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Sorption of Very Hydrophobic Organic Compounds (VHOCs) on Dissolved Humic Organic Matter (DOM). 2. Measurement of Sorption and Application of a Flory−Huggins Concept To Interpret the Data†

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Sorption phenomena of very hydrophobic compounds (VHOCs, log K_{OW} > 5) on dissolved humic organic matter (DOM) are overwhelmingly based on partitioning processes. In this respect, DOM is very similar to "rubbery" soil/sediment OM. To exclude system adsorption effects, the DOM sorption coefficients (K_{DOM}) of VHOCs were determined using a dynamic approach based on the VHOCs' aqueous solubility enhancement in the presence of DOM. Partition coefficients are strongly correlated to the analytes' K_{OW} across the alkane, PAH, and PCB groups under study. These three "families" are regarded to be good models of hydrophobic partitioning. On the basis of a uniform one-parameter concept characterizing sorption on amorphous polymers, Hildebrand solubility parameters of amorphous polymeric sorbents, including DOM, and of sorbates can be calculated on the basis of partition coefficients. Likewise, partition coefficients can be estimated using Hildebrand solubility parameters. Literature-based partition coefficients on DOM fit very well in this universal one-parameter concept. On using our own sorption data of PAHs, PCBs, and alkanes on DOM, an almost identical solubility parameter for the DOM polymer under study is obtained. The concept is also very useful in understanding both waterborne and airborne bioconcentration processes, which are considered to be partitioning phenomena.

Introduction

Sorption of very hydrophobic compounds including PCBs, PAHs, and alkanes, all of them possessing octanol−water coefficients (K_{OW}) of 10^5 and more, on humic organic matter (HOM) plays an important role in the environment (*1*). In natural waters, organic chemicals can exist freely dissolved or in a bound state associated with dissolved HOM (DOM), suspended particles, and other colloidal matter. Interactions with DOM [including porewater−DOM (*2*)] can increase aqueous solubility, slow volatilization, decrease sediment partitioning, and alter reactivity and bioavailability. Hydrophobic partitioning, consisting of nonspecific van der Waals forces and a substantial entropic term, accounts for absorption into amorphous, polymeric HOM (*3*). Hydrophobic partitioning is noncompetitive and strongly associated with the analyte's hydrophobicity, normally expressed by the octanol−water coefficient (K_{OW}).

$$\log K_{HOM} = a \log K_{OW} + b \quad (1)$$

where K_{HOM} is a partition coefficient referred to the organic matter of the sorbent and a and b are empirical correlation coefficients.

Basically, eq 1 is a linear free energy relationship (LFER). Numerous correlations between K_{HOM} and various molecular properties and descriptors have been summarized (*4*). However, a unified solubility parameter concept in the form of a one-parameter approach (see below) was not considered.

Solid Phase Microextraction To Determine Partition Coefficients. A relatively new approach to determine partition coefficients on HOM utilizes solid phase micro**e**xtraction (SPME; see ref *5* and references cited therein). The solvent-free SPME, introduced and pioneered by Pawliszyn and his group during the past decade (see reference cited in ref *5*), is a very efficient analytical method for the extraction of organic compounds of environmental significance. SPME uses a short piece of a fused silica fiber coated with a polymeric stationary phase. Analytes partition into the coating until equilibrium is reached between the coating and the sample. The analytes are thermally desorbed in a heated injection port of a gas chromatograph. The SPME approach to determine sorption on HOM is based on the valid assumption that the SPME fiber samples only the freely dissolved analyte fraction (C_{free}) rather than the fraction bound to the HOM matrix (C_{bound}), thus allowing the determination of K_{OM} (or K_{DOM}) data.

$$K_{OM} = \frac{n_0 - n_{sample}}{n_{sample}} \frac{1}{C_{OM}} \quad (2)$$

where n_0 and n_{sample} are analyte masses extracted from pure water and from a DOM solution, respectively, both of them spiked with the same analyte concentration. [The validity of this assumption is based on the fact that the thermodynamic activities of the freely dissolved solute fraction and the reversibly bound solute fraction are identical. A reversible sorption indicates a very fast solute exchange between these two phases (see ref *13*).] A significant advantage of the SPME method is that the fiber uptake of freely dissolved analytes is very small due to the low mass of fiber coating material (e.g., 2.57×10^{-5} mL in the case of the 7 μm PDMS fiber) (see Experimental Section). Thus, the (reversible) partitioning equilibrium sorbate−DOM is not disturbed by the SPME fiber. In the framework of our investigations we used "liquid" polymeric SPME coatings for which partitioning phenomena prevail rather than adsorption coatings (Carboxen, styrene−divinylbenzene-based coatings). In the latter case, competitive effects have to be considered.

This approach to determine sorption coefficients is more useful than established methods because it can be used for both dissolved and particulate organic matter, which facilitates their comparison and multicomponent systems can be investigated. In previous research with conventional static systems (*6*) we observed that VHOCs did not follow the strong $\log K_{DOM}$−$\log K_{OW}$ correlation observed for less hydrophobic surrogates of the same "analyte family". This might be attributed to losses in the system, which are ascribed mistakenly to the DOM-sorbed VHOC fraction, or might be a real phenomenon. In the first part of this paper we introduce

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dynamic systems, which compensate for losses in the system, to determine partitioning coefficients on SPME fiber coatings. To investigate PCBs and PAHs, a generator column approach was applied, whereas alkanes nC_8-nC_{14} were investigated by means of a flat sheet membrane setup (see Part 1). Fiber distribution coefficients on nonpolar SPME coatings were found to correlate strongly with analyte hydrophobicities. The prevailing partitioning processes on the fiber coatings are essential preconditions to utilize SPME (i) in environmental analysis and (ii) in the determination of partition coefficients on DOM. An analogous dynamic procedure should be used to determine K_{DOM} data for VHOCs including PAHs, PCBs, and alkanes, to demonstrate the validity of the $\log K_{DOM}-\log K_{OW}$ linear correlation for VHOCs. The dynamic approaches, which were basically described in Part 1, are based on the enhancement of analytes' intrinsic water solubilities (S_w) by means of DOM.

$$K_{DOM} = \frac{\frac{S_{w,DOM}}{S_w} - 1}{C_{DOM}} \quad (3)$$

A New Solubility Parameter Concept To Interpret Sorption on HOM. Although a strong $K_{HOM}-K_{OW}$ correlation exists (eq 1), the coefficients a and b in this basically linear free energy relationship have no fundamental physicochemical meaning. The processes of organic solute partitioning into octanol and into DOM are identical with respect to the entropic contribution of solute dissolution, which drives the VHOCs out of the aqueous phase. In the idealized case of two solutes with identical molecular sizes and intermolecular interactions, only the entropic term contributes to the solute's chemical potential; however, this is definitely not true for the sorbate−HOM system. The interactions between the solute−DOM and solute−octanol pairs might be quite different. The bulk (liquid) octanol cannot adequately recreate the interactions with the three-dimensional HOM; the same is valid for biomembranes (cf. below).

Several years ago, a unified "one-parameter" concept, based on the Flory−Huggins theory and the Scatchard−Hildebrand relation for regular solutions, was introduced by Kopinke to explain the partitioning (dissolution) into HOM on the basis of Hildebrand solubility parameters (*7*). According to the Hildebrand−Scatchard equation (cf. ref *7* and references cited therein), the miscibility of two solvents is inversely proportional to the change in energy on mixing, which, in turn, is directly proportional to the difference in solubility parameters. Therefore, the closer the solubility parameters (i.e., the cohesive energies expressing the strength of intermolecular interactions) for the two solvents, the more favorable is the mixing of the two. The proposed concept involves both the "compatibility" (affinity) of the target analyte with its amorphous, polymeric host (HOM including DOM in our special case here) and the analyte's "incompatibility" with water towards binding the analyte with the polymer phase dispersed in the aqueous system (eq 4). It should be noted that only those interactions that contribute to hydrophobic partitioning are considered. Therefore, application of the "one-parameter" concept (eq 4) toward polar compounds (e.g., nitrophenols) is not straightforward.

$$\ln \frac{K_{HOM,i}}{K_{OW,i}} = \frac{V_m}{RT}[(\delta_i - \delta_{octanol})^2 - (\delta_i - \delta_{HOM})^2] - \ln \rho_{HOM} \quad (4)$$

where V_m is the molar volume of the analyte under study (mL mol^{-1}); R is the universal gas constant (8.31 J K^{-1} mol^{-1}), T is the temperature (293 K); $\delta_{i,\ HOM,\ octanol}$ are solubility parameters for analyte i, HOM, and octanol, respectively [(J cm^{-3})$^{0.5}$]; and ρ_{HOM} is HOM density [to take into account the different dimensions of K_{OW} (g mL^{-1}) and K_{OM} (g g^{-1})].

Solubility parameters are tabulated both for organic compounds and for amorphous polymers (*8*−*11*). They can also be calculated on the basis of molar enthalpies of evaporation and molar volumes (see ref *7*). According to eq 4, the "compatibility" or "affinity" term between a defined analyte and HOM reaches its maximum when both solubility parameters are identical. The benefits of the proposed concept consist in the possibility of estimating partition coefficients (eq 4) or characterizing the solubility parameter of amorphous polymers, which is a rough measure of its polarity (*7*), via

$$\delta_{HOM} = \delta_i \pm \sqrt{(\delta_i - \delta_{octanol})^2 + \frac{RT}{V_m} 2.3\,(\log K_{OW} - \log K_{HOM} - \log \rho_{HOM})} \quad (5)$$

The solubility parameters of a variety of particulate and dissolved HOM were shown to be within a narrow range, $\delta_{HOM} = 25.5 \pm 1.5$ (J cm^{-3})$^{0.5}$, which is between the value of polar cellulose [32.0 (J cm^{-3})$^{0.5}$] and nonpolar polyethylene [16.3 (J cm^{-3})$^{0.5}$] (*7*). The solutes under study, on the basis of which the δ_{HOM} was calculated, included mainly organic pollutants of medium hydrophobicity ($1.5 < \log K_{OW} < 5.0$). Determination of the partition coefficients for solutes possessing $\log K_{OW} > 5$ is error-loaded and cumbersome when using static "batch" approaches (see Part 1). Obviously, biased K_{DOM} data would result in incorrect solubility parameters for the sorbent. Therefore, K_{DOM} data measured in the dynamic way should be used to evaluate the above-mentioned solubility parameter concept for its validity toward VHOCs. Further topics to be dealt with in the framework of this contribution include the following:

- calculation of the solubility parameters for a variety of particulate and dissolved HOM using different hydrophobic solutes (the calculation utilizes literature-based sorption data gathered after the publication of ref *7*, thus further evaluating the proposed concept) and
- extension of the HOM-designated solubility parameter concept to explanation of bioconcentration processes.

Experimental Section

Materials. Glass SPME vials (250 and 1000 mL), as well as homemade glass stir bars, were washed in an ultrasonic bath containing a detergent, rinsed with copious amounts of deionized water and pesticide-grade acetone, dried for 1 h at 120 °C, and then silanized with hexamethyldisilazane prior to every application. Vials (250 and 1000 mL) were sealed with polystyrene caps having small holes matching tightly the outside diameter of the SPME needles. PDMS fibers with 100, 30, and 7 μm film thicknesses were purchased from Supelco (Munich, Germany). Fibers were conditioned according to Supelco's recommendations. PCB standards containing monochloro through heptachloro congeners [PCB 1 (SIM target ion $m/z = 188$ amu, qualifier ion $m/z = 190$ amu), PCB 15 (222, 224), PCB 28 (256, 258), PCB 52 (292, 294), PCB 118 (326, 328), PCB 153 (360, 362), and PCB 180 (394, 396)], as well as the corresponding ^{13}C-labeled congeners PCB 15, 28, 52, 101, 153, and 180, were kindly supplied by K. Wenzel (Leipzig, Germany) and W. Vetter (Jena, Germany). They were diluted with HPLC grade methanol (Merck, Darmstadt, Germany) to give a concentration of 1 ppm. Alkanes and PAHs were purchased from Supelco and deuterated surrogates from Cambridge Isotope Laboratories (Andover, MA). Methanol was used as the solvent for stock solutions in conventional SPME work to minimize the reduction of PCB, PAH, and alkane activity coefficients in water on spiking.

Determination of K_{DOM} Data Using the Conventional Static System (Analytes of Low and Medium Hydrophobicities). This procedure is basically described in ref *5*. Briefly, SPME fibers were inserted in DOM solutions of known concentration (e.g., 100 ppm) and pure water solutions, and both solutions were spiked with analyte stock solutions in methanol. The analyte dissolved in pure water served for calibration purposes. The equilibration time to allow the analytes to partition into the DOM was 2 h; this should be appropriate according to both literature-based findings [e.g., pyrene binding to DOM within 3 min (*12*)] and our own results (*13*). The analyte sampling time (generally beyond 24 h) with the 250 or 1000 mL vials used was identical for pure water and for the DOM solutions. The differences in fiber uptakes were assigned to the analyte fraction bound to DOM. The vials were closed by means of polystyrene caps (no septum). Fibers under study were inserted through small holes in the caps as described in Part 1. The stirring rate was 430 rpm (higher rates were not possible with large stir bars used in the large vials). Stir bars, septa, and caps were not reused in the static SPME approach due to contamination problems. Just before the fiber was inserted into the splitless injector, water that may have wicked into the needle was removed by vigorous shaking of the fiber assembly and/or by touching the tip of the needle with a tissue.

Determination of K_{DOM} data for VHOCs Using the Dynamic Systems. Aqueous DOM solutions ($C_{DOM} = 10$ or 20 ppm; DOM, humic acid (Roth, Karlsruhe, Germany), pH was set to 6.0) were used in addition to DOM-free water. The DOM concentration should not be higher; otherwise, there may be DOM precipitation within the system. Moreover, higher C_{DOM} values would be inappropriate in the investigation of VHOCs, as the freely dissolved analyte concentration would be too low to allow the determination of partition coefficients with reasonable accuracy. For example, if K_{DOM} is 10^5 for an arbitrary analyte i and C_{DOM} of 10 ppm, the analyte mass ratio $m_{i,sorbed}/m_{i,free}$ is 1.0, which is appropriate (see eq 2). Less hydrophobic sorbates, which require higher C_{DOM} (otherwise the $n_0 - n_{sample}$ term in eq 2 is not significantly different from n_0), can easily be handled with static "batch" systems.

The analytes were delivered either by the generator column (target sorbates PCBs and PAHs) or by a semipermeable membrane (alkanes); the schematic setups are described in Part 1. Taking into account the demands of the multiphase system and the mutual cross-correlations of the activities, we preferred to use single analytes (e.g., *n*-decane) for a single experiment rather than analyte mixtures (e.g., *n*-heptane through *n*-tridecane). Attention should be paid to establishing equilibrium conditions (i.e., constant concentrations of target analytes in the solution) or conditions close to equilibrium in the system. To determine the total analyte concentration (consisting of freely dissolved and DOM-bound fractions) in the DOM solution, a 50 mL aliquot of the DOM solution was transferred with a 50 mL syringe into a 50 mL flask with a narrow neck and closed immediately after the sample transfer. Then, an aliquot of a standard solution of isotopically labeled surrogate in 500 μL of *n*-hexane was added. After the flask had been vigorously shaken for several hours in an end-over-end shaker, followed by phase separation, a 10 μL aliquot of the hexane layer was injected using the on-column technique. The total analyte concentration can therefore be determined by comparing the abundances of the target ions of the native analyte and the labeled surrogate. Analyte concentration in DOM-free water was also measured by applying liquid−liquid extraction with *n*-hexane (S_w in eq 3).

Devices. For GC-MS an HP 5973 A MSD (Hewlett-Packard, Palo Alto, CA), equipped with hardware for EI and NCI (the latter was run with methane as moderating gas) was used: multiplier set 200 eV above autotune using PFTBA as the calibrant for EI; threshold, 150; A/D samples, 8; SIM dwell time, 100 ms. For GC injection into an HP 6890A the following conditions were used: (a) split/splitless injector set at 290 °C (7 μm fiber) and 280 °C (30 μm, 100 μm fiber); (b) cold on-column injection to inject liquid samples [a 10 m piece of deactivated fused silica retention gap (poly(dimethylphenylsiloxane) deactivated, HP)] was used to protect the analytical column and to focus the analyte band. GC column: 30 m × 0.25 mm; film thickness, 0.25 μm HP-5 (HP); linear temperature program, 45 °C isothermal for 2 min, ramp at 12 °C min^{-1}, final temperature 295 °C (220 °C for *n*-alkanes nC_7−nC_{13}). The initial oven temperature was >100 °C below the boiling point of the lowest boiling analyte to ensure efficient thermal focusing.

Results and Discussion

Partition Coefficients of VHOCs Measured by the Dynamic Approach. Table 1 lists K_{DOM} data for alkanes, PCBs, and PAHs on dissolved humic acid purchased from the Roth Co. (Table 1 contains also the solubility parameters; see next section.) Application of the static approach to VHOCs as sorbates (e.g., *n*-decane and chrysene in Table 1) is not straightforward due to (i) analyte losses in the system as discussed above and (ii) very long SPME equilibration times. It should be kept in mind that the application of SPME for the study of analyte sorption on DOM is appropriate only under equilibrium conditions for the SPME coating (*5*). As was stated in Part 1, the VHOCs demand equilibrium times beyond 24 h. Also, vials of a volume of at least 250 mL should be used when VHOCs are investigated. Otherwise, highly biased partition coefficients result as was observed for the determination of SPME fiber distribution coefficients.

Figure 1 indicates a strong K_{DOM}−K_{OW} correlation over the entire range of analyte hydrophobicities. The regression lines $\log K_{DOM} = 0.98 \log K_{OW} - 0.39$ ($R^2 = 0.988$) for PAHs, $\log K_{DOM} = 0.93 \log K_{OW} - 0.54$ ($R^2 = 0.990$) for PCBs, and $\log K_{DOM} = 0.87 \log K_{OW} - 0.64$ ($R^2 = 0.986$) are in good agreement with literature-based data (see ref *35*) for soil and surrogate DOM (cf. Table 2). This indicates that basically the same partitioning processes occur for dissolved and particulate HOM. However, in the study of particulate HOM, further effects in addition to partitioning processes should be kept in mind (cf. below). Unfortunately, alkane sorption data on HOM are very scarce, possibly due to experimental problems faced with these VHOCs (e.g., high Henry's law constants).

Figure 1 also provides strong evidence that (i) K_{DOM} values at a given hydrophobicity change in the order PAH > PCB > alkane and (ii) the arbitrary coefficients a and b are sensible only across a defined "family" of analytes. When several analyte classes are investigated in the pursuit of a "universal" regression line for all sorbates under study, unsatisfactory confidence intervals result (see, for example, ref *14*). Theoretical explanation for findings i and ii can be given by means of the solubility parameter concept.

Application of the Solubility Parameter Concept to Sorption of VHOCs on DOM Using Our Own Data. Table 1 contains DOM solubility parameters (last column), calculated according to eq 5. Calculation of solubility parameters for analytes with $\log K_{OW} > 5.0$ should be based on "dynamic" data, where system losses are compensated for (see above). It follows from Table 1 that the calculated DOM solubility parameters were almost identical for all of the analytes covering the three compound "families". The averaged δ value of 24.0 $J^{0.5}\ cm^{-1.5}$ is at the lower level of the range $\delta = 25.5 \pm 1.5\ J^{0.5}\ cm^{-1.5}$ given in ref *7* for HOM of different genesis and polarity, which reflects pronounced hydrophobic moieties in the (coal-derived) DOM under study. The narrow interval of calculated solubility parameters across the three families points clearly to the prevalence of partitioning

TABLE 1. Sorption Coefficients for VHOCs and Calculated DOM Solubilities

analyte	V_m (mL mol^{-1})	δ_i (J$^{0.5}$ cm$^{-1.5}$)	log K_{OW}[a]	log K_{DOM} (static)	log K_{DOM} (dynam)	δ_{DOM}[b] (J$^{0.5}$ cm$^{-1.5}$)
n-heptane	148	15.3	4.51	3.36		23.8
n-octane	164	15.5	5.18[c] 4.93[c]	3.81	3.62	24.2
n-nonane	179	15.7	5.45 calcd	4.45	4.24	23.6
n-decane	195	15.9	5.98 calcd	4.71	4.57	23.9
n-undecane	211	15.9	6.51		5.20	23.5
n-dodecane	227	16.0	7.04		5.48	23.8
n-tridecane	243	16.1	7.57		6.00	23.7
PCB-1	172[d]	18.9	4.53		3.75	24.0
PCB-15	189[d]	19.0	5.58		4.52	24.6
PCB-28	204[d]	19.2	5.62		4.72	24.2
PCB-52	219[d]	19.5	6.09		5.13	24.4
PCB-118	234[d]	19.8	6.90		5.97	24.4
PCB-153	249[d]	19.9	7.16		6.06	24.8
naphthalene	126	20.2	3.30	2.99	2.93	23.8
fluorene	153	19.9	4.18	3.54	3.58	24.3
phenanthrene	159	20.0	4.44	4.00	3.93	23.9
pyrene	179	20.7	5.19	4.53	4.70	24.2
chrysene	196	20.6	5.50	4.74	5.06	23.7

[a] From ref *34*. [b] If both "dynamic" and "static" data are available, the former were used; SD between 0.06 and 0.16 log unit for "static" data and between 0.12 and 0.28 log unit for "dynamic" data; data replicate of three; ρ_{OM} =1.25 g mL^{-1} (i.e., 0.1 log unit). [c] Used K_{OW} = 5.05 (5.18 exptl; 4.93 calcd). [d] From ref *27* and increments given therein.

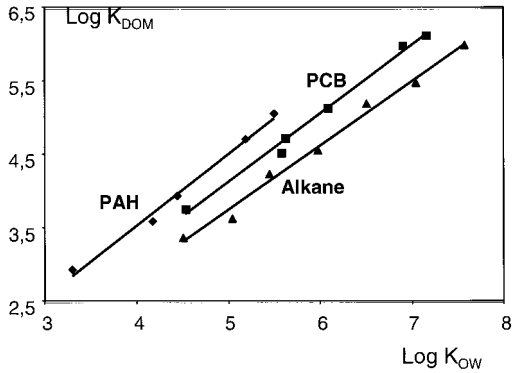

FIGURE 1. Organic matter normalized partition coefficients versus sorbate hydrophobicity of PAHs, PCBs, and alkanes on DOM (Roth Co.).

TABLE 2. Regression Data of Log K_{DOM} = *a* Log K_{OW} + *b* for PAHs, PCBs, and Alkanes

analyte class	*a* this work	*a* literature	*b* this work	*b* literature	R^2 (this work)
PAHs	0.98	1.00[a] 1.30[b]	−0.39	−0.51 −2.42	(0.988) 0.87
PCBs	0.93	0.904[a] 1.02[b]	−0.54	−0.84 −1.40	(0.990) 0.79
alkanes	0.87		−0.64		(0.986)

[a] Data from ref *35*; assumption: organic matter of the soil consists of 50% OC. [b] Data from ref *36*, Aldrich DOM.

processes, because in this case δ_{DOM} characterizes only the sorbent rather than the analyte. The better the compatibility between the sorbates and the DOM sorbent, expressed by smaller differences in solubility parameters ($\delta_{sorbate} - \delta_{DOM}$, see eq 4), the higher the K_{DOM} values. Clearly, alkanes show the highest incompatibility with the more polar DOM matrix. With PAHs, the solubility parameters of which are close to that of octanol, the term $\delta_{HOM} - \delta_{octanol}$ accounts overwhelmingly for the differences between K_{OW} and K_{DOM}.

Once calculated, the solubility parameter of a sorbent may be used to determine either the solubility parameters of the analytes or the partition coefficients. As an example, the solubility parameter of DDT (log K_{OW} = 6.00, log K_{DOM} = 5.19 measured by us via the dynamic approach using the Roth DOM, V = 228 mL mol^{-1}, δ_{HOM} = 24.0 J$^{0.5}$ cm$^{-1.5}$) amounts to 19.5 J$^{0.5}$ cm$^{-1.5}$, which is reasonable (*15*). In this respect, the finding of Chiou (see refs *16* and *17*) becomes plausible, according to which poly(ethylene glycol) (PEG; molecular weight around 10^3 Da) exhibited no significant solubility enhancement toward DDT. Assuming δ_{PEG} = 28.5 J$^{0.5}$ cm$^{-1.5}$ (*9*), a partition coefficient log K_{DDT} = 2.80 results, which translates into solubility enhancement by a factor of only 6 when using a 1% PEG solution. Furthermore, the log K_{DOM} of biphenyl (log K_{OW} = 4.01, δ = 17.0 J$^{0.5}$ cm$^{-1.5}$, V_m = 177 mL mol^{-1}, δ_{HOM} = 24.0 J$^{0.5}$ cm$^{-1.5}$; for data sources, see Table 1) can be calculated to be 3.08, which is close to the experimental value of log K_{DOM} = 3.13. Therefore, SPME as a new approach to determine DOM partition coefficients may serve to calculate solubility parameters that are not abundant in the literature and often need to be estimated by increments.

Application of the Solubility Parameter Concept to Sorption of Organic Sorbates on Dissolved and Particulate HOM Based on Literature Data. There are only a few sorbates for which the DOM sorption coefficients and δ values are available or can be calculated with reasonable accuracy. Recent data based on pyrene sorption on various DOMs give solubility parameters of 27.3 , 26.5, and 23.8 J$^{0.5}$ cm$^{-1.5}$ for the Suwannee River (SR) fulvic acid, SR humic acid, and the commercial (coal-derived) Aldrich humic acid, respectively (*18*). We assume that the commercial humic acid from Aldrich is similar to our HOM purchased from the Roth Co. Results analogous to those obtained for the SR fulvic acid were obtained in ref *19* for fulvic acid isolated from soil: δ = 27.4 J$^{0.5}$ cm$^{-1.5}$. The Aldrich HA was claimed to be as "hydrophobic" as octanol because of the similarity between K_{DOC} and K_{OW} (*18*). This assumption should necessarily result in a DOM solubility parameter close to that of pyrene (20.7 J$^{0.5}$ cm$^{-1.5}$) according to eq 4, which is definitely not true. Thus, K_{DOM} (rather than the carbon-normalized K_{DOC}) should be compared with K_{OW}.

There have been some discrepancies between the above cited and our results, on the one hand, and the results reported in ref *12*, on the other hand. Findings in ref *12* result in quite different δ data for the HOM under study (SR humic acid) using perylene, pyrene, and anthracene as solutes. We consider peculiarities of the fluorescence quenching method,

TABLE 3. Sorbates and Sorbents for Calculation of Solubility Parameters (cf. Figure 2)

no.	analyte	matrix	ref
1, 2	CCl_4,[a] dichlorobenzene	average of 32 normal soils	*16*
3, 4	CCl_4, dichlorobenzene	average of 36 bed sediments	
5−7	naphthalene, phenanthrene, pyrene	average of 5 normal soils	*35*
8−10	naphthalene phenanthrene, pyrene	average of 7 bed sediments	
11−15	benzenes, PCB-8,[a] and PCB-28[a]	Woodburn soil (OM = 1.9%)	*16*
16	ethylbenzene	peat (86% OM)	
17, 18	tetra- and pentachlorobenzene[a]	Cape Cod Aquifer sediment	*37*
19−21	pyrene	Suwannee River FA and HA, Aldrich HA	*27*
22−25	iodobenzene,[a] biphenyl,[a] tri- and tetrachlorobiphenyls	soil	*38*
26−28	nitrobenzene, phenanthrene, pyrene	soil	*39*
29−31	1,2-dichlorobenzene, trichlorobenzene, naphthalene	lake sediment	*40*

[a] CCl_4: $\delta = 17.8$ J$^{0.5}$ cm$^{-1.5}$, $V = 97$ mL mol^{-1}, OM = 50% OC; assumed PCB solubility parameter, 19.7 J$^{0.5}$ cm$^{-1.5}$. Tetra- and pentachlorobenzene: $V = 132$ and 137 mL mol^{-1}, respectively. Iodobenzene: $\delta = 20.7$ J$^{0.5}$ cm$^{-1.5}$, $V = 111$ mL mol^{-1}, log $K_{OW} = 3.25$, Biphenyl: $\delta = 21.7$ J$^{0.5}$ cm$^{-1.5}$, $V = 177$ mL mol^{-1}, log $K_{OW} = 4.01$.

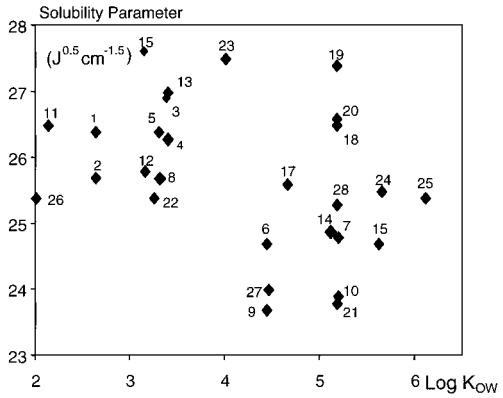

FIGURE 2. Solubility parameters for soils and sediments (based on literature data) versus analyte hydrophobicity.

which should be described elsewhere, to be the main reason for these findings rather than the steric effects assumed in ref *12*.

Although the validity of the partitioning concept for DOM has been widely acknowledged (and confirmed by this study), some recent results using peat-derived DOM show findings contradictory to partitioning-related phenomena (*20*). Desorption of pentachlorobenzene was shown to be biphasic, and the desorption rate of the resistant fraction was measured to be >1 order of magnitude lower than that of the labile fraction. The labile, reversible partitioning occurs in the time frame of ~10 s, which has already been established earlier (*12*, *13*). However, the slow-desorbing residual fraction of pentachlorobenzene accounts for only 1.3−3.7%, which might be ascribed to rigid and condensed DOM regions (such as "glassy" carbon, see below). In other words, ~97−99% of the sorbed analyte is accessible to reversible partitioning processes. Moreover, it should be noted that C_{DOM} was very high (500 ppm) in the framework of these studies. When solutes that can exercise specific interactions within the DOM are investigated, the Flory−Huggins interaction parameter (see ref *7*) might change with sorbate concentration, resulting in nonlinear partition behavior. However, this should be scrutinized elsewhere. Another topic that deserves further studies is steric hindrance. For example, planar PCB congeners are characterized by significantly stronger binding to DOM as well as to phytoplankton than less planar ortho-substituted congeners (*21*, *22*). This may be due to hindered rotation around the 1,1′ carbon bond with ortho-substituted congeners.

Sorption data measured on soils and sediments are much more readily available in the literature. Table 3 and Figure 2 give calculated δ values using literature-based partition coefficients published in the past few years (for reasons of simplicity an OC content of 50% and a density of 1.25 g mL^{-1} were assumed throughout all HOM, which is valid in the face of the uncertainties related to the sorption coefficients). The large set of soils investigated by Chiou from dispersed locations in the United States and China reveal quite similar solubility parameters (cf. Table 3 and ref *37*). The same holds true for the large set of bed sediments. These results confirm the assumption in ref *7* that the solubility parameter range of $\delta_{HOM} = 25.5 \pm 1.5$ (J cm^{-3})$^{0.5}$ is quite narrow. The lower polarity of the sediment HOM in comparison with the soil (cf. number 1−10 in Table 3) may be attributed to fractionation processes during sedimentation (*16*).

The suggested solubility parameter concept may also be very useful to predict sorption processes on a variety of environmentally relevant sorbents: As an example, sorption coefficients for benzene and carbon tetrachloride were determined using the sorbents cellulose, muck, peat, and treated peat (the last one having a lower oxygen content) (*23*). The K_{OM} data were correlated to carbon, oxygen, and nitrogen contents. However, as acknowledged by the authors and as stated by Chin et al. later (*18*), the oxygen content proved to be a poor predictor of HOM's propensity to sorb organic compounds in the order cellulose > muck > peat > treated peat. Using the benzene sorption data given in ref *23*, the solubility parameters amount to the following: cellulose, 31.4 J$^{0.5}$ cm$^{-1.5}$ [literature reference 32.0 J$^{0.5}$cm$^{-1.5}$ (*7*)] > muck, 28.0 J$^{0.5}$ cm$^{-1.5}$ > peat, 27.2 J$^{0.5}$ cm$^{-1.5}$ > treated peat, 26.3 J$^{0.5}$ cm$^{-1.5}$. Treated peat indicates the best compatibility with benzene (18.8 J$^{0.5}$ cm$^{-1.5}$) and CCl_4 (17.8 J$^{0.5}$ cm$^{-1.5}$). A similar ranking was observed in ref *24*, based on BTX sorption data: lignin ($\delta = 21.6$ J$^{0.5}$ cm$^{-1.5}$) > HOM ($\delta = 25.3$ J$^{0.5}$ cm$^{-1.5}$, averaged for the five soils under their study) > cellulose ($\delta = 32.1$ J$^{0.5}$ cm$^{-1.5}$).

Although Table 3 and Figure 2 give strong evidence of the validity of the solubility parameter concept for particulate HOM, attention should be paid to adsorption effects. In our former work (*6*) with nonpolar PAHs, we observed sorption linearity (C_{bound}/C_{free}) on DOM over a wide concentration interval. In contrast to that, nonlinear sorption, expressed by a significant concave-downward shape, is observed on soils and sediments (*17*, *25*). Obviously, more than one mechanism is operative when considering particulate HOM. Conceptual models to explain the deviations from sorption linearity include (i) at least two different HOM entities, that is, "hard" ("glassy") and "soft" ("rubbery") carbon; (ii) the presence of charcoal-like carbonaceous material with high specific surface areas; and (iii) internal holes ("pore filling" mechanisms) (*17*, *26*). Obviously, the Flory−Huggins theory cannot describe these effects in these heterogeneous sorbents, for which partitioning is not the main sorption mechanism by nature. A topic that deserves more attention in future work is the consideration of local cohesive energy

TABLE 4. Calculated Solubility Parameters of Biomatrices Based on Bioconcentration Factors (Assumption: Density = 1 g mL^{-1} Across All Matrices)

matrix/analyte	analyte	δ_{matrix} ($J^{0.5}cm^{-1}$)	ref
lipid tissue trout/referred to lipid content	benzene, trichloroethane	20.9/21.0	*41*
lipid tissue fathead minnow/referred to lipid content	hexachlorobenzene	21.1	*42*
lipid tissues guppy (*Poecilia reticulata*)/data referred to lipid content	chlorobenzenes, nitroaromatics	20.7 ± 0.9	*43*
dimyristoylphosphatidylcholine[a]	semivolatiles	21.8 ± 0.5	*44*
bovine serum albumin	nitrobenzene/phenols	28.9 ± 1.0	*45*
	ethylbenzene	28.3	*46*
	propylbenzene	29.4	*46*

[a] The higher solubility parameter of the choline (to simulate phospholipids) in comparison with octanol is evident, because solutes with $\delta_i > \delta_{octanol}$ show hgher partition coefficients on the choline, whereas solutes with $\delta_i < \delta_{octanol}$ possess higher K_{OW} values.

densities of the HOM domains, which are available to the solutes (see refs *18* and *28*). An indication that a significant adsorption term may also be operative in addition to partitioning is provided by a negative value under the square root in eq 5 [i.e., the negative value of $(2.3RT/V_m) \times (\log K_{OW} - \log K_{DOM})$ overcompensates $(\delta_i - \delta_{octanol})^2$]. For example, this occurs when literature data on pyrene sorption on an aquitard material were used (cf. ref *26*). The solubility parameter concept also fails when polar solutes (e.g., nitrophenols) are investigated because only hydrophobic interactions are involved in the concept.

Application of the Solubility Parameter Concept To Describe Bioconcentration Processes/Waterborne Organic Compounds. The environmental fate and effect of hydrophobic organic chemicals depend among others on their partitioning into aquatic organisms. The widely accepted hydrophobicity model considers bioconcentration as partitioning between water and the lipid phase of the aquatic organism, with no physiological barriers to impede accumulation of the chemical. Bioconcentration factors (BCF), the determination of which is expensive, demanding, and considered to be somewhat "idealized", have been estimated using the common relationship $\log BCF = a \log K_{OW} + b$, which was first outlined in the pioneering work of Chiou (*47*). This equation has the same shortcomings as those described for $\log K_{OM}$ data ($\log K_{OM} = a \log K_{OW} + b$, see eq 1). In our opinion, BCF data may be estimated for nonionic organics on the basis of analyte and matrix solubility parameter data via a modification of eq 4. The sorption coefficient on HOM and the HOM solubility parameter should be replaced by the BCF and the solubility parameters of the tissue, respectively. Table 4 gives δ values of several biological matrices calculated on the basis of (randomly selected) literature-available BCFs. Analogously to HOM, across all matrices under study, quite similar solubility parameters result. This provides strong evidence that (under equilibrium conditions) application of the solubility parameter concept is also very useful in estimating BCFs, although this approach simplifies the complex processes (e.g., no natural variations between type-identical organisms; no loss processes including respiration, metabolism, growth dilution considered, with respiration further divided into "active" and "passive" by means of dermal diffusion in the case of phytoplankton, etc.). We feel that this concept may be more efficient in explaining translocation and partitioning phenomena to plant tissue than the K_{OW} data (*48*).

With the solubility parameter of lipid tissue of aquatic organisms being close to that of the reference octanol (cf. Table 4), a similarity of lipid content-normalized BCF at equilibrium and K_{OW} is plausible for nonionic organic compounds of low and medium polarities. In the literature, tricaprylin (or triolein) is suggested to be a better reference standard to simulate bioconcentration processes (cf. refs *47* and *49* and references cited therein). For obvious reasons, tricaprylin is structurally more similar to lipid tissues. The overall solubility parameter of tricaprylin is assumed to be close to that of lipid tissues of aquatic organisms including rainbow trout. In this sense, the very nonpolar C_{18} Empore disks are likely not the best surrogate lipid phase to simulate bioconcentration processes (as was proposed in ref *50*). In our opinion, the SPME method to determine BCF data should be faster and less error-prone for volatile compounds than the cumbersome disk techniques. On the basis of the conclusions drawn above, it is advisable to run biomimetic extractions (i.e., to simulate bioconcentration processes) with the polar polyacrylate (PA) fiber, due to its compatibility with respect to solubility parameters with the lipid tissues. Another opportunity would be to use homemade SPME coatings with dimyristoylphosphatidylcholine to simulate biomembranes. Clearly, when BCFs in DOM solutions are investigated, the freely dissolved analyte concentration should be considered rather than the total concentration.

Application of the Solubility Parameter Concept To Describe Bioconcentration Processes/Airborne Organic Compounds. A key descriptor of a chemical's tendency to partition between air and lipid/wax/natural organic matter is the octanol−air partition coefficient (K_{OA}) (cf. ref *29* and references cited therein). We suggest extending the solubility parameter concept to describe the partitioning-based uptake of airborne organics by plants (another topic, which will not be detailed here, is the gas/particle partitioning on urban particulate material, which contains amorphous OM). In this approach, the octanol−air partition coefficient describing the "hydrophobicity" (or, more precisely, the aerophobicity) of organic compounds present in air is substituted for the octanol−water coefficients (eq 4). This suggestion proves to be right when (arbitrarily chosen) literature findings are considered. For example, the averaged solubility parameter value of pine needles under study in ref *30* amounts to 24.4 $J^{0.5}$ $cm^{-1.5}$ using aromatic hydrocarbons as sorbates. In this consideration (i) the matrix is considered to be an amorphous polymer and (ii) partitioning processes are assumed to prevail. On the basis of this (very simplified) consideration, a finding, which is surprising at a first glance, becomes plausible: the significant accumulation of PCBs (congeners with Cl_5−Cl_6; $\delta \sim 19.8$ $J^{0.5}$ $cm^{-1.5}$, cf. Table 1) in the polymeric inner needle matrix (*31*) ($\delta \sim 24.5$ $J^{0.5}$ $cm^{-1.5}$) in competition with the nonpolar wax layer on the needle surface. Therefore, when two airborne pollutants with similar octanol−air coefficients are considered, the analyte with the solubility parameter closer to that of the averaged pine needle δ value is expected to accumulate to a larger extent under equilibrium conditions.

The uptake of chlorinated pollutants in *Lolium multiflorum* (ryegrass) was correlated to the octanol−air coefficient in ref *32*. Bioconcentration of the more volatile PCBs, PCDDs, and PCDFs that reach equilibrium was found to correlate

strongly with the K_{OA} value. According to the physical–chemical data given in ref *32* and solubility parameters given in ref *15*, the matrix δ value amounts to $\delta_{ryegrass} = 30.3 \pm 0.6$ $J^{0.5}$ $cm^{-1.5}$), which is close to that of cellulose [31.8 $J^{0.5}$ $cm^{-1.5}$ (*7*)] (matrix density is assumed to be 1.0 g mL^{-1} in this consideration). The BCF–K_{OA} correlation was found to be invalid for highly hydrophobic analytes (e.g., Cl_6-PCBs, Cl_7- and Cl_8-PCDDs, and PCDFs). We argue that very slow diffusion in the amorphous matrix, which hinders equilibration with the air, contributes to this finding.

The usefulness of the proposed concept was confirmed by findings given in ref *33*. The authors determined partition coefficients between vapor and dewaxed cuticula matrices (isolated from mature tomato fruits), as well as between water and the cuticula, for 50 reference volatile organic compounds. On the basis of their measured partition coefficients and available K_{OW} and K_{OA} data for 12 analytes (cf. refs *34* and *51*), we calculated the dewaxed isolated cuticula's solubility parameter to be in a narrow range, $\delta_{cuticula} = 22.2 \pm 0.7$ $J^{0.5}$ $cm^{-1.5}$ and $\delta_{cuticula} = 22.3 \pm 0.6$ $J^{0.5}$ $cm^{-1.5}$, when using vapor/matrix and water/matrix partition coefficients, respectively. Important conclusions include the following:

(i) Once calculated, the solubility parameter of the sorbent may serve to predict bioconcentration processes for both waterborne and airborne pollutants.

(ii) Partitioning phenomena prevail in bioconcentration processes of both waterborne and airborne pollutants.

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Literature Cited

(1) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: New York, 1993.
(2) Chin, Y.-P.; Gschwend, P. M. *Environ. Sci. Technol.* **1992**, *26*, 1621–1626.
(3) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1–10.
(4) Seth, R.; Mackay, D.; Muncke, J. *Environ. Sci. Technol.* **1999**, *33*, 2390–2394.
(5) Poerschmann, J.; Kopinke, F.-D.; Pawliszyn, J. *J. Chromatogr. A* **1998**, *816*, 159–167; *Environ. Sci. Technol.* **1997**, *31*, 3629–3636.
(6) Poerschmann, J.; Kopinke, F.-D.; Plugge, J.; Georgi, A. Interaction of Organic Chemicals (PAH, PCB, Triazines, Nitroaromatics and Organotin Compounds) with Dissolved Humic Organic Matter. In *Understanding Humic Substances—Advanced Methods, Properties and Applications*; Ghabbour, E. A., Davies, G., Eds.; RCS: Cambridge, U.K., 1999; pp 223–240.
(7) Kopinke, F.-D.; Poerschmann, J.; Stottmeister, U. *Environ. Sci. Technol.* **1995**, *29*, 941–950.
(8) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1991; Chapter VII. Horvath, A. L. Molecular Design. In *Studies in Physical and Theoretical Chemistry 75*; Elsevier: New York, 1992; p 425.
(9) van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, The Netherlands, 1997; Chapter 7 (Cohesive Properties and Solubilities), pp 189.
(10) Mackay, D.; Shiu, W. Y.; Ching Ma, Y. *Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals, Vol. I, Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*; Lewis Publishers: Boca Raton, FL, 1991.
(11) Barton, A. F. M. *CRC Handbook of Solubility Parameters and other Cohesive Parameters*; CRC Press: Boca Raton, FL, 1985; p 257.
(12) Schlautman, M. A.; Morgan, J. A. *Environ. Sci. Technol.* **1993**, *27*, 961–969.
(13) Poerschmann, J.; Zhang, Zh.; Kopinke, F.-D.; Pawliszyn, J. *Anal. Chem.* **1997**, *69*, 597–600.
(14) Baker, J. R.; Mihelcic, J. R.; Luehrs, D. C., Hickey, J. P. *Water Environ. Res.* **1997**, *69*, 136–145.
(15) Govers, H. A. J.; Wielen, V. D.; Olie, F. W. M. *J. Chromatogr. A* **1995**, *715*, 267–278.
(16) Chiou, C. T. *Soil Sorption of Organic Pollutants and Pesticides*; Wiley Encyclopedia Series in Environmental Science; Myers, R. A., Ed.; Wiley: New York, 1998; Vol. 8, p 4517.
(17) Chiou, C. T.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 338–343.
(18) Chin, Y.-P.; Aiken, G. R.; Danielsen, K. M, *Environ. Sci. Technol.* **1997**, *31*, 1630–1635.
(19) Lee, D.-Y.; Farmer, W. J. *J. Environ. Qual.* **1989**, *18*, 468–474.
(20) Schlebaum, W.; Badora, A.; Schraa, G.; Riemsdijk, W. H. v. *Environ. Sci. Technol.* **1998**, *32*, 2273–2277.
(21) Skoglund, R. S.; Swackhamer D. L. *Environ. Sci. Technol.* **1999**, *33*, 1516–1519.
(22) Uhle, M. E.; Chin, Y.-P.; Aiken, G. R.; Mcknight, D. M. *Environ. Sci. Technol.* **1999**, *33*, 2715–2718.
(23) Rutherford, D. W.; Chiou, C. T.; Kile, D. E. *Environ. Sci. Technol.* **1992**, *26*, 336–339.
(24) Xing, B.; McGill, W. B.; Dudas, M. J. *Environ. Sci. Technol.* **1994**, *28*, 1929–1933.
(25) Xing, B.; Pignatello, J. J.; Gigliotti, B. *Environ. Sci. Technol.* **1996**, *30*, 2432–2440.
(26) Xia, G.; Ball, W. P. *Environ. Sci. Tec*hnol. **1999**, *33*, 262–269.
(27) Spurlock, F. C.; Biggar, J. W. *Environ. Sci. Technol.* **1994**, *28*, 989–995.
(28) Chiou, C. T.; Kile, D. E.; Rutherford, D. W.; Sheng, G.; Boyd, S. A. *Environ. Sci. Technol.* **2000**, *34*, 1254–1258.
(29) Simonich, L. S.; Hites, R. A. *Environ. Sci. Technol.* **1995**, *29*, 2905–2914.
(30) Hiatt, M. H. *Environ. Sci. Technol.* **1999**, *33*, 4126–4133.
(31) Wenzel, K.-D.; Weissfolg, L.; Paladini, E.; Gantuz, M.; Guerreiro, P.; Puliafito, C.; Schüürmann, G. *Chemosphere* **1997**, *34*, 2505–2518.
(32) Mclachlan, M. S.; Welsch-Pausch, K.; Tolls, J. *Environ. Sci. Technol.* **1995**, *29*, 1998–2004.
(33) Welke, B.; Ettlinger, K.; Riederer, M. *Environ. Sci. Technol.* **1998**, *32*, 1099–1104.
(34) Daylight Chemical Information Systems, Database Medchem, Irvine, CA, 1999.
(35) Chiou, C. T.; Mcgroddy, S. E.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 264–270.
(36) Ozretich, R. J.; Smith, L. M.; Roberts, F. A. *Environ. Toxicol. Chem.* **1995**, *14*, 1261–1272.
(37) Barber, L. B. *Environ. Sci. Technol.* **1994**, *28*, 890–897.
(38) Sabljic. A.; Güsten, H.; Verhaar, H.; Hermens, J. *Chemosphere* **1995**, *31*, 4489–4514.
(39) Poole, S. K.; Poole, C. F. *Anal. Commun.* **1996**, *33*, 417–419.
(40) Chen, W.; Kann, A. T.; Fu, G.; Vignona, L. C.; Tomson, M. B. *Environ. Toxicol. Chem.* **1999**, *18*, 1610–1616.
(41) Bertelsen, S. H.; Hoffmann, A. D.; Gallinat, C. A.; Elonen, C. M.; Nichols, J. W. *Environ. Toxicol. Chem.* **1998**, *17*, 1447–1455.
(42) Meylan, W. M.; Howard, P. H.; Boethling, R. S.; Aronsson, D.; Printup, H.; Gouchie; S. *Environ. Toxicol. Chem.* **1999**, *18*, 664–672.
(43) Schüürmann, G. *Z. Umweltchem. Ökotox.* **1997**, *9*, 345–352.
(44) Vaes, W. H. J.; Ramos, E. U.; Hamwijk, C.; Holsteijn, I. v.; Blaauboer, B. J.; Seinen, W.; Verhaar, W. J. M.; Hermens, J. L. M. *Chem. Res. Toxicol.* **1997**, *10*, 1067–1072.
(45) Vaes, W. H. J.; Ramos, E. U.; Verhaar, H. J. M.; Seinen, W.; Hermens, J. L. M. *Anal. Chem.* **1996**, *68*, 4463–4467.
(46) Yuan, H.; Ranatunga, R.; Carr, P. W.; Pawliszyn, J. *Analyst* **1999**, *124*, 1443–1448.
(47) Chiou, C. T. *Environ. Sci. Technol.* **1985**, *19*, 57–62.
(48) Burken, J. G.; Schnoor, J. L. *Environ. Sci. Technol.* **1998**, *32*, 3379–3385.
(49) Bahadur, N. P.; Shiu, W. Y.; Boocock, D. G. B.; Mackay, D. J. *J. Chem. Eng. Data* **1999**, *44*, 40–43.
(50) Loon, W. M. G. M. v.; Wijnker, F. G.; Verwoerd, M. E.; Hermens, J. L. M. *Anal. Chem.* **1996**, *68*, 2916–2926.
(51) Keymeulen, R.; Parewijck, B.; Gorna-Binkul, A.; Langenhove, H. v. *J. Chromatogr. A* **1997**, *765*, 247–253.

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