds were removed from the data set, and the fitting coefficients were calculated again using the remaining data.

The resulting regression coefficients are presented in Table 1 of the main manuscript. The PP-LFERs with these re-calculated regression coefficients are used for discussions throughout the manuscript. The coefficients based on Nguyen's data set have appreciably changed, chiefly due to the updated descriptors for PCBs. For the data set from Poole and Poole, the re-determined coefficients are not different from those published originally by the authors.

Table S5. List of sorbates from Nguyen et al. (16) with their LSER descriptors.

	<i>E</i>	<i>S</i>	<i>A</i>	<i>B</i>	<i>V</i>	<i>L</i>	ref
<b>halo-aliphatic compounds</b>							
trichloromethane	0.425	0.49	0.15	0.02	0.617	2.480	(1)
tetrachloromethane	0.458	0.38	0.00	0.00	0.739	2.823	(1)
1,2-dichloroethane	0.416	0.64	0.10	0.11	0.635	2.573	(1)
1,2-dibromoethane	0.747	0.76	0.10	0.17	0.740	3.382	(1)
1,1,1-trichloroethane	0.369	0.41	0.00	0.09	0.758	2.733	(1)
trichloroethene	0.524	0.37	0.08	0.03	0.715	2.997	(21)
1,1,2,2-tetrachloroethane	0.595	0.76	0.16	0.12	0.880	3.803	(1)
tetrachloroethene	0.639	0.44	0.00	0.00	0.837	3.584	(21)
1,2-dichloropropane	0.371	0.60	0.10	0.11	0.776	2.857	(1)
<b>nonpolar aromatic compounds</b>							
benzene	0.610	0.52	0.00	0.14	0.716	2.786	(1)
toluene	0.601	0.52	0.00	0.14	0.857	3.325	(1)
<i>p</i> -xylene	0.613	0.52	0.00	0.16	0.998	3.839	(1)
<i>o</i> -xylene	0.663	0.56	0.00	0.16	0.998	3.939	(1)
ethylbenzene	0.613	0.51	0.00	0.15	0.998	3.778	(1)
1,3,5-trimethylbenzene	0.649	0.52	0.00	0.19	1.139	4.344	(1)
1,2,3-trimethylbenzene	0.728	0.61	0.00	0.19	1.139	4.565	(1)
1,2,4,5-tetramethylbenzene	0.739	0.60	0.00	0.19	1.280	5.926	(1)
<i>n</i> -propylbenzene	0.604	0.50	0.00	0.15	1.139	4.230	(1)
<i>n</i> -butylbenzene	0.600	0.51	0.00	0.15	1.280	4.730	(1)
chlorobenzene	0.718	0.65	0.00	0.07	0.839	3.657	(1)
1,2-dichlorobenzene	0.872	0.78	0.00	0.04	0.961	4.518	(1)
1,4-dichlorobenzene	0.825	0.75	0.00	0.02	0.961	4.435	(1)
1,3-dichlorobenzene	0.847	0.73	0.00	0.02	0.961	4.410	(1)
1,2,3-trichlorobenzene	1.030	0.86	0.00	0.00	1.084	5.419	(1)
1,2,4-trichlorobenzene	0.980	0.81	0.00	0.00	1.084	5.248	(1)
1,2,3,4-tetrachlorobenzene	1.180	0.92	0.00	0.00	1.206	6.171	(1)
1,2,4,5-tetrachlorobenzene	1.160	0.86	0.00	0.00	1.206	5.926	(1, 3)
PCB-1	1.480	1.07	0.00	0.20	1.447	6.336	(18)
PCB-4	1.600	1.22	0.00	0.20	1.569	6.815	(18)
PCB-8	1.620	1.20	0.00	0.18	1.569	7.197	(18)
PCB-28	1.760	1.33	0.00	0.15	1.691	7.904	(18)
PCB-52	1.900	1.48	0.00	0.15	1.814	8.144	(18)
PCB-153	2.180	1.74	0.00	0.11	2.059	9.587	(18)
PCB-70	1.890	1.46	0.00	0.13	1.814	8.694	(18)
PCB-54	1.840	1.48	0.00	0.15	1.814	7.753	(18)
PCB-155	2.120	1.74	0.00	0.11	2.059	8.715	(18)
PCB-95	2.020	1.61	0.00	0.13	1.936	8.631	(18)
PCB-97	2.040	1.61	0.00	0.13	1.936	9.033	(18)
PCB-101	2.040	1.61	0.00	0.13	1.936	8.868	(18)
PCB-128	2.180	1.74	0.00	0.11	2.059	9.957	(18)
PCB-136	2.140	1.74	0.00	0.11	2.059	9.117	(18)
PCB-194	2.480	2.00	0.00	0.06	2.303	11.186	(18)
PCB-202	2.440	2.00	0.00	0.06	2.303	10.141	(18)
naphthalene	1.340	0.92	0.00	0.20	1.085	5.161	(1)
phenanthrene	2.055	1.29	0.00	0.26	1.454	7.632	(1)
anthracene	2.290	1.34	0.00	0.26	1.454	7.568	(1)
fluoranthene	2.377	1.55	0.00	0.24	1.585	8.827	(8)
1-methylnaphthalene	1.344	0.90	0.00	0.20	1.226	5.789	(1)
2-methylnaphthalene	1.304	0.88	0.00	0.20	1.226	5.617	(2, 22)

1-ethylnaphthalene	1.371	0.87	0.00	0.20	1.367	6.136	(1, 3)
2-ethylnaphthalene	1.331	0.90	0.00	0.20	1.367	6.140	(2, 3)
9-methylanthracene	2.290	1.30	0.00	0.26	1.595	8.438	(2, 3)
pyrene	2.808	1.71	0.00	0.28	1.585	8.833	(8)
naphthacene	2.847	1.70	0.00	0.33	1.823	10.748	(2)
<b>monopolar aromatic compounds</b>							
acetophenone	0.818	1.01	0.00	0.49	1.014	4.501	(1)
<i>N,N</i> -dimethylbenzamide	0.950	1.40	0.00	0.98	1.255	5.457 <sup>a</sup>	(2)
acridine	2.356	1.33	0.00	0.58	1.414	7.644	(2, 3)
methyl phenyl ether (anisole)	0.708	0.74	0.00	0.29	0.916	3.890	(1)
nitrobenzene	0.871	1.11	0.00	0.28	0.891	4.557	(1)
<b>bipolar aromatic compounds</b>							
2,3-dichlorophenol	0.960	0.94	0.48	0.20	1.020	4.989	(23)
2,4-dichlorophenol	0.960	0.99	0.58	0.14	1.020	4.943	(10)
2,4,6-trichlorophenol	1.010	1.01	0.82	0.08	1.142	5.664	(10)
pentachlorophenol	1.220	0.87	0.96	0.01	1.387	6.822	(24)
<i>m</i> -toluidine	0.946	0.95	0.23	0.45	0.957	4.463	(2, 3)
4-bromoaniline	1.190	1.19	0.31	0.35	0.991	5.276	(3, 20)
4-methoxyaniline	1.050	1.19	0.23	0.61	1.016	4.949	(1)
fluometuron	0.650	1.19	0.41	0.79	1.548	6.680	(19)
diuron	1.280	1.60	0.57	0.70	1.599	8.060	(19)
benzamide	0.990	1.50	0.49	0.67	0.973	5.767	(1)
<i>N</i> -methylbenzamide	0.950	1.44	0.35	0.73	1.114	5.367 <sup>a</sup>	(2)
phenylurea	1.110	1.40	0.77	0.77	1.073	5.777 <sup>a</sup>	(17)
3-nitroaniline	1.200	1.71	0.40	0.35	0.990	5.880	(1)
4-nitroaniline	1.220	1.91	0.42	0.38	0.990	6.343	(1)
benzyl alcohol	0.803	0.87	0.33	0.56	0.916	4.221	(1)

<sup>a</sup>Estimated by SPARC May 2008 release w4.2.1405-s4.2.1408 (<http://ibmlc2.chem.uga.edu/sparc/>; accessed July 2008) (11, 12).

Table S6. List of sorbates from Poole and Poole (17) with their LSER descriptors.

	<i>E</i>	<i>S</i>	<i>A</i>	<i>B</i>	<i>V</i>	<i>L</i>	ref
<b>halo-aliphatic compounds</b>							
dichloromethane	0.387	0.57	0.10	0.05	0.494	2.019	(1)
trichloromethane	0.425	0.49	0.15	0.02	0.617	2.480	(1)
tetrachloromethane	0.458	0.38	0.00	0.00	0.739	2.823	(1)
tribromomethane	0.974	0.68	0.15	0.09	0.775	3.784	(1)
1,1-dichloroethane	0.322	0.49	0.10	0.10	0.635	2.316	(1)
1,2-dichloroethane	0.416	0.64	0.10	0.11	0.635	2.573	(1)
1,2-dibromoethane	0.747	0.76	0.10	0.17	0.740	3.382	(1)
1,1,1-trichloroethane	0.369	0.41	0.00	0.09	0.758	2.733	(1)
1,1,2-trichloroethane	0.499	0.68	0.13	0.08	0.758	3.290	(1)
1,1,2,2-tetrachloroethane	0.595	0.76	0.16	0.12	0.880	3.803	(1)
1,1-dichloroethene	0.362	0.34	0.00	0.05	0.592	2.110	(1)
trichloroethene	0.524	0.37	0.08	0.03	0.715	2.997	(21)
tetrachloroethene	0.639	0.44	0.00	0.00	0.837	3.584	(21)
1,2-dichloropropane	0.371	0.60	0.10	0.11	0.776	2.857	(1)
<b>monopolar aliphatic compounds</b>							
<i>N,N</i> -diethylacetamide	0.296	1.30	0.00	0.78	1.070		(2)
ethyl pentanoate	0.049	0.58	0.00	0.45	1.169	3.769	(1)
ethyl hexanoate	0.043	0.58	0.00	0.45	1.310	4.251	(1)
ethyl heptanoate	0.027	0.58	0.00	0.45	1.451		(17)
ethyl octanoate	0.024	0.58	0.00	0.45	1.592		(17)
<b>bipolar aliphatic compounds</b>							
methanol	0.278	0.44	0.43	0.47	0.308	0.970	(1)
ethanol	0.246	0.42	0.37	0.48	0.449	1.485	(1)
1-propanol	0.236	0.42	0.37	0.48	0.590	2.031	(1)
1-butanol	0.224	0.42	0.37	0.48	0.731	2.601	(1)
1-pentanol	0.219	0.42	0.37	0.48	0.872	3.106	(1)
1-hexanol	0.210	0.42	0.37	0.48	1.013	3.610	(1)
1-heptanol	0.211	0.42	0.37	0.48	1.154	4.115	(1)
1-octanol	0.199	0.42	0.37	0.48	1.295	4.619	(1)
1-nonanol	0.193	0.42	0.37	0.48	1.435	5.124	(1)
1-decanol	0.191	0.42	0.37	0.48	1.576	5.628	(1)
trichloroacetamide	0.710	0.63	0.47	0.56	0.873		(17)

acetic acid	0.265	0.65	0.61	0.45	0.465	1.750	(1)
hexanoic acid	0.174	0.60	0.60	0.45	1.028	3.920	(1)
<b>nonpolar aromatic compounds</b>							
benzene	0.610	0.52	0.00	0.14	0.716	2.786	(1)
toluene	0.601	0.52	0.00	0.14	0.857	3.325	(1)
ethylbenzene	0.613	0.51	0.00	0.15	0.998	3.778	(1)
<i>o</i> -xylene	0.663	0.56	0.00	0.16	0.998	3.939	(1)
<i>m</i> -xylene	0.623	0.52	0.00	0.16	0.998	3.839	(1)
<i>p</i> -xylene	0.613	0.52	0.00	0.16	0.998	3.839	(1)
<i>n</i> -propylbenzene	0.604	0.50	0.00	0.15	1.139	4.230	(1)
1,3,5-trimethylbenzene	0.649	0.52	0.00	0.19	1.139	4.344	(1)
1,2,3-trimethylbenzene	0.728	0.61	0.00	0.19	1.139	4.565	(1)
styrene	0.849	0.65	0.00	0.16	0.955	3.856	(1)
1,2,4,5-tetramethylbenzene	0.739	0.60	0.00	0.19	1.280	5.926	(2, 3)
<i>n</i> -butylbenzene	0.600	0.51	0.00	0.15	1.280	4.730	(1)
naphthalene	1.340	0.92	0.00	0.20	1.085	5.161	(1)
1-methylnaphthalene	1.344	0.90	0.00	0.20	1.226	5.789	(1)
2-methylnaphthalene	1.304	0.88	0.00	0.20	1.226	5.617	(2, 22)
1-ethylnaphthalene	1.371	0.87	0.00	0.20	1.367	6.136	(1, 3)
2-ethylnaphthalene	1.331	0.90	0.00	0.20	1.367	6.140	(2, 3)
biphenyl	1.360	0.99	0.00	0.26	1.324	6.014	(14)
anthracene	2.290	1.34	0.00	0.26	1.454	7.568	(1)
9-methylanthracene	2.290	1.30	0.00	0.26	1.595	8.438	(2, 3)
phenanthrene	2.055	1.29	0.00	0.26	1.454	7.632	(1)
fluorene	1.588	1.03	0.00	0.20	1.357	6.922	(1)
fluoranthene	2.377	1.55	0.00	0.24	1.585	8.827	(8)
naphthacene	2.847	1.70	0.00	0.33	1.823	10.748	(2, 3)
pyrene	2.808	1.71	0.00	0.28	1.585	8.833	(8)
benz[a]anthracene	2.992	1.70	0.00	0.33	1.823	10.291	(2, 3)
dibenz[a,h]anthracene	4.000	1.93 <sup>a</sup>	0.00	0.44 <sup>a</sup>	2.192	12.960	(3)
benzo[a]pyrene	3.625	1.98	0.00	0.44	1.954	11.715	(2, 3)
chlorobenzene	0.718	0.65	0.00	0.07	0.839	3.657	(1)
1,2-dichlorobenzene	0.872	0.78	0.00	0.04	0.961	4.518	(1)
1,3-dichlorobenzene	0.847	0.73	0.00	0.02	0.961	4.410	(1)
1,4-dichlorobenzene	0.825	0.75	0.00	0.02	0.961	4.435	(1)
1,2,3-trichlorobenzene	1.030	0.86	0.00	0.00	1.084	5.419	(1)
1,2,4-trichlorobenzene	0.980	0.81	0.00	0.00	1.084	5.248	(1)
1,3,5-trichlorobenzene	0.980	0.73	0.00	0.00	1.084	5.045	(1)
1,2,3,4-tetrachlorobenzene	1.180	0.92	0.00	0.00	1.206	6.171	(1)
1,2,3,5-tetrachlorobenzene	1.160	0.85	0.00	0.00	1.206	5.922	(1)
pentachlorobenzene	1.330	0.96	0.00	0.00	1.329	6.716	(2, 3)
hexachlorobenzene	1.490	0.99	0.00	0.00	1.451	7.624	(2, 3)
bromobenzene	0.882	0.73	0.00	0.09	0.891	4.041	(1)
iodobenzene	1.188	0.82	0.00	0.12	0.975	4.502	(1)
dibenzothiophene	1.959	1.31	0.00	0.18	1.379	7.575	(2, 3)
<b>monopolar aromatic compounds</b>							
<i>N,N</i> -dimethylaniline	0.957	0.84	0.00	0.41	1.098	4.701	(1)
dimethyl phthalate	0.780	1.41	0.00	0.88	1.429	6.051	(2, 3)
diethyl phthalate	0.729	1.40	0.00	0.88	1.711		(2)
methyl benzoate	0.733	0.85	0.00	0.48	1.073	4.704	(1)
ethyl benzoate	0.689	0.85	0.00	0.46	1.214	5.075	(1)
phenyl benzoate	1.330	1.42	0.00	0.47	1.540		(2)
ethyl 4-nitrobenzoate	0.950	1.38	0.00	0.61	1.388		(17)
ethyl phenylacetate	0.660	1.01	0.00	0.57	1.355		(2)
nitrobenzene	0.871	1.11	0.00	0.28	0.891	4.557	(1)
methyl phenyl ether (anisole)	0.708	0.74	0.00	0.29	0.916	3.890	(1)
1,2-dimethoxybenzene	0.810	1.00	0.00	0.47	1.116		(17)
diphenyl ether	1.216	1.08	0.00	0.20	1.383		(2)
benzophenone	1.447	1.50	0.00	0.50	1.481		(2)
acetophenone	0.818	1.01	0.00	0.49	1.014	4.501	(1)
azobenzene	1.680	1.20	0.00	0.44	1.481		(2, 3)
acridine	2.356	1.33	0.00	0.58	1.414	7.644	(2, 3)
<b>bipolar aromatic compounds</b>							
acetanilide	0.870	1.36	0.46	0.69	1.114		(25)
3-methylacetanilide	0.870	1.40	0.50	0.66	1.254		(2)
4-methoxyacetanilide	0.970	1.63	0.48	0.86	1.313		(17)
1-phenylethanol	0.784	0.83	0.30	0.66	1.057	4.394	(2, 3)
benzamide	0.990	1.50	0.49	0.67	0.973	5.767	(1)
4-nitrobenzamide	1.250	2.17	0.75	0.60	1.147		(17)
4-methylbenzamide	0.990	1.50	0.49	0.65	1.114		(17)
2-chlorobenzamide	1.140	1.60	0.45	0.75	1.095		(17)
<i>N</i> -methylbenzamide	0.950	1.44	0.35	0.73	1.114		(2)
aniline	0.955	0.96	0.26	0.41	0.816	3.934	(2, 3)

<i>m</i> -toluidine	0.946	0.95	0.23	0.45	0.957	4.463	(2, 3)
<i>p</i> -toluidine	0.923	0.95	0.23	0.45	0.957	4.452	(1)
4-chloroaniline	1.060	1.13	0.30	0.32	0.939	4.889	(1)
4-bromoaniline	1.190	1.19	0.31	0.35 <sup>b</sup>	0.991	5.276	(3, 20)
<i>N</i> -methylaniline	0.948	0.90	0.17	0.43	0.957	4.478	(1)
diphenylaniline	0.700	0.88	0.60	0.38	1.424		(17)
ethyl 4-hydroxybenzoate	0.860	1.35	0.69	0.45	1.272		(17)
benzoic acid	0.730	0.90	0.59	0.40	0.932		(2)
4-hydroxybenzoic acid	0.930	0.92	0.87	0.53	0.990		(17)
4-nitrobenzoic acid	0.990	1.43	0.68	0.51	1.172		(2)
4-methylbenzoic acid	0.730	0.90	0.60	0.38	1.073		(2)
phenylacetic acid	0.730	0.95	0.60	0.63	1.073		(17)
phenol	0.805	0.89	0.60	0.30	0.775	3.766	(1)
3,5-dimethylphenol	0.820	0.84	0.57	0.36	1.057	4.856	(1)
2-chlorophenol	0.853	0.88	0.32	0.31	0.898	4.178	(1)
3-chlorophenol	0.909	1.06	0.69	0.15	0.898	4.773	(1)
2,3-dichlorophenol	0.960	0.94	0.48	0.20	1.020	4.989	(23)
2,4-dichlorophenol	0.960	0.99	0.58	0.14	1.020	4.943	(10)
3,4-dichlorophenol	1.020	1.20	0.74	0.00	1.020	5.708	(2)
2,4,6-trichlorophenol	1.010	1.01	0.82	0.08	1.142	5.664	(10)
pentachlorophenol	1.220	0.87	0.96	0.01	1.387	6.822	(24)
4-bromophenol	1.080	1.17	0.67	0.20	0.950	5.135	(1)
4-nitrophenol	1.070	1.72	0.82	0.26	0.949	5.876	(1)
2-methoxyphenol	0.837	0.91	0.22	0.52	0.975	4.449	(1)
3-methoxyphenol	0.879	1.17	0.59	0.38	0.975	4.803	(1)
catechol	0.970	1.07	0.85	0.52	0.834	5.060	(2, 3)
resorcinol	0.980	1.00	1.10	0.58	0.834	6.216	(2, 3)
1-naphthol	1.520	1.05	0.61	0.37	1.144	6.130	(1)
phenylurea	1.110	1.40	0.77	0.77	1.073		(17)
carbazole	1.787	1.42	0.47	0.26 <sup>b</sup>	1.315	7.982	(3, 20)

<sup>a</sup>*S* and *B* are for dibenz[*a,c*]anthracene (2). <sup>b</sup>*B*<sup>0</sup> descriptor.

## SI-6. Comparison between lignite and peat.

Figure S2 compares the experimental  $\log K_{\text{OC}, \text{Low}}$  of lignite and peat for 49 sorbates of which data are available for both sorbents. There is an excellent correlation between the two data sets, and the data points are parallel to but slightly above the 1:1 line. Thus, values of  $\log K_{\text{OC}, \text{Low}}$  for lignite are generally higher than those for peat. In our earlier publication (13), we suggested with a smaller data set that these differences in  $\log K_{\text{OC}}$  between lignite and peat are mainly due to the difference in the accessibility of organic carbon between the two sorbents. On the whole, the extended data set from this study led to the same conclusion, as there are no large deviations from the correlation for specific types of sorbates.

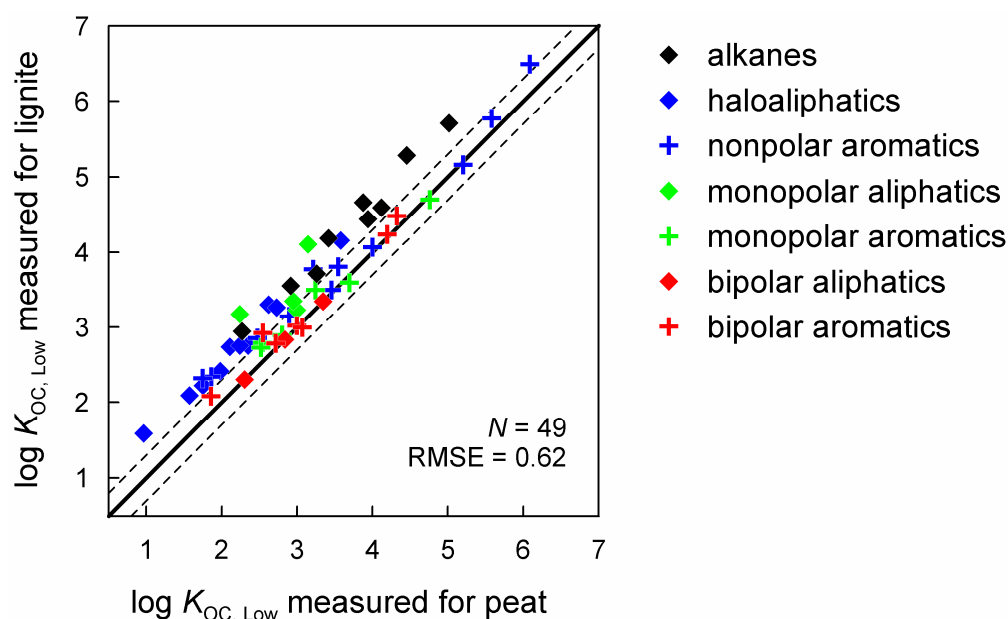


Figure S2. Comparison of measured  $\log K_{\text{OC}, \text{Low}}$  for peat and lignite. The solid line shows the 1:1 agreement. The dashed lines indicate 0.3 log-unit deviations (a factor of 2 for  $K_{\text{OC}}$ ).  $N$  = number of data points; RMSE = root mean square error.

#### **SI-7. Comparison of $\log K_{OC}$ for lignite to the literature PP-LFERs.**

The measured  $\log K_{OC, Low}$  for lignite are generally larger than the predicted  $\log K_{OC}$  by the literature PP-LFERs (16, 17), whereas the PP-LFER based on the lignite data overpredicted the experimental  $K_{OC}$  values in the literature (Figure S3). Nonlinear sorption for lignite cannot completely explain the deviations, because the nonlinearities for the lignite used are relatively small (13). In light of the conclusion from SI-6, the larger site accessibility of organic carbon in lignite may be the main cause of the deviations. Due to the generally high  $K_{OC}$  values toward many sorbates, we conclude that the lignite sample used may not be an appropriate model sorbent to obtain representative values of  $\log K_{OC}$  in typical soil organic matter.



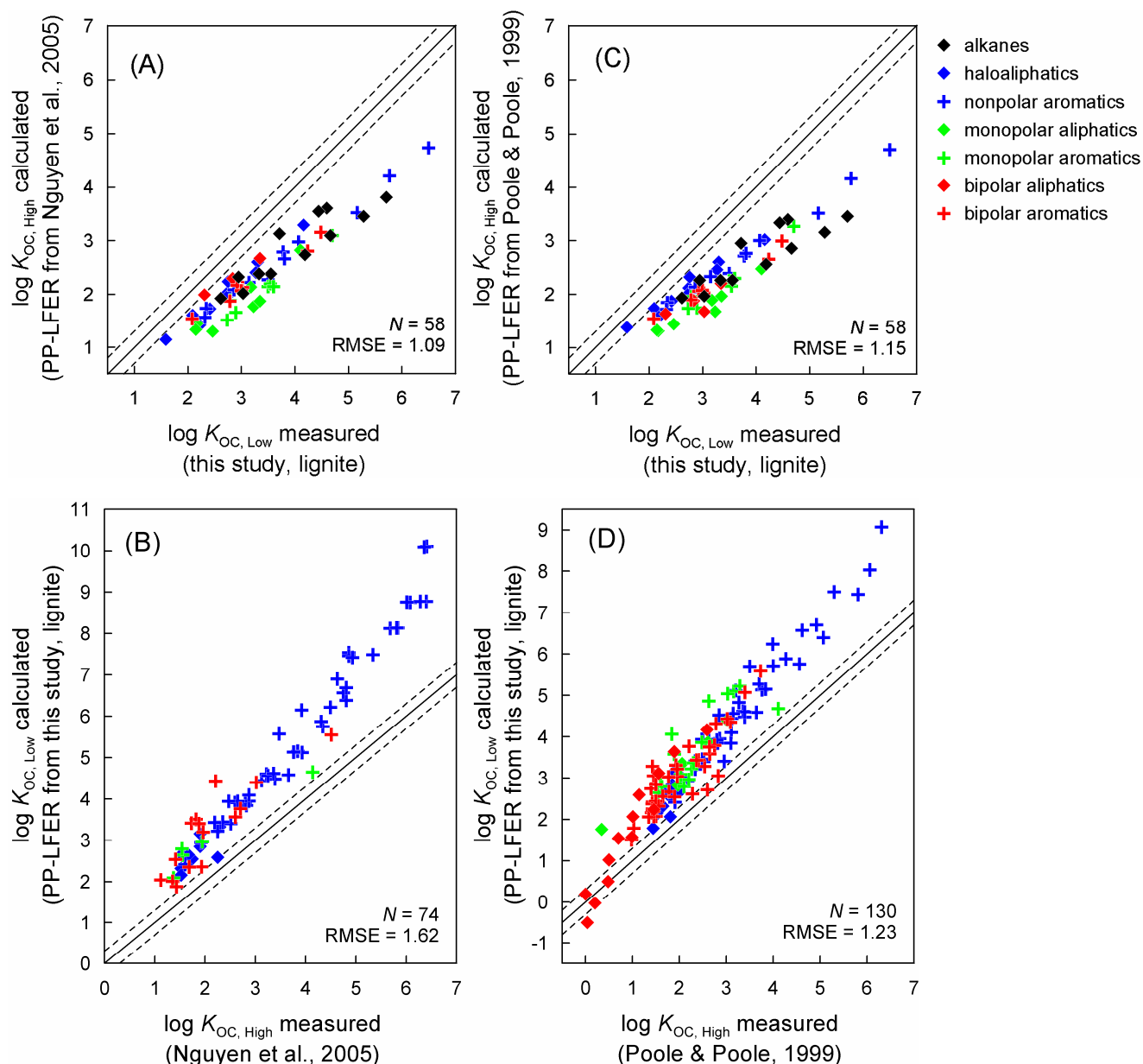


Figure S3. (A) and (C): Log  $K_{OC}$  values measured for lignite and predicted by literature PP-LFERs (16, 17). (B) and (D): Log  $K_{OC}$  values listed in the literature (16, 17) and predicted by the PP-LFER based on the lignite data. Solid lines represent the 1:1 agreement, and dashed lines indicate 0.3 log-unit deviations (a factor of 2 for  $K_{OC}$ ).  $N$  = number of data points; RMSE = root mean square error.

#### SI-8. Comparison of PP-LFERs from this study for peat and from Poole & Poole (1999).

Discussions regarding the PP-LFER from Poole and Poole (17) lead to very similar conclusions compared to the presented discussions on the PP-LFER from Nguyen et al. (16). That is, the PP-LFER from Poole and Poole underpredicts the  $\log K_{OC, Low}$  of many sorbates measured for peat (Figure S4A), and the PP-LFER calibrated on  $\log K_{OC, Low}$  for peat overpredicts the  $\log K_{OC, High}$  collected by Poole and Poole (Figure S4B). Moreover,  $\log K_{OC, High}$  for peat shows a good agreement with the literature data (Figures S4C, D). Also, the data points for *n*-alkanes are not parallel to the 1:1 line in Figure S4C, as was the case when the PP-LFER from Nguyen et al. was used. The data set by Poole and Poole does contain a series of aliphatic sorbates, namely, 1-alkanols from methanol to 1-decanol. However, these data have an unexpected inflection point (see the red lines in Figure S4D), indicating that these  $\log K_{OC}$  values of alkanols are self-inconsistent and do not accurately reflect the influence of  $-CH_2-$  increments on  $\log K_{OC}$ .

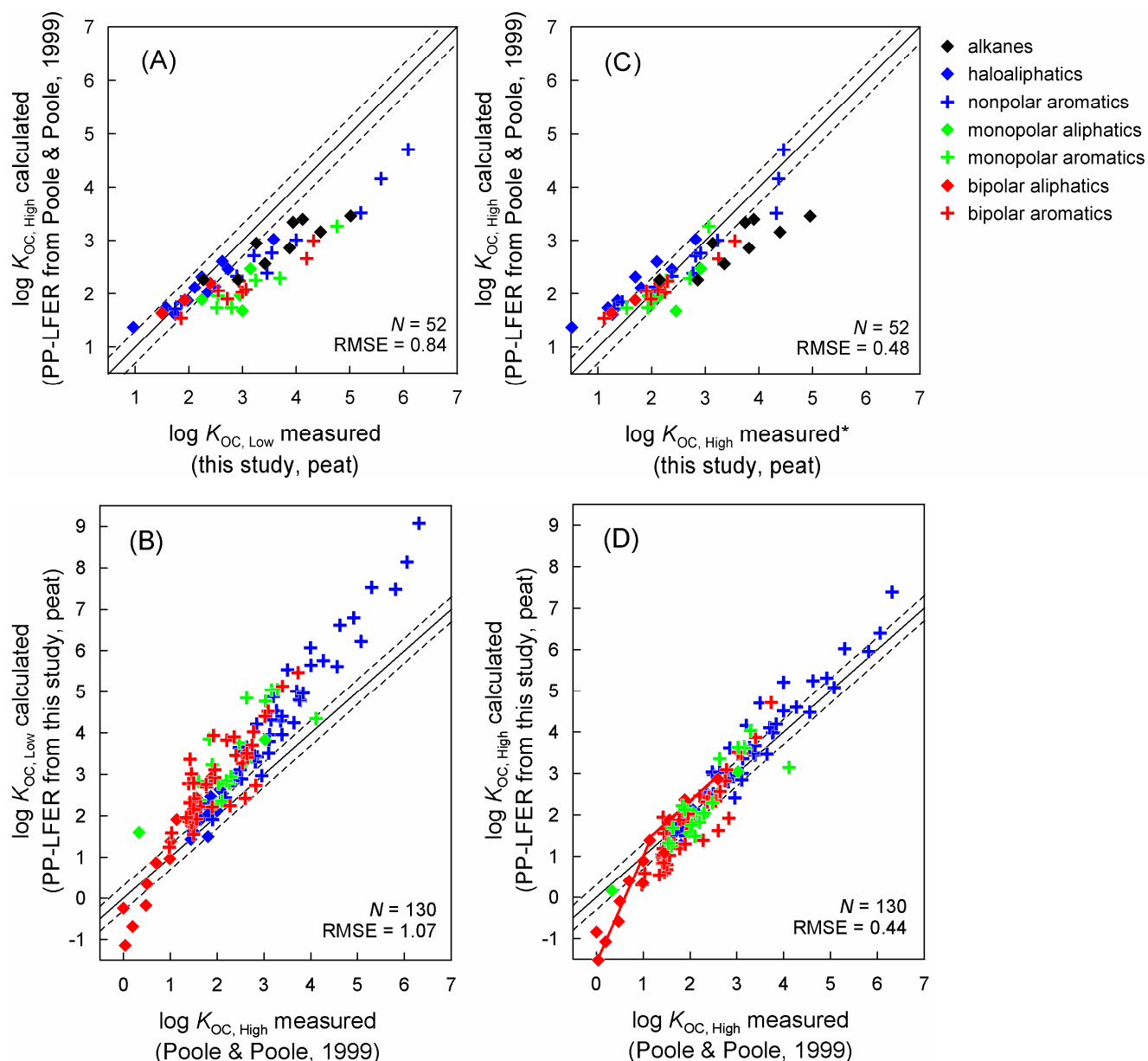


Figure S4. Comparison between calculated (predicted) and measured  $\log K_{OC}$ . (A) Predictions by the PP-LFER from Poole and Poole (1999) vs measured  $\log K_{OC, Low}$  for peat. (B) Predictions by the PP-LFER calibrated on  $\log K_{OC, Low}$  for peat vs measured  $\log K_{OC, High}$  collected by Poole and Poole. (C) Predictions by the PP-LFER from Poole and Poole vs measured  $\log K_{OC, High}$  for peat. (D) Predictions by PP-LFER calibrated on  $\log K_{OC, High}$  for peat vs measured  $\log K_{OC, High}$  collected by Poole and Poole. Solid lines represent the 1:1 agreement, and dashed lines indicate 0.3 log-unit deviations (a factor of 2 for  $K_{OC}$ ). Red lines in panel D are linear regressions for methanol to 1-heptanol and for 1-heptanol to 1-decanol.  $N$  = number of data points;  $RMSE$  = root mean squared error. \*Estimated values based on experimental data, see the main manuscript for details.

**SI-9. Agreement between the  $\log K_{OC, High}$  estimated for peat and the  $\log K_{OC, High}$  predicted by the literature PP-LFER in relation to the sorbed concentration ( $C_s$ ).**

The choice of  $\Delta(\log C_s)$  in eq 4 influences the degree of agreement between the  $\log K_{OC, High}$  estimated for peat and the  $\log K_{OC, High}$  predicted by the literature PP-LFER of Nguyen et al. (16). It is, however, not possible to judge a priori which  $C_s$  is the best representative concentration for the literature data, as experimental concentrations in the literature vary to a large extent. Figure S5 sketches the  $\Delta(\log C_s)$ -dependence of the root mean square errors (RMSE) between the estimated  $\log K_{OC, High}$  for peat and the PP-LFER-predicted  $\log K_{OC, High}$ . The RMSE at  $\Delta(\log C_s) = 0$  in the plot is the RMSE between the measured  $\log K_{OC, Low}$  and the PP-LFER-predicted  $\log K_{OC, High}$ . The RMSE improves with increasing  $\Delta(\log C_s)$  and reaches the smallest value at around  $\Delta(\log C_s) = 2$ . At higher concentrations, the RMSE apparently increases because the resulting  $\log K_{OC, High}$  for aromatic and/or polar compounds (i.e., high  $S$ ) become too low. However, in the range of  $\Delta(\log C_s)$  between 3 and 4 (i.e., 2000–20,000 mg/kg-dry), the equilibrium aqueous phase concentrations of many sorbates reach the solubility limits. Therefore, such higher concentrations would not be realistic.

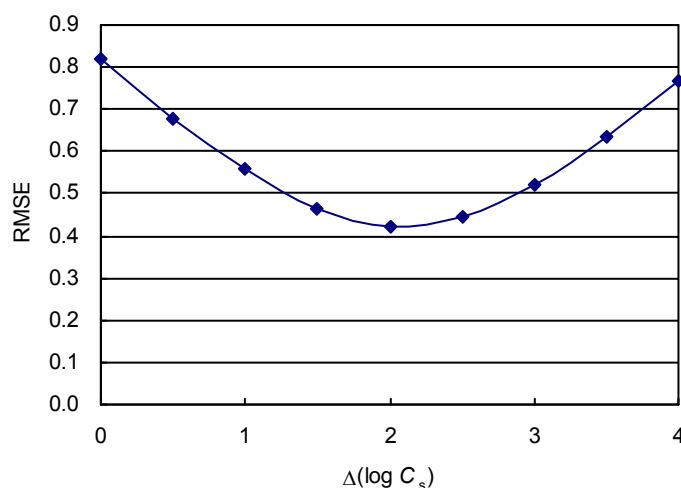


Figure S5. Root mean square errors (RMSE) between the  $\log K_{OC, High}$  estimated for peat and the  $\log K_{OC, High}$  predicted by the literature PP-LFER of Nguyen et al. (16) plotted against  $\Delta(\log C_s)$ . The line simply connects the data points for visual aid.

# SI-10. List of sorbates analyzed individually and sorbates mixed and analyzed together.

Table S7. List of sorbates analyzed individually and sorbates mixed and analyzed together.

sorbates analyzed individually		sorbates mixed
<i>n</i> -pentane	anisole	3-ethyl-3-hexanol
<i>n</i> -hexane	4-ethylphenol	phenol
<i>n</i> -octane	2,6-dimethylphenol	
<i>n</i> -nonane	2-naphthol	2,6-dimethyl-2-heptanol
<i>n</i> -decane	2,4,5-trichlorophenol	4-methyl-4-nonanol
isohexane		
cyclopentane		octan-2-ol
cyclohexane		2,4,6-trimethylphenol
cyclooctane		
<i>cis</i> -decaline		2-chlorophenol
<i>trans</i> -decaline		4-chlorophenol
tetrachloromethane		
pentachloroethane		trichloroethene
$\gamma$ -hexachlorocyclohexane		chlorobenzene
tetrachloroethene		
tribromomethane		acetophenone
1,2-dibromoethane		benzonitrile
di- <i>n</i> -propyl ether		
di- <i>n</i> -butyl ether		chloroform
di- <i>n</i> -pentylether		<i>cis</i> -dichloroethene
octan-2-one		<i>n</i> -heptane
hexanenitrile		
1-nitrohexane		butylacetate
toluene		benzene
<i>n</i> -propylbenzene		thiophene
1,2-dichlorobenzene		dichloromethane
naphthalene		
phenanthrene		ethylbenzoate
fluoranthene		benzofuran
dibenzofuran		4-nitrotoluene
1-nitronaphthalene		benzothiazole

Table S8. Comparison of measured log  $K_{OC}$  between single and mixed sorbate cases.

	single sorbate	mixture
<i>n</i> -heptane (peat)	3.11	3.08
trichloromethane (lignite)	1.86	1.82
trichloroethene (lignite)	2.55	2.48
benzene (lignite)	2.08	2.07

## SI-11. Comparison with PP-LFERs from Niederer et al. (2007).

Niederer et al. (26) measured humic substances–air distribution coefficients for 76–114 compounds in an inverse gas chromatography system. Based on these data, they estimated  $K_{OC}$  through a thermodynamic cycle that uses the air–water partitioning coefficients, and derived PP-LFER equations for  $\log K_{OC}$  for each humic substance. Although there are many differences between their and our experimental settings (listed below), it may be interesting to compare the  $K_{OC}$  data sets as well as the resulting PP-LFERs from both studies.

Comparison was made in mutual directions as was done in the manuscript with the data from Nguyen et al. (16), i.e., Figures S6–S8 compare predictions for  $\log K_{OC}$  from Niederer’s PP-LFERs to our experimental data, and Figures S9–S11 compare predictions from our PP-LFERs to Niederer’s experimental data. Note that a slightly different form of PP-LFER model was fitted in ref 26. Moreover, LSER parameters were not available for a few compounds. These compounds were not included in the comparison.

Three findings can be addressed from the comparison.

- (i) The values of  $\log K_{OC}$  for the Leonadite humic acid and Amherst peat humic acid are in excellent agreement with our values for peat. The agreement is less substantial with humic acids from aquatic environments or fulvic acids in general.
- (ii) Niederer’s experimental/predicted  $\log K_{OC}$  agree better with  $\log K_{OC, \text{High}}$  than  $\log K_{OC, \text{Low}}$  for peat from this study.
- (iii) Lignite is generally a stronger sorbent than the sorbents that Niederer et al. investigated.

These observations appear to be reasonable, and finding (ii) suggests that the experimental concentrations of Niederer et al. were relatively high.

However, it is important to bear in mind that there are numerous differences between the experimental settings of Niederer et al. and ours such as, respectively:

- (I) Base-extracted organic matter vs bulk organic matter
- (II) Sorbent–air vs sorbent–water systems
- (III) Column vs batch experiments
- (IV) Unknown, variable concentrations vs consistent concentrations

Therefore, the conclusions here should rather be considered as preliminary.

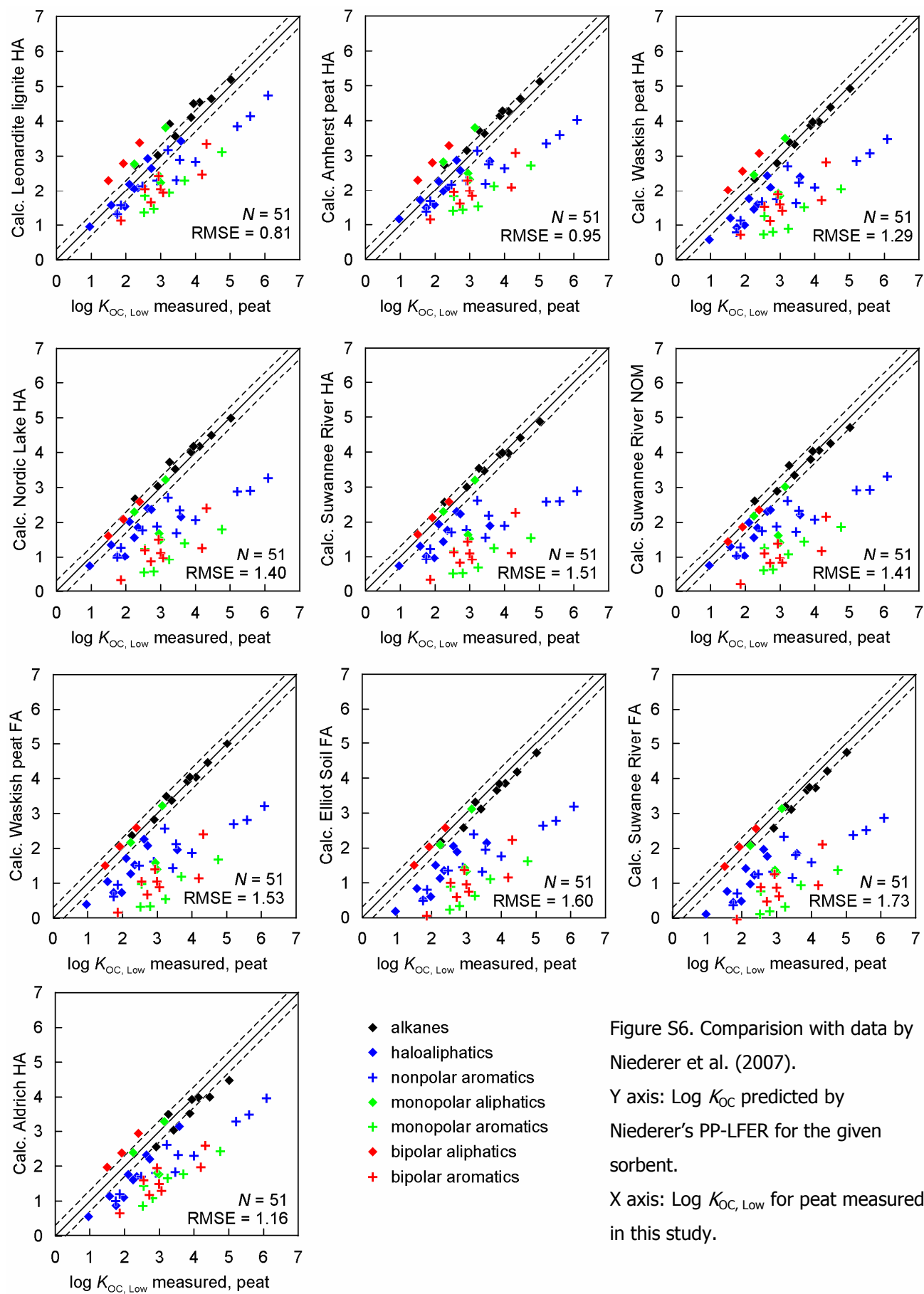


Figure S6. Comparison with data by Niederer et al. (2007).

Y axis:  $\log K_{OC}$  predicted by Niederer's PP-LFER for the given sorbent.

X axis:  $\log K_{OC, Low}$  for peat measured in this study.



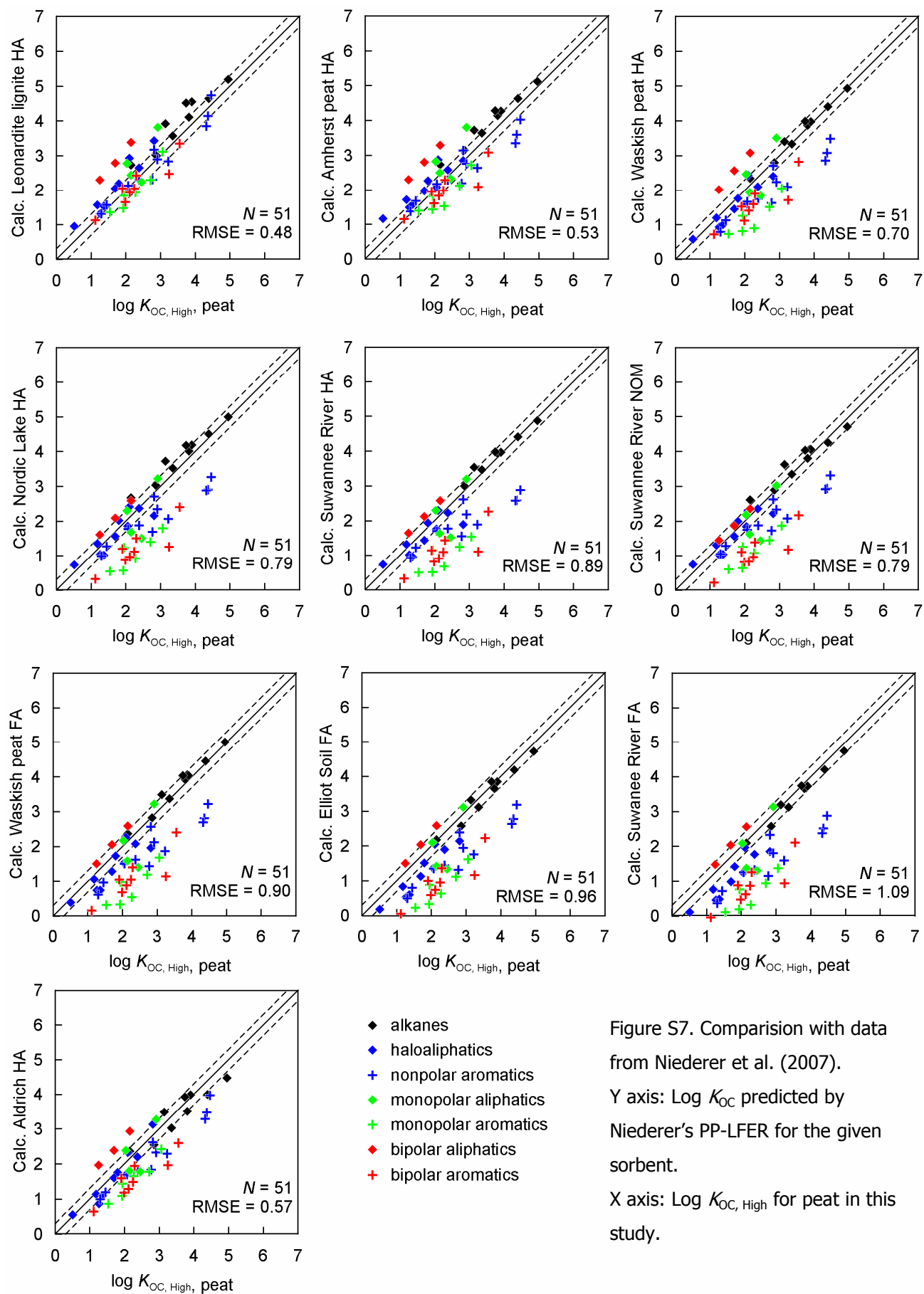


Figure S7. Comparison with data from Niederer et al. (2007).

Y axis: Log  $K_{OC}$  predicted by Niederer's PP-LFER for the given sorbent.

X axis: Log  $K_{OC, High}$  for peat in this study.

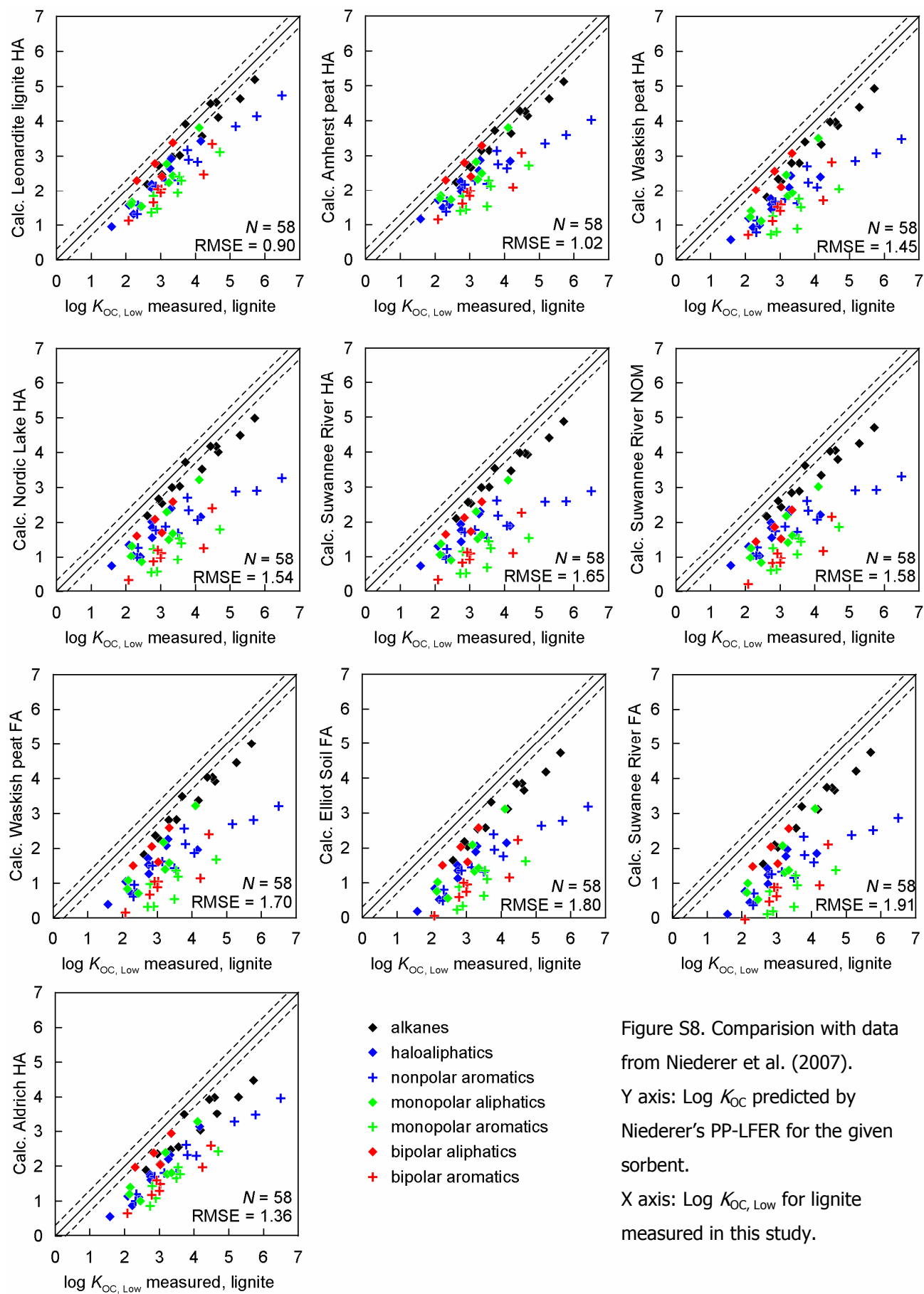


Figure S8. Comparison with data from Niederer et al. (2007).

Y axis: Log  $K_{OC}$  predicted by Niederer's PP-LFER for the given sorbent.

X axis: Log  $K_{OC, Low}$  for lignite measured in this study.

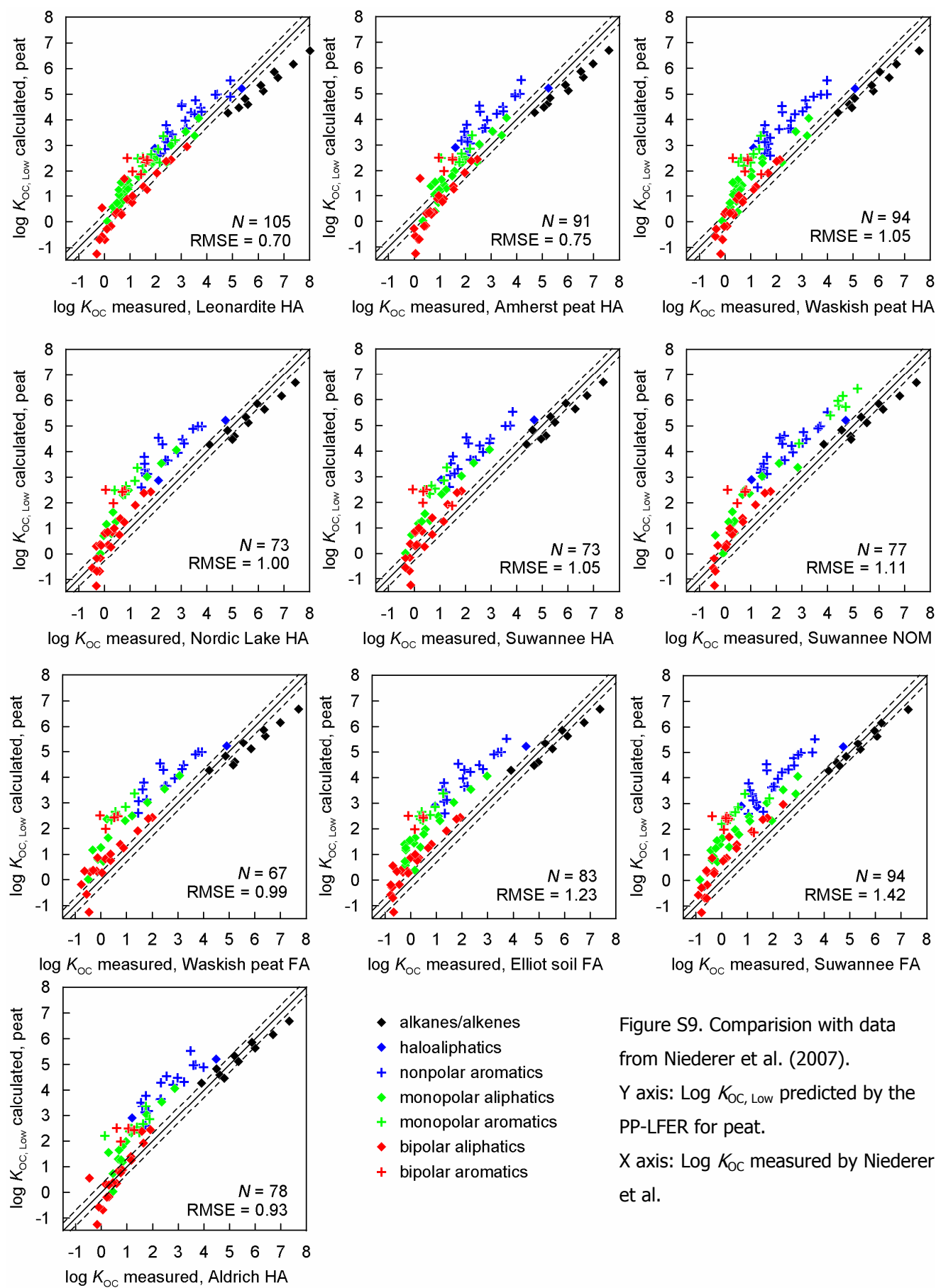
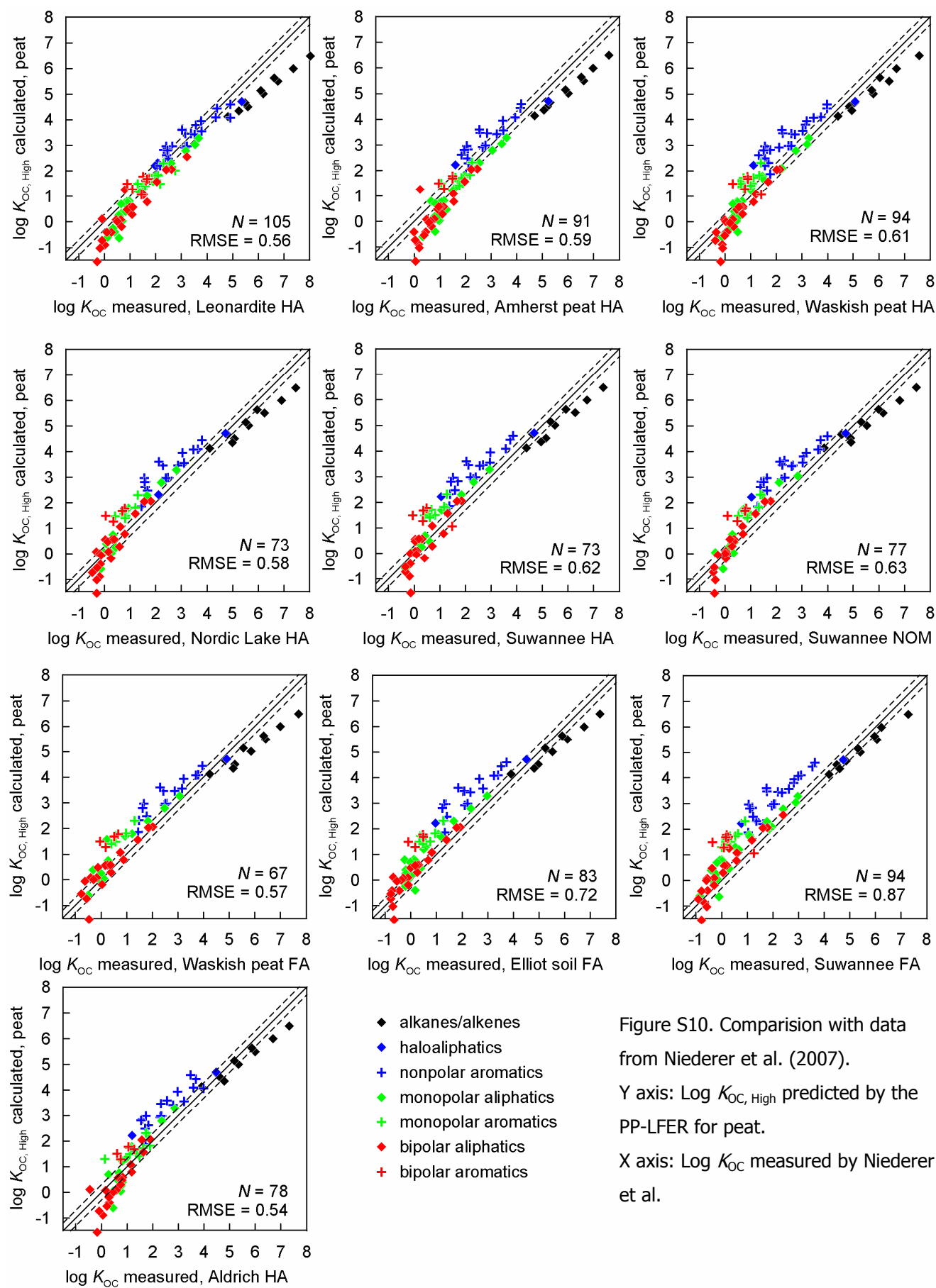


Figure S9. Comparison with data from Niederer et al. (2007).

Y axis:  $\log K_{OC, Low}$  predicted by the PP-LFER for peat.

X axis:  $\log K_{OC}$  measured by Niederer et al.



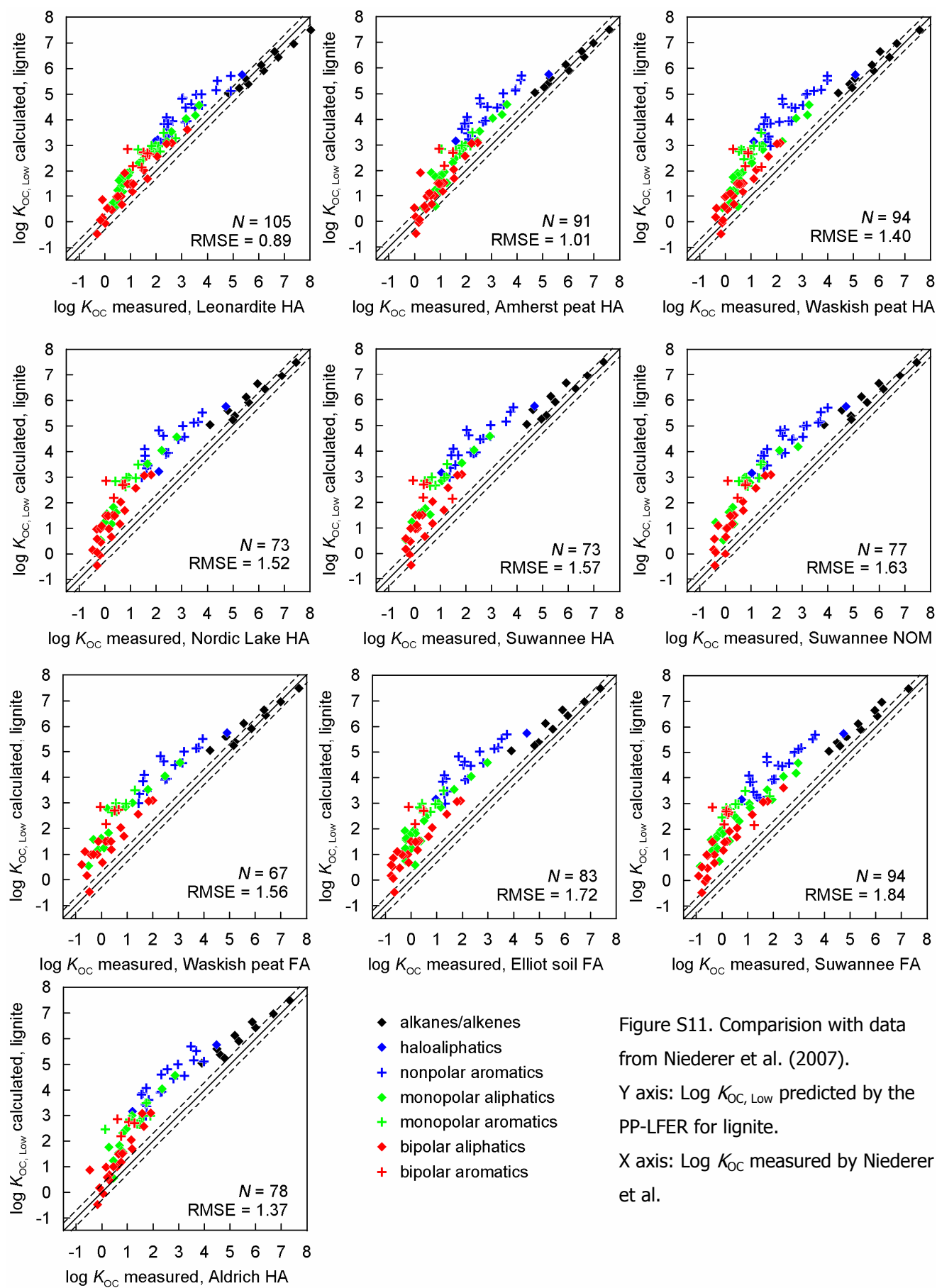


Figure S11. Comparison with data from Niederer et al. (2007).  
Y axis:  $\log K_{OC,Low}$  predicted by the PP-LFER for lignite.  
X axis:  $\log K_{OC}$  measured by Niederer et al.

## Literature Cited in the Supporting Information

- (1) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G. S.; Leo, A.; Taft, R. S. Hydrogen bonding. Part 34. The factors that influence the solubility of gases and vapors in water at 298 K, and a new method for its determination. *J. Chem. Soc. Perkin Trans. 2* **1994**, 1777-1791.
- (2) Abraham, M. H.; Chadha, H. S.; Whiting, G. S.; Mitchell, R. C. Hydrogen bonding. 32. An analysis of water-octanol and water-alkane partitioning and the Dlog P parameter of seiler. *J. Pharm. Sci.* **1994**, 83, 1085-1100.
- (3) Abraham, M. H. Hydrogen bonding. XXVII. Solvation parameters for functionally substituted aromatic compounds and heterocyclic compounds, from gas-liquid chromatographic data. *J. Chromatogr.* **1993**, 644, 95-139.
- (4) Abraham, M. H.; Enomoto, K.; Clarke, E. D.; Sexton, G. Hydrogen bond basicity of the chlorogroup; hexachlorocyclohexanes as strong hydrogen bond bases. *J. Org. Chem.* **2002**, 67, 4782-4786.
- (5) Endo, S.; Schmidt, T. C. Partitioning properties of linear and branched ethers: Determination of linear solvation energy relationship (LSER) descriptors. *Fluid Phase Equilibr.* **2006**, 246, 143-152.
- (6) Weckwerth, J. D.; Carr, P. W.; Vitha, M. F.; Nasehzadeh, A. A comparison of gas-hexadecane and gas-apolane partition coefficients. *Anal. Chem.* **1998**, 70, 3712-3716.
- (7) Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. Hydrogen bonding. XVI. A new solute solvation parameter,  $\pi_2^H$ , from gas chromatographic data. *J. Chromatogr.* **1991**, 587, 213-228.
- (8) Acree, W. E.; Abraham, M. H. Solubility predictions for crystalline polycyclic aromatic hydrocarbons (PAHs) dissolved in organic solvents based upon the Abraham general solvation model. *Fluid Phase Equilibr.* **2002**, 201, 245-258.
- (9) Hoover, K. R.; Acree, W. E. Jr.; Abraham, M. H. Correlation of the solubility behavior of crystalline 1-nitronaphthalene in organic solvents with the Abraham solvation parameter model. *J. Solution Chem.* **2005**, 34, 1121-1133.
- (10) Hoover, K. R.; Acree, W. E. Jr.; Abraham, M. H. Chemical toxicity correlations for several fish species based on the Abraham solvation parameter model. *Chem. Res. Toxicol.* **2005**, 18, 1497-1505.
- (11) Hilal, S. H.; Karickhoff, S. W.; Carreira, L. A. Prediction of the solubility, activity coefficient and liquid/liquid partition coefficient of organic compounds. *QSAR Comb. Sci.* **2004**, 23, 709-720.
- (12) Hilal, S. H.; Saravanaraj, A. N.; Whiteside, T.; Carreira, L. A. Calculating physical properties of organic compounds for environmental modeling from molecular structure. *J. Comput.-Aided Mol. Des.* **2007**, 21, 693-708.

- (13) Endo, S.; Grathwohl, P.; Haderlein, S. B.; Schmidt, T. C. Compound-specific factors influencing sorption nonlinearity in natural organic matter. *Environ. Sci. Technol.* **2008**, *42*, 5897-5903.
- (14) Abraham, M. H.; Benjelloun-Dakhama, N.; Gola, J. M. R.; Acree, W. E., Jr.; Cain, W. S.; Cometto-Muniz, J. E. Solvation descriptors for ferrocene, and the estimation of some physicochemical and biochemical properties. *New J. Chem.* **2000**, *24*, 825-829.
- (15) Karickhoff, S. W. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* **1981**, *10*, 833-846.
- (16) Nguyen, T. H.; Goss, K.-U.; Ball, W. P. Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. *Environ. Sci. Technol.* **2005**, *39*, 913-924.
- (17) Poole, S. K.; Poole, C. F. Chromatographic models for the sorption of neutral organic compounds by soil from water and air. *J. Chromatogr. A* **1999**, *845*, 381-400.
- (18) Abraham, M. H.; Al-Hussaini, A. J. M. Solvation parameters for the 209 PCBs: Calculation of physicochemical properties. *J. Environ. Monitor.* **2005**, *7*, 295-301.
- (19) Green, C. E.; Abraham, M. H.; Acree, W. E. Jr.; De Fina, K. M.; Sharp, T. L. Solvation descriptors for pesticides from the solubility of solids: Diuron as an example. *Pest Manage. Sci.* **2000**, *56*, 1043-1053.
- (20) Abraham, M. H. Hydrogen-bonding. 31. Construction of a scale of solute effective or summation hydrogen-bond basicity. *J. Phys. Org. Chem.* **1993**, *6*, 660-684.
- (21) Grate, J. W.; Abraham, M. H.; Du, C. M.; McGill, R. A.; Shuely, W. J. Examination of vapor sorption by fullerene, fullerene-coated surface acoustic wave sensors, graphite, and low-polarity polymers using linear solvation energy relationships. *Langmuir* **1995**, *11*, 2125-2130.
- (22) Abraham, M. H.; Autenrieth, R.; Dimitriou-Christidis, P. The estimation of physicochemical properties of methyl and other alkyl naphthalenes. *J. Environ. Monitor.* **2005**, *7*, 445-449.
- (23) Abraham, M. H.; Chadha, H. S.; Dixon, J. P.; Rafols, C.; Treiner, C. Hydrogen bonding .41. Factors that influence the distribution of solutes between water and hexadecylpyridinium chloride micelles. *J. Chem. Soc. Perkin Trans. 2* **1997**, 19-24.
- (24) Abraham, M. H.; Martins, F.; Mitchell, R. C.; Salter, C. J. Hydrogen bonding. 47. Characterization of the ethylene glycol-heptane partition system: Hydrogen bond acidity and basicity of peptides. *J. Pharm. Sci.* **1999**, *88*, 241-247.
- (25) Abraham, M. H.; Platts, J. A.; Hersey, A.; Leo, A. J.; Taft, R. W. Correlation and estimation of gas-chloroform and water-chloroform partition coefficients by a linear free energy relationship method. *J. Pharm. Sci.* **1999**, *88*, 670-679.
- (26) Niederer, C.; Schwarzenbach R. P.; Goss, K.-U. Elucidating differences in the sorption properties of 10 humic and fulvic acids for polar and nonpolar organic chemicals. *Environ. Sci. Technol.* **2007**, *41*, 6711-6717.