Supporting Information for

"Compound-Specific Factors Influencing Sorption Nonlinearity in Natural Organic Matter"

in *Environmental Science and Technology*

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SI-1. Physico-chemical properties of probe compounds

compound	Abb.	E[a]	S[a]	A[a]	B[a]	L[a]	log S_w (25 °C)[b] [mg/L]	log K_{ow} (25 °C)[b] [-]	log K_{aw} (20 °C) [-]
n-pentane	nPEN	0.000	0.00	0.00	0.00	2.162	1.62[g]	3.39	1.61[g]
n-hexane	nHEX	0.000	0.00	0.00	0.00	2.668	1.05[g]	3.90	1.73[g]
n-heptane	nHEP	0.000	0.00	0.00	0.00	3.173	0.46[g]	4.66	1.84[g]
n-octane	nOCT	0.000	0.00	0.00	0.00	3.677	-0.13[g]	5.18	1.95[g]
n-nonane	nNON	0.000	0.00	0.00	0.00	4.182	-0.74[g]	5.65	2.07[g]
cyclopentane	cPEN	0.263	0.10	0.00	0.00	2.477	2.19	3.00	0.79[j]
cyclohexane	cHEX	0.305	0.10	0.00	0.00	2.964	1.74	3.44	0.78[j]
cyclooctane	cOCT	0.413	0.10	0.00	0.00	4.329	0.90	4.45	0.51[j]
isohexane[c]	iHEX	0.000	0.00	0.00	0.00	2.503	1.15	3.21[h]	1.75[j]
di-*n*-propyl ether	DNPE	0.008	0.22[d]	0.00	0.45[d]	2.803[d]	3.69	2.03	-0.87[k]
di-*n*-butyl ether	DNBE	0.000	0.24[d]	0.00	0.45[d]	3.924[d]	2.48	3.21	-0.58[k]
benzene	BENZ	0.610	0.52	0.00	0.14	2.786	3.25	2.13	-0.74[j]
toluene	TOL	0.601	0.52	0.00	0.14	3.325	2.72	2.73	-0.70[j]
n-propyl benzene	PrBZ	0.604	0.50	0.00	0.15	4.230	1.72	3.69	-0.49[j]
trichloromethane	TrCM	0.425	0.49	0.15	0.02	2.480	3.90	1.97	-0.90[l]
tetrachloromethane	TeCM	0.458	0.38	0.00	0.00	2.823	2.90	2.83	-0.02[l]
trichloroethylene	TCE	0.524	0.37	0.08	0.03	2.997	3.11	2.42	-0.50[l]
tetrachloroethylene	PCE	0.639	0.44	0.00	0.00	3.584	2.31	3.40	-0.27[l]
2-octanone	OCTON	0.108	0.68	0.00	0.51	4.257	2.95	2.37	-2.31[m]
hexanenitrile	HXNTRL	0.166	0.90	0.00	0.36	3.472[e]	3.39[h]	1.66	-2.55[n]
1-nitrohexane	NTRHX	0.203	0.95	0.00	0.29	4.441[f]	2.26[h]	2.70	-2.04[o]
4-ethylphenol	4EtP	0.800	0.90	0.55	0.36	4.737	3.89[i]	2.58	-4.85[o]
2,6-dimethylphenol	26DMP	0.860	0.79	0.39	0.39	4.680	4.02[i]	2.36	-4.16[o]
naphthalene	NAPH	1.340	0.92	0.00	0.20	5.161	2.02[i]	3.30	-1.90[l]

[a] Linear solvation energy relationship parameters. Data from Abraham et al. (*1-5*) unless otherwise noted.

[b] S_w, aqueous solubility; K_{ow}, octanol-water partitioning coefficients; Ref *6*.

[c] Properties shown are for 2-methylpentane.

[d] Ref *7*.

[e] Ref *8*.

[f] Extrapolated from data for nitromethane to 1-nitropentane.

[g] Calculated by LSER. See SI-3.

[h] Estimated values.

[i] Subcooled liquid solubilities. The value for NAPH is from ref *9*; Solid solubilities for 4EtP and 26DMP are from ref *6* and fugacity ratios from ref *10*.

[j] Ref *11*.

[k] Determined experimentally in this study by the method presented in ref *12*.

[l] Ref *13*.

[m] Interpolated from values for 2-butanone to 2-nonanone (*14*).

[n] Interpolated from values for propanenitrile to octanenitrile (*15*).

[o] Estimated by the LSER equation (*16*).

SI-2. Details of materials and sorption experiments

Materials. The lignite sample (BK-II) was collected from the Oberlausitz area in Saxony, Germany. Pahokee peat soil (PP) was purchased from the International Humic Substances Society. These humified materials were pulverized with a zirconium oxide planet ball mill (Laborette, Fritsch) to shorten the time necessary to attain sorption equilibrium. Particle size distribution analysis for BK-II using laser diffraction showed that 50 % were < 20 μm and 90 % < 100 μm in diameter. Properties of the pulverized sorbents are presented in Table 1. The BET adsorption experiment using nitrogen gas (Gemini surface area analyzer, Micrometrics GmbH) was carried out for the specific surface area measurement. C and N content was determined by elemental analysis (Vario EL, Elementar). Polydimethylsiloxane (PDMS) and polyacrylate (PA) SPME fibers were obtained from Supelco. Chemicals were purchased from different providers and used without further purification. Stated purities were 98 % or better. List of the probe compounds used and their abbreviations are given in Table 2 and in SI-1. Isohexane was a mixture of 2-methylpentane and 3-methylpentane. These were assumed to behave identically during sorption, as relative chromatographic peak areas before and after sorption were the same. Sorption experiments for naphthalene were conducted with deuterated naphthalene, because the background concentrations of native naphthalene were significant.

Stock Solutions. Stock solutions were prepared in methanol at various concentrations (0.2 ppm to 20 vol%) in methanol. For liquid compounds, high concentration stock solutions (≥ 2000 ppm) were made by dissolving pure liquid into methanol. Excess volumes of mixing were assumed to be negligible. Stock solutions with lower concentrations were prepared by diluting the high concentration solutions (usually one step). The densities of pure liquids at 25 °C were used to convert the concentrations to mg/L. High concentration stock solutions of solid compounds were prepared in 10-mL volumetric flasks which were filled up with methanol. Lower concentrations were then obtained by step dilution

(max. 2 steps). Fresh stock solutions were made every two months, except for small alkanes (nPEN, nHEX, cPEN, cHEX) for which stock solutions were remixed about weekly owing to their relatively high air-methanol distribution coefficients (0.005–0.02, estimated by LSER).

Batch Sorption Experiments. Generally, 12 different concentrations ranging over more than 4 orders of magnitude were prepared in duplicate for each probe compound. The maximum equilibrium concentration was 0.01–0.8 times the aqueous solubility (S_w) and the minimum was 10^{-7}–10^{-5} times S_w, depending on the compounds. Sorption batches were prepared with 20-mL crimp-top headspace glass vials. Sorbents of 0.02 to 1 g were weighed into vials and 10 or 15 mL of water containing 200 mg/L NaN_3 as biocide and 5 mM $CaCl_2$ as ionic strength regulator were added. Amounts of sorbent were adjusted so that 40–95 % of the added compound was sorbed at equilibrium. Preliminary experiments were performed with 4–6 batches to find appropriate amounts of sorbent. Most of sorbent particles floated when mixed with water. To wet the sorbent, the vials were closed with polyethylene caps lined inside with aluminum-foil-covered silicon/PTFE septa, and shaken at 150 strokes/min on a horizontal shaker for 1 d (> 20 h). Subsequently, the caps and aluminum foil were removed and the top of the vials was wiped with clean tissue. Separate experiments with 0.5 g of BK-II suggested that the aluminum foil and tissue would remove just < 0.2 wt% of the sorbent in the batch. The batches were then spiked with methanolic stock solutions and crimped with metal caps with butyl rubber/PTFE septa. Methanol content did not exceed 0.25 vol% in water to avoid cosolvent effects in the aqueous phase. Instead, to achieve desired concentrations in water, stock solutions of different concentrations were prepared as described above. For nPEN, cPEN, cHEX, DNPE, 2-octanone and 1-nitrohexane, pure liquid had to be injected into batches to realize highest concentrations. After spiking, the sorption batches were horizontally shaken at 150 strokes/min in a temperature-controlled room at 20 °C. The batches were occasionally shaken also by hand to mix the sorbent. Sorption time of 10 d was given for equilibrium. Separate experiments for DNBE and PrBZ on BK-II indicated that aqueous concentrations after 1, 2, 3

and 4 weeks do not significantly differ. Other studies using lignite or peat samples chose comparable times (7–21 d, refs *17-19*).

Aqueous Concentration Determination. Headspace was analyzed for volatile compounds, namely, alkanes, ethers, alkyl benzenes and chlorinated compounds in the entire concentration ranges, and 2-octanone, hexanenitrile, 1-nitrohexane, 4EtP, 26DMP and NAPH were measured by SPME at low concentrations and by headspace injection at high concentrations. Repeated headspace analysis suggested that reproducibilities of headspace measurements are 1–5 %, except for alkanes (2–10 %). For the compounds analyzed by SPME, sorption batches were recovered on the 9th day and suspended particles were allowed to settle for 1 d. The supernatant was then filtered with an alumina membrane filter (0.2 μm pore, Anodisc 13, Whatman) hosted by a stainless steel filter holder (Whatman) under pressure. Filtrates were adjusted to 5 or 10 g and spiked with an internal standard. Internal standards used were 1-nitrohexane for 2-octanone, methyl *t*-butyl ether for hexanenitrile, 2-octanone for 1-nitrohexane, 2-ethylphenol for 4EtP and 26DMP, and native NAPH for deuterated NAPH. Although some of the internal standards are not best analogues to the target compounds, repeated experiments with spiked water and DOM solutions (made by mixing BK-II or PP with water and filtration) showed that relative standard deviations improved from 5–16% to 2–4 % by the correction to the internal standards. The filtration procedure significantly decreased the concentration only for NAPH and 1-nitrohexane (up to 10 %), as examined in separate experiments without sorbent. Corrections for this were not made because coexisting substances (e.g., DOM) in sorbent/water suspensions presumably compete with the analyte at the filter surface and reduce loss of the analyte to the filter. Indeed, the uncorrected isotherms are more continuous with the data measured by headspace compared to corrected isotherms (data not shown).

Calibration standards were made in water without $CaCl_2$, NaN_3 and sorbent. To cover wide

concentration ranges, 14–22 standards were prepared for each isotherm measurement. The standard solutions were mixed one day before measurements and shaken occasionally by hand to ensure complete dissolution of the compounds in water and equilibrium between air and water.

A GC/MS (TraceGC 2000/TraceDSQ, ThermoFinnigan) equipped with an autosampler (CombiPAL, CTC Analytics) and a temperature-adjustable sample tray (PAL Tray Cooler 2) was used throughout the experiments. The temperature of the sample tray was set to 20 °C. An RTX-VMS capillary column (60 m × 0.32 mm i.d., 1.8 μm film thickness, Restek Corp.) with a deactivated precolumn (0.4 m × 0.53 mm i.d.; BGB Analytik) was installed for chromatographic separation. Helium was used as carrier gas at 1.5 mL/min. The temperatures of the transfer line and the ion source were set to 250 and 220 °C, respectively. SIM mode monitoring two to four ions for each compound was employed for quantification.

In headspace extraction methods, 250–1000 μL of the headspace were taken and injected into the GC using the autosampler. For some high concentration samples, 50 μL were taken manually by a valve-lock gas-tight syringe. The split mode was applied for injection, with the split ratio being 20 to 100. A high injection volume and a small split ratio were selected for low concentration measurements, and vice versa. Analytes were measured isothermally at an oven temperature between 70 and 160 °C depending on the compound retention. The injection port was set at 150–250 °C, always at least 30 °C higher than the oven temperature. The sample solutions were placed on the sample tray at least 1 h prior to measurements to ensure the equilibrium between the headspace and water. After each measurement, the syringe was cleaned with nitrogen stream for 1–2 min to avoid carry-over. For phenols, the syringe had to be flushed for 5 min at 60 °C.

SPME fibers were conditioned in the GC injection port at 250 °C for 30 min (PDMS) or at 300 °C for 2

h (PA). For extraction, the fibers were dipped into the water for 15 min. For relatively high concentration samples, sorption time was shortened to 5 min. Desorption was carried out in the GC injection port at 250 °C for 2 min (PDMS) or at 280 °C for 3 min (PA). The purge valve was initially closed, and opened when the desorption time had elapsed. The fiber was further heated for 3 to 6 min to avoid carryover. The GC oven temperature was initially 40 °C and, after desorption, ramped up to 200 °C at the rate of 10 °C/min. For phenols, the temperature was increased from 40 °C to 140 °C at 20 °C/min, to 200 °C at 5 °C/min and held for 3 min.

Mass Balance Calculation. Sorbed concentrations were computed by mass balance. Control batches spiked with a sorbate compound but without sorbent were run in parallel to check the sorbate loss. For most compounds, nearly 100 % of injected amounts in control batches remained after 10 d. Significant loss (5–20 %) from controls was observed for nHEP, nOCT, nNON, PCE, PrBZ and 1-nitrohexane. Loss relative to the injected amount was nearly constant for each compound and independent of the injected amounts. Leak of the gas from headspace is unlikely because, if so, concentration decrease should have been greatest for alkanes, of which K_{aw} values are the highest of our probe compounds. It is likely that the loss was due to diffusion through septa. The loss was corrected in mass balance calculation by assuming that the escaped amount is proportional to the final concentration in water. Degradation of sorbate compounds in the presence of the sorbents was examined for nOCT, DNBE, TeCM and 2-octanone in separate experiments, where the sorbate compounds in sorption batches were extracted with 5 mL isohexane. The recovery of 85–100 % was obtained in both BK-II and PP, confirming no significant degradation during the sorption experiments. The only exception was 2-octanone in PP, which showed a significantly smaller recovery (60%). In fact, after the 10-d sorption experiment for 2-octanone with PP, we found a significant peak for a reduction product, 2-octanol in water (identified from the mass spectrum by the scan mode analysis). With the increasing initial concentration of 2-octanone, the 2-octanol peak became almost negligible compared to the growing

2-octanone peak. Further, if no mass loss is assumed for 2-octanone, the resulting isotherms would be too nonlinear in low concentrations compared to the other compounds (see figure below), whereas the isotherms at C_w > 0.5 mg/L are comparable to the other compounds. A similar isotherm shape was obtained for 1-nitrohexane in PP as well, although no degradation product of 1-nitrohexane was found. This is likely because the reduction product (expectedly 1-hexylamine) is very water soluble and thus a significant amount was not extracted by the PDMS-SPME fiber. To prevent reduction of 2-octanone, 5 mM $NaNO_2$ or 5 mM Fe(III)-citrate were introduced into water, but in both cases the resulting isotherms were identical to that before. For the discussion about nonlinearities and molecular interactions in the main manuscript, log K_d and log $K_{soil(h)/air}$ of 2-octanone and 1-nitrohexane at low concentrations were extrapolated from C_w > 0.5 mg/L as first approximations. In BK-II, the 2-octanol peak was not found, and the isotherms for 2-octanone and 1-nitrohexane match the trend of the other compounds. This agrees with the fact that almost 100 % of 2-octanone in BK-II was recovered by solvent extraction.

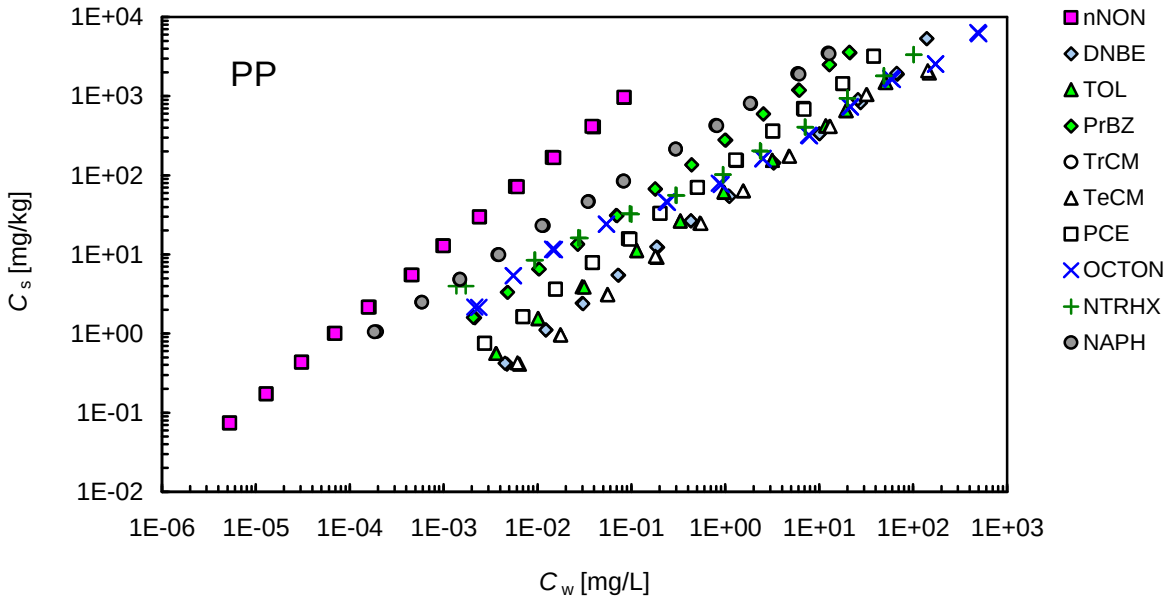

Figure SI-2. Apparent sorption isotherms for 2-octanone (OCTON) and 1-nitrohexane (NTRHX) in PP, likely influenced by degradation. Isotherms for some selected compounds are shown for comparison.

Background concentrations and procedural contaminations of the analytes were monitored by non-spiked vials with and without sorbent. Background concentrations were detectable for nPEN, nHEX, cHEX, iHEX, BENZ and TOL. For these compounds, only measured concentrations above 10-fold background concentrations were considered.

For volatile compounds, the fraction in the headspace was taken into account by calculating the gas phase concentration with K_{aw} and the volume of the headspace. Internal volumes of 20-mL headspace vials were measured in advance by weighing pure water, and the mean value (21.1 ± 0.1 mL, n = 20) was used for all vials. The volume occupied by sorbent is accounted for by using the measured volume increases of 0.68 and 0.61 mL/g for BK-II and PP, respectively. Inaccuracies in K_{aw} do not cause errors in sorbed concentrations, because the resultant variations in C_w are compensated with those in the air phase concentration. However, inaccurate K_{aw} does influence K_d as well as $K_{soil(h)/air}$. Accurate K_{aw} values of *n*-alkanes are extremely difficult to obtain (see SI-3). Fortunately, variations in K_{aw} do not cause errors in the $K_{soil(h)/air}$ values for *n*-alkanes determined in our experimental systems, because (i) the fraction in water does not contribute to the mass balance due to high K_{aw} and (ii) in standard batches nearly all (> 94 %) of the compound is estimated to be in the headspace, so the peak area can be directly calibrated to the headspace concentration. Freundlich exponents ($1/n$) of *n*-alkanes do not change due to the variation of K_{aw} values, but K_d and Freundlich coefficients (K_{Fr}) do.

SI-3. Air-water distribution coefficients (K_{aw}) of *n*-alkanes

Although the K_{aw} value at a certain temperature should be unique for each compound, reported K_{aw} (and aqueous solubility; S_w) data exhibit considerably large variations owing to experimental difficulties associated with alkanes' high volatility and scarce solubility (Figure SI-3-1). Note that K_{aw} and S_w are equivalent if the saturation vapor pressure is known, since S_w values of alkanes are so low that K_{aw} values between the saturated and diluted solutions do not differ. Thus, S_w data were converted to K_{aw} and shown together in Figure SI-3-1. There is a relatively good agreement in experimental data for short *n*-alkanes up to C_7, but plots are considerably scattered for larger alkanes. Data for > C_8 are not only scattered, but exhibit some upwards deviations from the linear increase till C_{11} and a sudden drop at C_{12}. This suggests that there exist systematic errors in the experimental data sets and taking the mean of many values does not solve the problems.

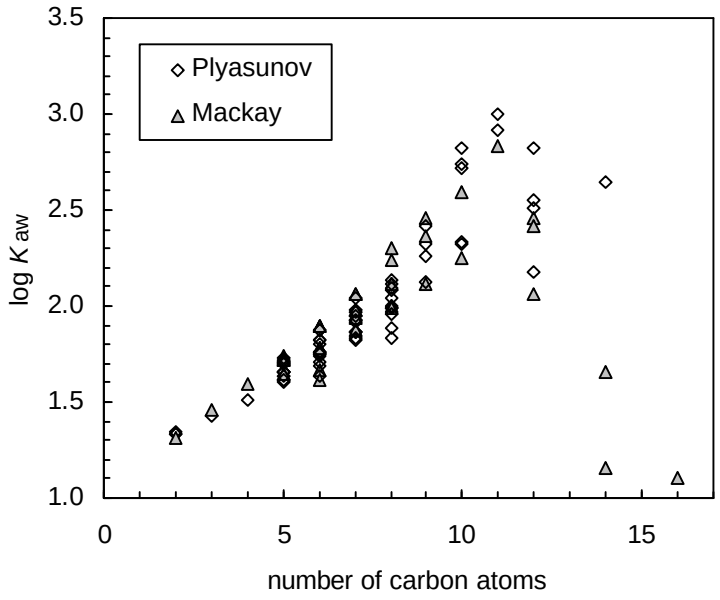

Figure SI-3-1. Experimental log K_{aw} at 25 °C for *n*-alkanes (data collected by Mackay and Shiu (*20*) and by Plyasunov and Shock (*11*)).

To evaluate consistency of K_{aw} values for *n*-alkanes, we compared the following values (all for 25 °C).

- Recommended values by Mackay and Shiu (*20*).
- Values chosen by Plyasunov and Shock (*11*).
- Estimated values by a linear solvation energy relationship (LSER) equation (*1*).
- Estimated values by HenryWin implemented in EPI-Suite (*21*).

The two recommended experimental data sets are nearly identical and show a good linearity up to C_8 (Figure SI-3-2). Mackays' data are always slightly higher than Plyasunovs'. This is due partially to the different data sets they used, and also because the former researchers principally took the arithmetic means, while the latter the geometric means (or the arithmetic means of "log" K_{aw}). However, for alkanes longer than C_9, linearity does not exist any longer. HenryWin provides two estimations for each compound, one based on the bond contribution method and the other on the fragment method. The LSER and the bond contribution method in HenryWin are in good agreement, and almost identical to the extrapolated line from Mackays' recommended values up to C_8. This may be partly due to the fact that some data are shared by the calibration data sets of HenryWin and LSER and by Mackays' set. Nevertheless, both HenryWin and LSER are calibrated with experimental data for many compounds (408 in LSER) which affect fitting parameters and, accordingly, estimations for *n*-alkanes. Therefore, in this study, log K_{aw} values from LSER were considered as currently the most consistent values for *n*-alkanes. The group contribution method in HenryWin resulted in steeper lines than the experimental C_2-C_8 data, and thus are considered less consistent.

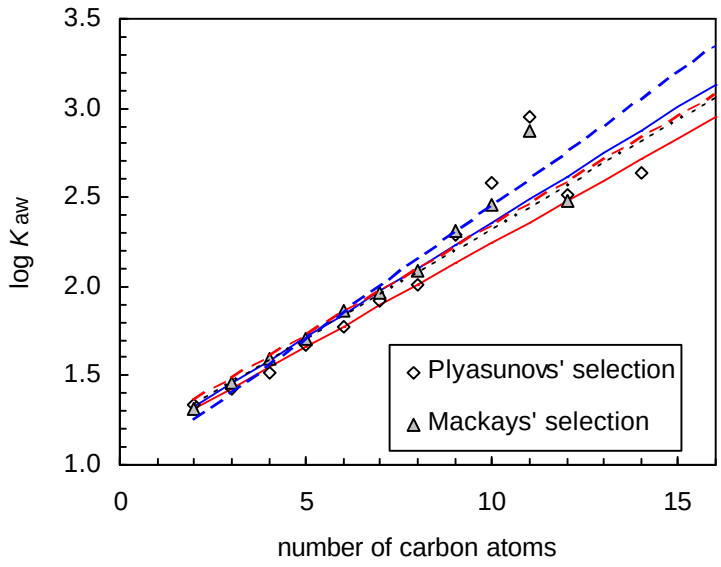

Figure SI-3-2. Recommended values by Plyasunov and Shock (*11*) and Mackay and Shiu (*20*). Lines indicate extrapolations from C_2-C_8 data of Plyasunov and Shock (solid, red), extrapolations from C_2-C_8 data of Mackay and Shiu (solid, blue), estimations by LSER (dotted, black) and by the bond contribution method (dashed, red) and the group contribution method (dashed, blue) in HenryWin.

Values of log K_{aw} at 20 °C were computed using the enthalpy values given in ref *11*. The enthalpy values in ref *11* are linear against the number of carbon atoms and thus regarded as consistent. The enthalpy for *n*-nonane was obtained by extrapolation. Small differences in the enthalpy do not significantly affect the results, since the temperature difference is small.

SI-4. Maximum and minimum sorbed concentrations (mg/kg-dry) of measured sorption isotherms

	BK-II (lignite)		PP (peat)	
	min	max	min	max
nPEN	0.13	1700	n.a.	
nHEX	1.2	4500	0.49	520
nHEP	n.a.		0.12	1100
nOCT	0.30	2500	0.13	790
nNON	0.59	3900	0.074	960
cPEN	0.021	10000	n.a.	
cHEX	0.10	9800	0.025	740
cOCT	0.18	5600	0.11	2300
iHEX	0.98	420	n.a.	
DNPE	2.6	9400	n.a.	
DNBE	2.1	8500	0.41	5300
BENZ	0.82	24000	n.a.	
TOL	5.2	6600	0.56	1500
PrBZ	3.4	26000	1.6	3600
TrCM	0.42	4500	n.a.	
TeCM	0.079	2400	0.41	2100
TCE	0.79	9800	n.a.	
PCE	1.8	15000	0.75	3200
OCTON	26	43000	76	6400
HXNTRL	0.69	19000	n.a.	
NTRHX	7.6	22000	100	3400
4EtP	1.2	9800	1.4	3500
26DMP	1.8	15000	1.0	3200
NAPH	4.0	16000	1.1	3500

SI-5. Measured sorption isotherms

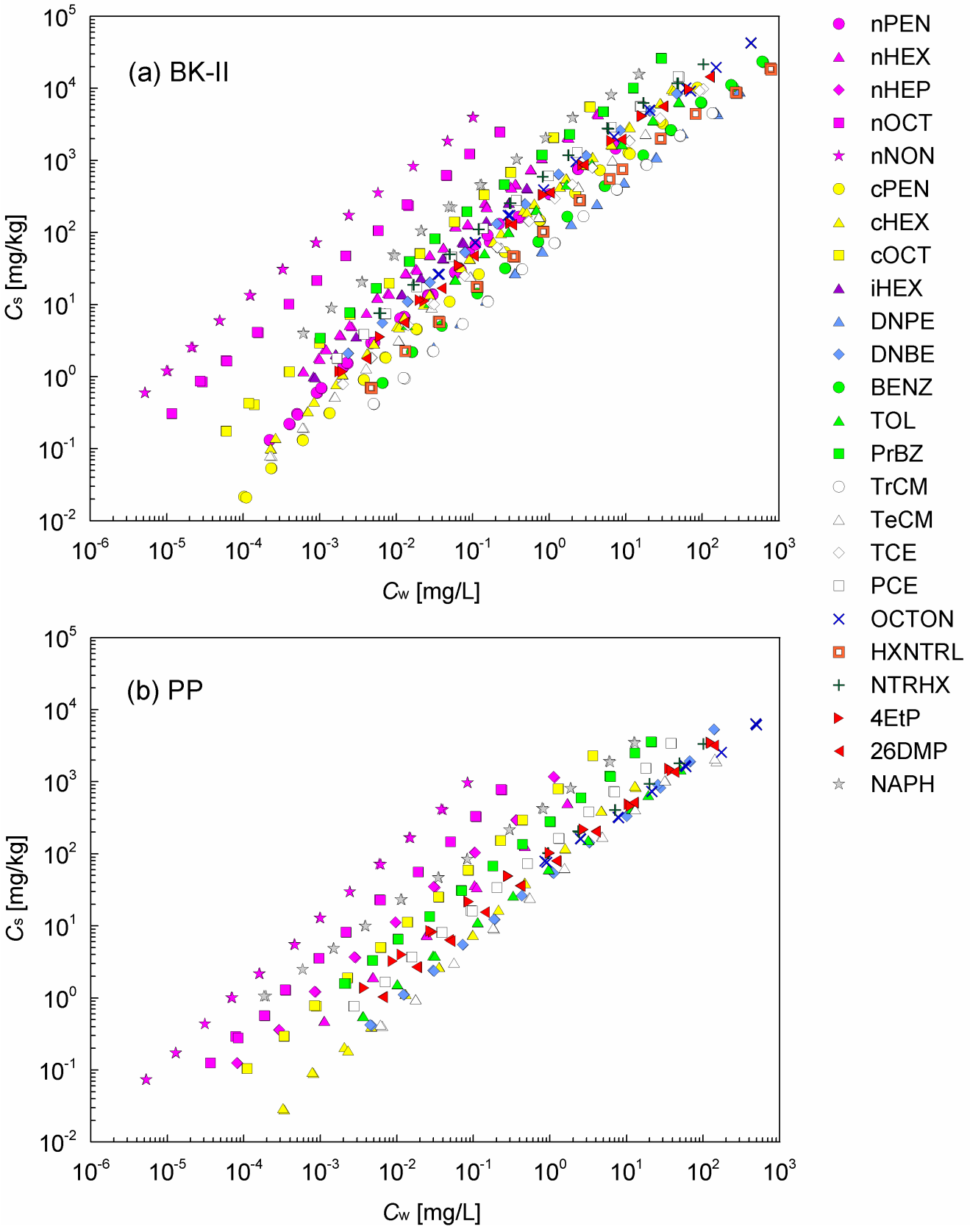

Figure SI-5. Measured sorption isotherms on BK-II (lignite) and PP (peat).

SI-6. Log K_d change against sorbed concentration

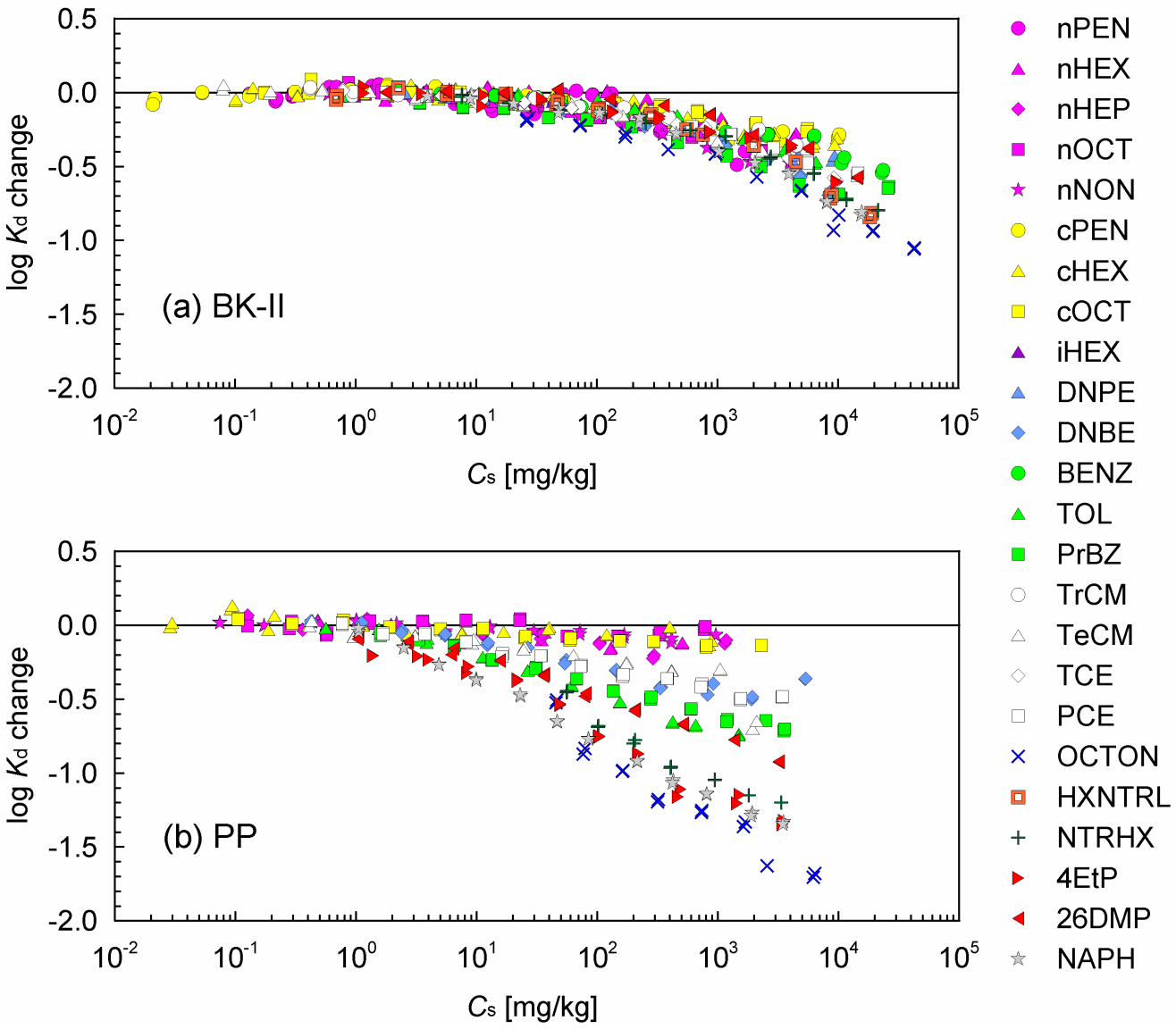

Figure SI-6. Log K_d change against sorbed concentration with respect to log K_d value at reference concentration (2 mg/kg for BK-II (lignite) and 1 mg/kg for PP (peat)). This figure is identical to Figure 1 in our present article.

SI-7. Slopes and intercepts of nonspecific interaction lines (NSILs)

BK-II (lignite)

C_s [mg/kg]	*l*		*c*	
	value	S.E.	value	S.E.
2	0.90	0.03	-0.81	0.09
20	0.88	0.02	-0.80	0.07
200	0.87	0.02	-0.87	0.06
2000	0.89	0.06	-1.14	0.20

S.E.: standard errors

PP (peat)

C_s [mg/kg]	*l*		*c*	
	value	S.E.	value	S.E.
2	0.77	0.04	-1.18	0.14
20	0.80	0.03	-1.31	0.10
200	0.82	0.01	-1.44	0.05
2000	0.85	0.002	-1.57	0.01

S.E.: standard errors

SI-8. Plots of contributions of specific interactions vs. *E* and *B*

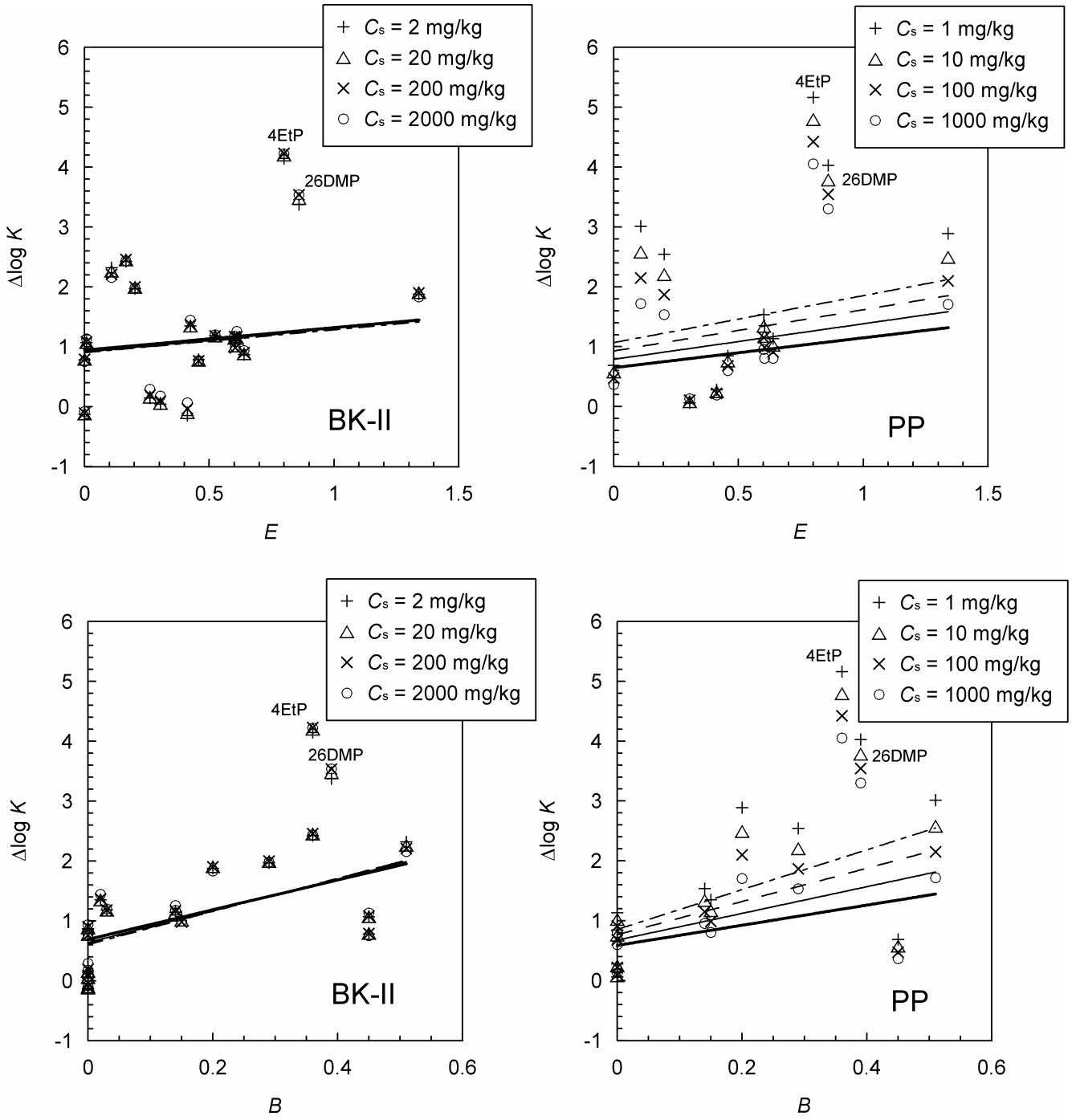

Figure SI-8. Contributions of specific interactions vs. *E* and *B* parameters. Linear regressions are indicated, from low to high concentrations, with dash-dotted, dashed, solid, and bold solid lines. Two phenols (4EtP and 26DMP) were excluded from regressions. R^2 is 0.03 (with *E* for BK-II), 0.08–0.10 (*E*, PP), 0.38–0.41 (*B*, BK-II) and 0.29–0.36 (*B*, PP).Correlations with *A* parameter are not shown because our probe compounds include only two strong H-donor compounds.

SI-9. Compound list for cited literature isotherms and their K_{aw} and LSER descriptors

	S	*A*	*B*	*L*	log K_{aw}
trichloromethane	0.49	0.15	0.02	2.480	-0.90
benzene	0.52	0.00	0.14	2.786	-0.74
1,2-dichlorobenzene	0.78	0.00	0.04	4.518	-1.26
1,3-dichlorobenzene	0.73	0.00	0.02	4.410	-0.93
1,4-dichlorobenzene	0.75	0.00	0.02	4.435	-0.95
1,2,3-trichlorobenzene	0.86	0.00	0.00	5.419	-1.39
1,2,4-trichlorobenzene	0.81	0.00	0.00	5.248	-1.31
1,3,5-trichlorobenzene	0.73	0.00	0.00	5.045	-1.21
2,4-dichlorophenol	0.99	0.58	0.14	4.943	-3.93
trichloroethylene	0.37	0.08	0.03	2.997	-0.50
phenanthrene	1.29	0.00	0.26	7.632	-2.80
benzothiophene	0.88	0.00	0.20	5.174	-2.27
acridine	1.33	0.00	0.58	7.644	-5.63
3-nitrophenol	1.57	0.79	0.23	5.692	-6.98
pyridine	0.84	0.00	0.52	3.022	-3.47
nitrobenzene	1.11	0.00	0.28	4.557	-3.14
anisole	0.74	0.00	0.29	3.890	-1.80

Sources: LSER descriptors (*1, 2, 4, 5*), K_{aw} (*6, 13, 15*). K_{aw} values at 25 °C were converted to 20 °C using enthalpy data from refs *15* and *22*. K_{aw} for benzothiophene, acridine and 3-nitrophenol were estimated by the LSER equation in ref *16*.

SI-10. Results of multiple regression analysis (MRA)

BK-II (lignite)

		3 variables				4 variables			
C_s [mg/kg]		2	20	200	2000	2	20	200	2000
value	*c*	-0.81	-0.81	-0.86	-1.01	-0.67	-0.67	-0.72	-0.88
	l	0.89	0.87	0.86	0.85	0.83	0.81	0.80	0.80
	s	2.43	2.43	2.41	2.38	2.01	2.02	2.01	2.00
	a	3.64	3.76	3.85	3.91	3.55	3.67	3.77	3.83
	b					1.58	1.55	1.51	1.43
S.E.	*c*	0.27	0.26	0.25	0.24	0.15	0.14	0.13	0.13
	l	0.09	0.08	0.08	0.08	0.05	0.04	0.04	0.04
	s	0.23	0.23	0.22	0.21	0.14	0.13	0.12	0.12
	a	0.49	0.47	0.46	0.44	0.27	0.25	0.23	0.23
	b					0.23	0.22	0.21	0.20
R^2 corrected		0.973	0.974	0.976	0.978	0.992	0.993	0.994	0.994
S.E.		0.28	0.28	0.27	0.25	0.16	0.14	0.14	0.14
N		23	23	23	23	23	23	23	23
AIC*		-54.4	-55.8	-57.5	-59.4	-81.4	-84.6	-87.2	-87.6

*Akaike Information Criterion = $2k + N \ln (RSS/N)$, where *k* is the number of adjustable parameters and RSS is the residual sum of squares (*23*).

PP (peat) using data from this study.

		3 variables				4 variables			
C_s [mg/kg]		1	10	100	1000	1	10	100	1000
value	*c*	-1.69	-1.69	-1.69	-1.70	-1.50	-1.54	-1.58	-1.62
	l	0.90	0.90	0.89	0.88	0.84	0.84	0.85	0.86
	s	2.98	2.59	2.20	1.81	2.69	2.36	2.02	1.69
	a	4.19	4.28	4.36	4.45	4.02	4.14	4.26	4.38
	b					1.17	0.94	0.71	0.49

S.E.	*c*	0.51	0.42	0.34	0.26	0.45	0.38	0.31	0.25
	l	0.15	0.12	0.10	0.08	0.13	0.11	0.09	0.07
	s	0.32	0.26	0.21	0.16	0.30	0.26	0.21	0.17
	a	0.57	0.47	0.38	0.29	0.50	0.42	0.35	0.28
	b					0.53	0.45	0.37	0.30
R^2 corrected		0.977	0.982	0.987	0.991	0.982	0.986	0.989	0.992
S.E.		0.31	0.26	0.21	0.16	0.27	0.23	0.19	0.15
N		16	16	16	16	16	16	16	16
AIC		-33.9	-39.9	-46.9	-55.0	-37.7	-43.3	-49.7	-56.6

PP (peat) using data from this study and cited references.

		all data				all but heterocyclic comps.			
		3 variables		4 variables		3 variables		4 variables	
C_s [mg/kg]		100	1000	100	1000	100	1000	100	1000
value	*c*	-1.71	-1.63	-1.78	-1.69	-1.31	-1.26	-1.34	-1.28
	l	0.84	0.81	0.85	0.82	0.78	0.76	0.78	0.76
	s	2.97	2.60	2.25	2.00	2.22	1.96	2.10	1.88
	a	3.04	3.23	3.15	3.32	4.21	4.23	4.15	4.19
	b			2.89	2.43			0.77	0.51
S.E.	*c*	0.54	0.47	0.44	0.40	0.16	0.15	0.14	0.14
	l	0.17	0.15	0.14	0.12	0.05	0.05	0.04	0.04
	s	0.55	0.48	0.48	0.43	0.15	0.14	0.13	0.13
	a	0.79	0.69	0.64	0.58	0.21	0.19	0.18	0.18
	b			0.72	0.65			0.22	0.22
R^2 corrected		0.899	0.910	0.933	0.938	0.991	0.992	0.994	0.993
S.E.		0.78	0.69	0.64	0.57	0.20	0.18	0.17	0.17
N		33	33	33	33	30	30	30	30
AIC		-12.5	-21.0	-25.4	-32.3	-92.6	-98.3	-102.3	-102.1

SI-11. Plots of Freundlich exponents (1/*n*) for BK-II vs. *S* parameter

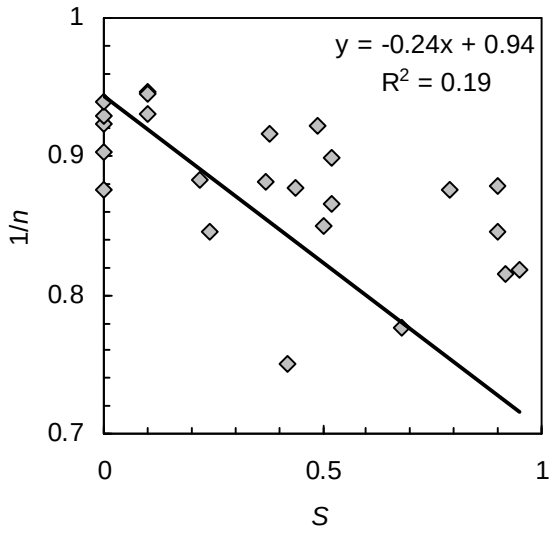

Figure SI-11. Freundlich exponents (1/*n*) for BK-II (lignite) vs. *S* parameter. The solid line indicates the linear regression.

SI-12. Discussion on multiparameter approach for K_{oc} using hexadecane-water partitioning coefficients

Zhu and Pignatello (*18*) proposed a multiparameter equation to model K_{oc} using hexadecane-water partitioning coefficients as following,

$$\ln K_{oc} = a \ln c_{HD\text{-}W} - b/RT + p^e S - G^{e,H\text{-}bond}{}_{OM}/RT - G^{e,EDA}{}_{OM}/RT + const_{OC}/RT \quad (S1)$$

where $c_{HD\text{-}W}$ is mole fraction-based hexadecane-water partitioning coefficients. According to the authors in ref *18*, the first two terms ($a\ln c_{HD\text{-}W} - b/RT$) quantify the hydrophobic effects on the compound from water to organic matter. The last constant term ($const_{OC}$/RT) stems from the Flory-Huggins theory with the assumption of full accessibility of organic carbon and is unchanged by the multiple regression. The remaining three terms refer to specific (polar) interactions. In eq S1, *a*, *b* and p^e are fitting parameters. $G^{e,H\text{-}bond}{}_{OM}/RT$ and $G^{e,EDA}{}_{OM}/RT$ terms drop if the considered compounds do not undergo the H-bond and additional electron donor-acceptor interactions, respectively. Here, we note two problems of this model.

First, the "hydrophobic driving force" from water to organic matter is not necessarily correlated with $\ln c_{HD\text{-}W}$ and thus cannot be expressed as "$a\ln c_{HD\text{-}W} - b/RT$" (see Derivation below). Correlations should be rather expected between nonspecific interactions in organic matter and those in hexadecane. If *a* in eq S1 is not 1, as for the three soils studied in ref *18*, eq S1 does not strictly hold. The multiple regression might still result in good fitting because the sufficient number of parameters are included, but the obtained coefficients do not reflect the molecular interactions as intended in eq S1.

Second, the assumption of fully accessible organic carbon is unrealistic and leads to miscalculation of free energies of sorption. Recently, Niederer et al. (*24*) demonstrated that variability of sorption coefficients in humic substances from different origins results heavily from different site accessibilities

and not much from molecular interactions. Based on the full accessibility assumption, the authors of ref *18* quantified ΔG of sorption as well as of individual interactions. However, because quantity of available sites in soils is unknown, it is generally difficult to obtain ΔG for transfer of a compound to soils. Further, if *ad*sorption is the dominant mechanism, concentrations in the soil phase should be expressed per surface area of the responsible material(s) to calculate ΔG. In the multiple regression analysis using eq 1, however, the b/RT term functions as an adjustable parameter, which corrects the full-accessibility assumption of the model. Nevertheless, in ref *18*, *b* was interpreted as part of hydrophobic "force" (i.e., molecular interactions), which clearly differs from the idea of site accessibilities that are not related to interactions.

Equation S1 might still be useful for practical purposes (not for analysis of molecular interactions), as it can directly handle K_{oc} (or K_d). For this purpose, a simplified equation is proposed here,

$$\log K_{oc} = h'\log K_{HD/w} + s'S + a'A + c' \qquad \text{(S2)}$$

where h', s' and a' are concentration-dependent fitting coefficients; c' is an adjustable parameter reflecting the accessibility difference between organic carbon and hexadecane, and any compound nonspecific factor. One might need to include the *B*–term if the organic matter has H-donating properties. Note again that if h' is significantly different from 1, eq S2 does not give information about molecular interactions. The figure below shows plots similar to Figure 2 in the present article. Because of large $\log K_{HD/w}$ of *n*-alkanes, the hydrophobic line had to be extrapolated considerably. The resulting polar interactions vs. *S* diagram is similar to Figure 3 in the article. In our case, h' was not much different from 1 (0.8–0.9). Thus, eq S2 still holds.

In conclusion, to assess molecular interactions we prefer our method that converts K_d to $K_{soil(h)/air}$ and regresses it with *L* etc. to the method that uses hexadecane-water partitioning coefficients, because (i) $K_{soil(h)/air}$ directly quantifies the overall soil-sorbate interactions, (ii) when eq S2 is used, a large

extrapolation of the nonspecific line is necessary, and (iii) if the coefficient *h*' in eq S1 is not 1, this approach leads to erroneous interpretations for polar interactions. Errors due to non-unity *h*' are large for polar compounds because of strong polar interactions in the water phase. Furthermore, specifically to this study employing headspace measurements, K_d of *n*-alkanes is influenced by inaccuracies in K_{aw}, but $K_{soil(h)/air}$ is not.

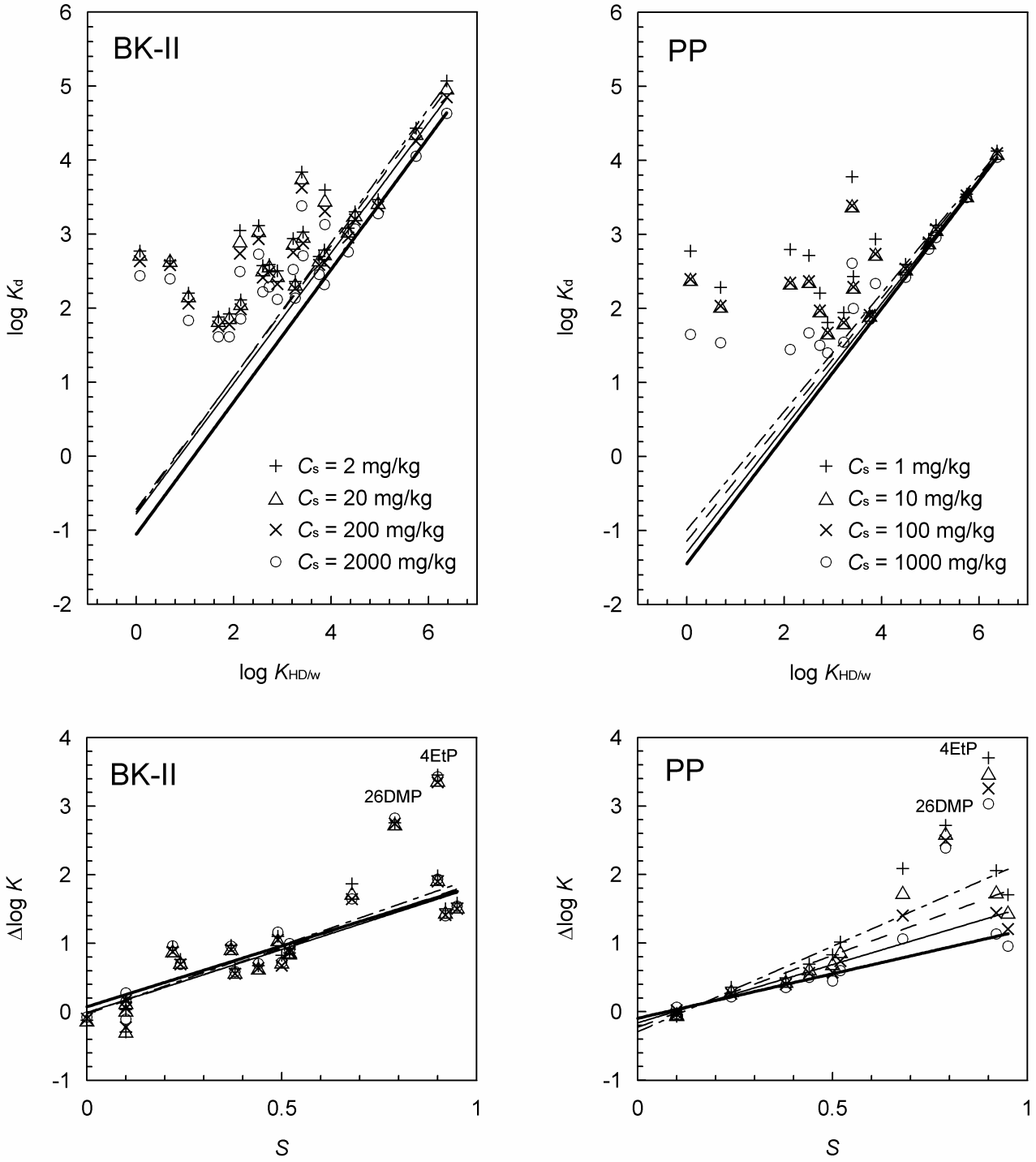

Figure SI-12. Plots of log K_d against log $K_{HD/w}$ (top) and of the resulting Dlog K against S (bottom).

Derivation

The free energy of solute transfer from water to organic carbon $\Delta G_{oc\text{-}w}$ (= $RT \ln K_{oc}$ + $const_{OC}$) is split into excess free energies of the solute in organic carbon (G^e_{oc}) and in water (G^e_w) with respect to an

arbitrary reference state.

$$\Delta G_{oc\text{-}w} = G^{e}_{oc} - G^{e}_{w} \quad \text{(S3)}$$

These excess free energies are subdivided for each phase into excess free energies resulting from nonspecific interactions (cavity formation and induced dipole-induced dipole interaction) and from specific interactions (all the other interactions).

$$\Delta G_{oc\text{-}w} = (G^{e,\,nonsp}{}_{oc} + G^{e,\,sp}{}_{oc}) - (G^{e,\,nonsp}{}_{w} + G^{e,\,sp}{}_{w}) \quad \text{(S4)}$$

By reformulation,

$$\Delta G_{oc\text{-}w} = (G^{e,\,nonsp}{}_{oc} - G^{e,\,nonsp}{}_{w} - G^{e,\,sp}{}_{w}) + G^{e,\,sp}{}_{oc} \quad \text{(S5)}$$

In ref *18*, the first term is redefined as the "hydrophobic driving force" $G^{e,hyd}{}_{oc}$,

$$G^{e,hyd}{}_{oc} = G^{e,\,nonsp}{}_{oc} - G^{e,\,nonsp}{}_{w} - G^{e,\,sp}{}_{w} \quad \text{(S6)}$$

and is assumed to have a linear relationship with the free energy of transfer from water to hexadecane $\Delta G_{HD\text{-}W}$ (= $RT \ln\chi_{HD\text{-}W}$); thus,

$$G^{e,hyd}{}_{oc} = a\,\Delta G_{HD\text{-}W} + b \quad \text{(S7)}$$

Equations similar to eqs S3 and S4 can be also written for $\Delta G_{HD\text{-}W}$,

$$\Delta G_{HD\text{-}W} = G^{e}_{HD} - G^{e}_{w} \quad \text{(S8)}$$

$$\Delta G_{HD\text{-}W} = G^{e,\,nonsp}{}_{HD} - G^{e,\,nonsp}{}_{w} - G^{e,\,sp}{}_{w} \quad \text{(S9)}$$

Note that $G^{e,\,sp}{}_{HD} = 0$.

Inserting eqs S6 and S9 in eq S7,

$$G^{e,\,nonsp}{}_{oc} - G^{e,\,nonsp}{}_{w} - G^{e,\,sp}{}_{w} = a\,(G^{e,\,nonsp}{}_{HD} - G^{e,\,nonsp}{}_{w} - G^{e,\,sp}{}_{w}) + b \quad \text{(S10)}$$

It is generally accepted that nonspecific interactions in different phases are nearly proportional (i.e., $G^{e,\,nonsp}{}_{oc}$, $G^{e,\,nonsp}{}_{HD}$ and $G^{e,\,nonsp}{}_{w}$ are all proportional to each other) since cavity formation and the induced dipole-induced dipole interaction are both closely related to the size of molecule (unless perfluorinated compounds are considered) (*25*). However, $G^{e,\,sp}{}_{w}$ is completely independent from these nonspecific-interaction-related excess free energies. Therefore, eq S10 holds only if coefficient *a* is 1, so that the $G^{e,\,sp}{}_{w}$ terms in both sides are cancelled out. If *a* is significantly different from 1, eq S10 is

not generally fulfilled. In particular, errors may be large for polar compounds since $G^{e,\,sp}{}_{w}$ is large. To avoid this problem, $G^{e,\,sp}{}_{w}$ should not be multiplied by a. This can be done by moving $G^{e}{}_{w}$ in eqs S3 and S8 to the left hand side of the equations,

$$\Delta G_{oc\text{-}w} + G^{e}{}_{w} = G^{e}{}_{oc} \qquad \text{(S3')}$$

$$\Delta G_{HD\text{-}W} + G^{e}{}_{w} = G^{e}{}_{HD} \qquad \text{(S8')}$$

Subdividing $G^{e}{}_{oc}$ and $G^{e}{}_{HD}$ as was done above,

$$\Delta G_{oc\text{-}w} + G^{e}{}_{w} = (G^{e,\,nonsp}{}_{oc} + G^{e,\,sp}{}_{oc}) \qquad \text{(S11)}$$

$$\Delta G_{HD\text{-}W} + G^{e}{}_{w} = G^{e,\,nonsp}{}_{HD} \qquad \text{(S12)}$$

Because of the correlation between excess free energies representing nonspecific interactions,

$$G^{e,\,nonsp}{}_{oc} = a\, G^{e,\,nonsp}{}_{HD} + b \qquad \text{(S13)}$$

Inserting eqs S13 and S12 in eq S11,

$$\Delta G_{oc\text{-}w} + G^{e}{}_{w} = a\,(\Delta G_{HD\text{-}W} + G^{e}{}_{w}) + b + G^{e,\,sp}{}_{oc} \qquad \text{(S14)}$$

If the air phase is taken as the reference phase for the excess free energies, eq S14 becomes,

$$\Delta G_{oc\text{-}w} + \Delta G_{w\text{-}air} = a\,(\Delta G_{HD\text{-}W} + \Delta G_{w\text{-}air}) + b + G^{e,\,sp}{}_{oc} \qquad \text{(S15)}$$

where $\Delta G_{w\text{-}air}$ is the free energy of transfer from air to water. By the thermodynamic cycle,

$$\Delta G_{oc\text{-}air} = a\,\Delta G_{HD\text{-}air} + b + G^{e,\,sp}{}_{oc} \qquad \text{(S16)}$$

Equation S16 is nothing but eq 3 in the article with free energy notations.

SI-13. Contribution of *E*-term in the LSERs to log $K_{soil(h)/air}$

Multiple regression analysis for log $K_{soil(h)/air}$ at different sorbate concentrations in BK-II and PP was performed using all five LSER descriptors in eq 3 in the manuscript (i.e., *E*, *S*, *A*, *B*, *L*). The results below show that addition of the *E*-term does not improve the fitting (compare the AIC values with SI-10) and that the resultant regression coefficient (*e*) is not significantly different from 0. This confirms that the contribution of the E-term to the log $K_{soil(h)/air}$ is negligibly small in our cases and the *L*-term alone can explain the nonspecific interactions.

		BK-II (lignite)				PP (peat)*	
C_s [mg/kg]		2	20	200	2000	100	1000
value	*c*	-0.68	-0.68	-0.73	-0.88	-1.30	-1.23
	l	0.84	0.82	0.81	0.80	0.77	0.74
	s	2.09	2.08	2.05	2.01	2.01	1.78
	a	3.59	3.70	3.79	3.83	4.18	4.23
	b	1.47	1.47	1.45	1.42	0.87	0.63
	e	-0.09	-0.07	-0.05	-0.01	0.11	0.13
S.E.	*c*	0.15	0.14	0.14	0.14	0.15	0.15
	l	0.05	0.05	0.05	0.05	0.05	0.05
	s	0.19	0.18	0.17	0.17	0.18	0.18
	a	0.28	0.27	0.25	0.25	0.18	0.18
	b	0.30	0.28	0.26	0.26	0.26	0.26
	e	0.16	0.15	0.14	0.14	0.14	0.14
R^2 corrected		0.992	0.993	0.993	0.993	0.994	0.993
S.E.		0.16	0.15	0.14	0.14	0.17	0.17
N		23	23	23	23	30	30
AIC		-79.8	-82.9	-85.4	-85.6	-101.1	-101.1

*Including all compounds from this study and the cited references except for the three heterocyclic aromatic compounds, see the text.

SI-14. Comparison with literature data for PP

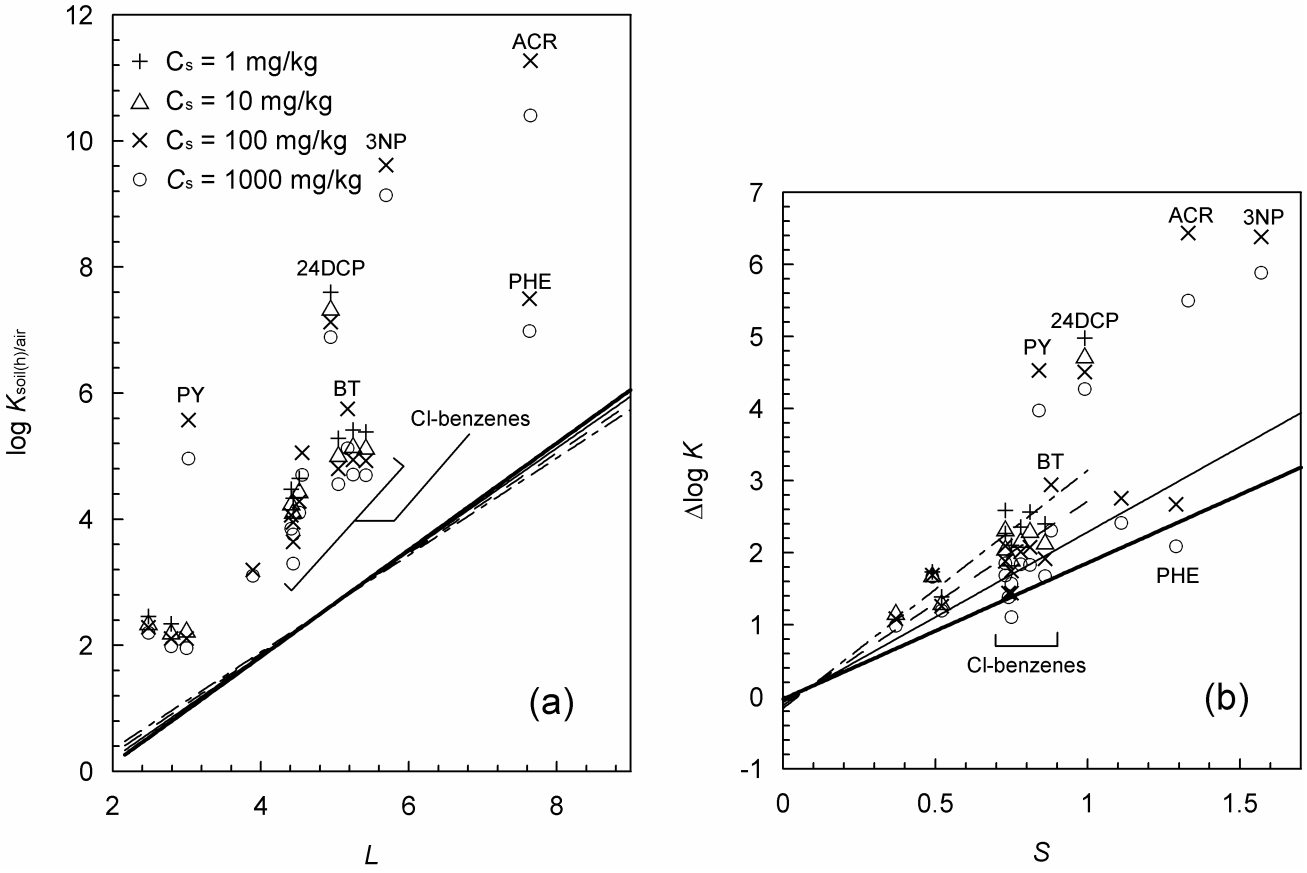

Figure SI-14. Comparison with literature data for PP: (a) log $K_{soil(h)/air}$ vs. log hexadecane-air partitioning constants (*L*); (b) contributions of specific interactions (Dlog *K*) vs. polarizability/dipolarity parameter (*S*). Lines are the linear regressions for data in this study as shown in Figures 2 and 3. Selected compounds were indicated as PY (pyridine), BT (benzothiophene), ACR (acridine), PHE (phenanthrene), 24DCP (2,4-dichlorophenol) and 3NP (3-nitrophenol).

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