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## Chromatographic models for the sorption of neutral organic compounds by soil from water and air

Salwa K. Poole<sup>a</sup>, Colin F. Poole<sup>b,\*</sup>

<sup>a</sup>Chemistry Department, Parke-Davis Pharmaceutical Research Division, Warner-Lambert Company, 2800 Plymouth Road, Ann Arbor, MI 48105, USA

<sup>b</sup>Room 171, Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

### Abstract

The solvation parameter model is used to construct models for the estimation of the soil–water and soil–air distribution constants and to characterize the contribution of fundamental intermolecular interactions to the underlying sorption processes. Wet soil is shown to be quite cohesive and polar but relatively non-selective for dipole-type, lone-pair electron and hydrogen-bond interactions. Using a comparison of system constant ratios chromatographic systems employing reversed-phase liquid chromatography on polar bonded phases are shown to provide suitable models for estimating soil–water distribution constants. No suitable gas chromatographic models were found for the soil–air distribution constant but the requirements for such a system are indicated. Models are also provided for adsorption at the air–water interface. Estimation methods based on either the solvation parameter model or chromatographic model reproduce experimental distribution constants for a wide variety of compounds with a similar error (0.2–0.3 log units) to that expected in the experimental data. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The sorption of organic chemicals by soils is a complex process but one of great importance for an understanding of the transport and fate of organic chemicals in the environment. Reliable data for the sorption of organic chemicals from water is required to establish the fate of contaminants in natural waters, the transport of organic compounds through soil, the leaching of contaminants from hazardous waste sites, and for the correct use of crop protecting agents in agriculture [1–7]. Such is the economic and ecological importance of these processes that

they are part of the cornerstones of public policy, quality of life and health issues, and wealth creation.

For nonionic compounds the dominant phase for the sorption of organic compounds by soils, sediments and sewage sludges from water is the soil organic matter provided that this exceeds a minimum threshold for bulk composition of about 0.5% (w/w) [1,2,8–13]. The soil organic matter is usually present as a layer coating the surface of the mineral fraction of the soil and masking mineral sorption sites. In addition, the strong dipole interactions of mineral surface sites with water results in exclusion of neutral compounds from mineral sorption sites. It is these factors that make it feasible to develop a simple sorption model for the uptake of organic compounds by soil from water by considering the organic matter phase only. Such general models will

\*Corresponding author. Tel.: +1-313-577-2881; fax: +1-313-577-1377.

E-mail address: cfp@chem.wayne.edu (C.F. Poole)

of course fail when significant site-specific (mineral) interactions result in increased physical or chemical binding of solutes to soil [14–17].

The extent to which a particular organic compound is distributed between soil and water is described by the appropriate sorption isotherm for the compound and its concentration in the system. The soil sorption distribution constant ( $K_d$ ) varies widely with soil type and cannot be utilized as a solute property. A large part, but not all, of this variation can be eliminated by normalizing the sorption distribution constant to the amount of organic matter ( $K_{OM}$ ), or more commonly to the fraction of organic carbon ( $K_{OC}$ ), for individual soils. But since the composition of the soil organic matter is not fixed, variations in experimental soil organic matter–water distribution constants can be expected for soils with extreme property differences. In addition, experimental soil–water distribution isotherms are frequently nonlinear over an extended solute concentration range, and are usually fit to the Freundlich isotherm model

$$\log C_s = \log K_F + (1/z) \log C_w \quad (1)$$

where  $C_s$  is the amount of solute sorbed by the soil ( $\mu\text{g/g}$ ),  $K_F$  the Freundlich sorption coefficient,  $C_w$  the concentration of analyte in solution ( $\mu\text{g/ml}$ ), and  $z$  is a unitless exponent. Only when  $z=1$  is  $K_F=K_d$  and a comparison of sorption properties to other soils is possible in consistent units. These conditions can be met in many instances for a limited (low) concentration range when site-specific solute-soil interactions are negligible [1,2,4,6,10].

The determination of the soil organic carbon–water distribution constant is a time consuming and difficult task requiring a number of measured  $K_d$  values for several varied soils obtained over a reasonable concentration range [18–20]. Because of experimental complications, and the need to access values for undetermined soil–water distribution constants in environmental modeling, there is considerable interest in estimation methods based on surrogate solute properties that are more amenable to experimental determination [3,6,21–24].

The majority of quantitative structure–property relationship models for estimating soil–water distribution constants use either topological indices [3,25–29], quantum chemical parameters [30], oc-

tanol–water distribution constants ( $\log K_{OW}$ ) [1,2,6,21,24,29,31] or aqueous solubility ( $\log S_w$ ) [1,2,6,21] as compound descriptors. Topological indices and quantum chemical parameters allow soil sorption distribution constants to be estimated solely from chemical structure. These models generally employ connectivity indices to encode information about solute size, steric factors, branching, unsaturation, number of heteroatoms and aromatic rings, etc. Reasonable results have been obtained for nonpolar compounds but for polar compounds empirical correction factors based on structural fragments are required. Water solubility and the octanol–water distribution constant are the most widely used descriptors for predicting  $\log K_{OC}$  and provide reasonable estimates of  $\log K_{OC}$  for nonpolar compounds and less reliable results for polar compounds. Models based on  $\log K_{OW}$  and  $\log S_w$  are compound class specific and exhibit a large variation in slopes and intercepts, indicating the large uncertainty and low reliability of estimates for compounds with diverse structural properties. Typical uncertainties for within class estimates of  $\log K_{OC}$  are 0.2–0.6. For polar compounds the predictive accuracy can be improved by adding additional terms to the model containing  $\log K_{OW}$  to allow for specific polar interactions and acid–base effects poorly model by octanol [6,17,27,28].

The defining principle in the above studies is that the sorption of neutral organic compounds by soil from water can be modeled by a distribution mechanism analogous to liquid–liquid distribution and retention in reversed-phase liquid chromatography (RPLC). The analogy with RPLC is strongly supported by the notion of water percolating through a somewhat porous inert microstructure (mineral matter in soil and silica in chromatography), supporting an immobilized solvated organic layer (humus in soil and chemically bonded phase in chromatography), which is responsible for the selective retention of organic compounds. This being the case, it should be possible to model the uptake of organic compounds by soil from water using models successfully applied to the retention of organic compounds in reversed-phase chromatography and to use characteristic chromatographic parameters for the estimation of soil–water distribution constants. A number of such applications have already been described using

chemically bonded sorbents [28,32–39], immobilized humic acid [39–44], and immobilized salicylic acid or 8-hydroxyquinoline [45] for RPLC, and by soil thin-layer chromatography [46]. In a number of studies only low polarity solutes were considered and extrapolation methods employed to determine  $\log K_w$  (the assumed retention factor for the solute with water as the mobile phase) without adequate validation of the linearity of the model used. More detailed studies using the retention factor at a fixed mobile phase composition indicate that retention factors are more suitable for estimating  $\log K_{OC}$  than are  $\log K_w$  values when compounds from different classes are considered [30,36–38].

In this paper we present a single model, the solvation parameter model, to characterize the sorption properties of the soil–water and soil–air distribution systems, and to identify surrogate chromatographic models with suitable properties for the estimation of soil–water and soil–air distribution constants. Preliminary results for the sorption of organic compounds by soil [47] and activated carbon [48] from water for a restricted number of compounds were presented previously. Applications of the solvation parameter model to solid-phase extraction and reversed-phase column, thin-layer, micellar electrokinetic and gas chromatography are now quite extensive, and a few representative references are indicated from which a more detailed bibliography can be constructed [49–56]. In related studies the solvation parameter model was used to establish models for the estimation of distribution constants for biological systems of pharmaceutical interest and to establish suitable chromatographic models for estimating octanol–water distribution constants [56–59].

## 2. Methodology

The solvation parameter model in a form suitable for characterizing the contributions of different intermolecular interactions to the sorption of organic compounds by soil from water and the retention factor in reversed-phase liquid chromatography is set out below:

$$\log SP = c + mV_x + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^0 \quad (2)$$

where  $SP = K_{OC}$ ,  $K_{OW}$ ,  $K_S$  or  $k$ , and for sorption of organic compounds by soil from air

$$\log SP = c + l \log L^{16} + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H \quad (3)$$

where  $SP = K_{OCA}$  or  $K_{AW}$  (the distribution constants are defined in Section 3). The equations are made up of product terms representing solute properties (descriptors) and chromatographic (system) properties. Each product term represents the contribution of a defined intermolecular interactions to the retention mechanism. The solute descriptors are McGowan's characteristic volume  $V_x$  (in  $\text{cm}^3 \text{mol}^{-1}/100$ ),  $\log L^{16}$  is the distribution constant for the solute between a gas and *n*-hexadecane at 298 K,  $R_2$  excess molar refraction (in  $\text{cm}^3/10$ ),  $\pi_2^H$  the solute's dipolarity/polarizability, and  $\Sigma\alpha_2^H$  and  $\Sigma\beta_2^0$  the solute's effective hydrogen-bond acidity and hydrogen-bond basicity, respectively. The system constants in Eq. (2) are defined by their complementary interactions with the solute descriptors. The *r* constant determines the difference in capacity of wet soil (or solvated sorbent in chromatography) and water or air (or the mobile phase in chromatography) to interact with solute *n*- or  $\pi$ -electrons; the *s* constant to the difference in capacity of wet soil and water or air to take part in dipole–dipole and dipole-induced dipole interactions; the *a* constant is a measure of the difference in hydrogen-bond basicity of wet soil and water or air; the *b* constant is a measure of the difference in hydrogen-bond acidity of wet soil and water or air; and the *m* and *l* constants are a measure of the relative ease of forming a cavity for the solute in wet soil compared to water or air together with the difference in dispersion interactions between the solute and wet soil and water or air (referred to as the cavity term). Solute descriptors are available for about 4000 compounds [55,57]. For new compounds the  $V_x$  and  $R_2$  descriptors can be calculated from atomic constants [57]. The other solute descriptors must be determined by either parameter estimates or experiment [58,60,61].

## 3. Data sources and calculations

Values for  $\log K_{OC}$ ,  $\log K_{OW}$  and  $\log k$  are taken

from literature sources as indicated in the text. In various instances data recorded as the Freundlich sorption coefficient ( $K_d$ ) were normalized through division by the fraction of soil organic carbon  $f_{OC}$  (100/percent organic carbon),

$$K_{OC} = K_d / (f_{OC}) \quad (4)$$

and data presented as the soil organic matter distribution constant ( $K_{OM}$ ) was converted to  $K_{OC}$  assuming that the soil organic matter is 58% carbon.

$$\log K_{OC} \approx \log K_{OM} + 0.24 \quad (5)$$

The water saturated soil–air distribution constant normalized per unit of soil organic carbon,  $\log K_{OCA}$ , was calculated through the relationship

$$\log K_{OCA} = \log K_{OC} + \log L^w \quad (6)$$

with the values for  $\log L^w$ , the air–water distribution constant for organic vapors taken from [62]. Where more than one experimental value for  $K_{OC}$  are available for a single compound an average value was taken after exclusion of values where  $z$  in Eq. (1) is  $0.8 < z < 1.1$  (if this information was provided). Solutes with known descriptors were used without resorting to parameter estimates to avoid introducing additional uncertainty into the model fits (in general this meant excluding the majority of data available for crop protection agents and polychlorinated biphenyls). Solute descriptors were taken from several sources [57,58,62–64] and supplemented by additional values from our laboratory data base (all values used are recorded in the tables).

There are few experimental distribution constants for the adsorption of neutral organic compounds at the air–water interface. A valuable collection of distribution constants for the transfer of solute from bulk water to the air–water interface,  $\log K_s$ , is given by Valsaraj [65]. The distribution constants for adsorption of neutral organic compounds at the air–water interface,  $\log K_{AW}$ , were calculated using Eq. (7)

$$\log K_{AW} = \log K_s + \log L^w \quad (7)$$

where  $K_{AW}$  (in cm) is the ratio of the surface concentration ( $\text{mol}/\text{cm}^2$ ) to the molar gas (air) phase concentration ( $\text{mol}/\text{cm}$ ) and  $K_s$  (in cm) is the ratio of the surface concentration ( $\text{mol}/\text{cm}^2$ ) to the bulk

aqueous phase concentration ( $\text{mol}/\text{cm}^3$ ). The agreement between calculated and available experimental  $K_{AW}$  values is good given the small differences in temperature between the calculated ( $25^\circ\text{C}$ ) and experimental values ( $12.5^\circ\text{C}$ ) [66].

The system constants were obtained from the individual data sets by multiple linear regression analysis using the program SPSS/PC+ Ver. 5.0 (SPSS, Chicago, IL, USA) running on a Hewlett-Packard Vectra computer (Wilmington, DE, USA). Statistical outliers in the data sets were removed one at a time based on the difference between the predicted and experimental value being greater than twice the standard error in the estimate for the model. When a stable model was obtained the experimental values were put back in one at a time to confirm if rejection was justified. All experimental values identified as statistical outliers are indicated in the text.

## 4. Results and discussion

### 4.1. Model for the sorption of neutral organic compounds by soil from water

One of the largest data bases of  $\log K_{OC}$  values meeting our selection criteria in the public domain has been assembled by Sabljic et al. [24]. Additional values taken from Maylen et al. [26] and Bahnick and Doucette [67] were added to this collection. We had solute descriptors for 138 of these compounds (Table 1) yielding the following model

$$\begin{aligned} \log K_{OC} = & 0.55 (\pm 0.14) + 1.76 (\pm 0.15) V_x \\ & + 0.95 (\pm 0.10) R_2 - 0.39 (\pm 0.14) \pi_2^H \\ & - 0.39 (\pm 0.14) \Sigma \alpha_2^H - 1.51 (\pm 0.19) \Sigma \beta_2^0 \end{aligned} \quad (8)$$

where  $\rho = 0.940$ ,  $S.E. = 0.391$ ,  $F = 202$  and  $n = 138$ , where  $\rho$  is the multiple correlation coefficient,  $S.E.$  the standard error in the estimate,  $F$  the Fischer statistic, and  $n$  is the number of solutes. The data contains seven outliers (urea:  $ex = 0.90$ ,  $pre = -0.03$ ; 2,3,5-trimethylphenol:  $ex = 3.61$ ,  $pre = 2.34$ ; dimethylamine:  $ex = 2.63$ ,  $pre = 0.50$ ; 1-aminonaphthalene:  $ex = 3.51$ ,  $pre = 2.83$ ; diethylacetamide:

Table 1  
Solute descriptors and soil–water, soil–air and octanol–water distribution constants

Solute	Descriptors						Distribution constants		
	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	$\text{Log } L^{16}$	$\text{Log } K_{OC}$	$\text{Log } K_{OW}$	$\text{Log } K_{OCA}$
Benzene	0.716	0.610	0.52		0.14	2.714	1.91	2.19	2.54
Toluene	0.857	0.601	0.52		0.14	3.325	2.18	2.79	2.83
Ethylbenzene	0.998	0.613	0.51		0.15	3.778	2.41	3.15	2.99
1,2-Dimethylbenzene	0.998	0.663	0.56		0.16	3.939	2.41	3.12	3.07
1,3-Dimethylbenzene	0.998	0.623	0.52		0.16	3.839	2.34	3.20	2.95
1,4-Dimethylbenzene	0.998	0.613	0.52		0.16	3.839	2.52	3.15	3.11
<i>n</i> -Propylbenzene	1.139	0.604	0.50		0.15	4.230	2.86	3.72	3.25
1,3,5-Trimethylbenzene	1.139	0.649	0.52		0.19	4.344	2.82	3.42	3.48
1,2,3-Trimethylbenzene	1.139	0.728	0.61		0.19	4.565	2.80	3.59	3.69
Styrene	0.955	0.849	0.65		0.16	3.856	2.96	2.95	3.87
1,2,4,5-Tetramethylbenzene	1.280	0.748	0.61		0.19		3.12	4.00	
<i>n</i> -Butylbenzene	1.280	0.600	0.51		0.15	4.730	3.39	4.38	3.68
Naphthalene	1.085	1.340	0.92		0.20	5.161	3.11	3.30	4.87
1-Methylnaphthalene	1.226	1.344	0.90		0.20	5.789	3.36	3.87	5.15
2-Methylnaphthalene	1.226	1.304	0.92		0.20		3.64	3.86	
1-Ethyl-naphthalene	1.367	1.371	0.87		0.20	6.136	3.78	4.39	5.54
2-Ethyl-naphthalene	1.367	1.331	0.87		0.20		3.76	4.38	
Biphenyl	1.324	1.360	0.99		0.26	6.014	3.27	4.01	5.22
Anthracene	1.454	2.290	1.34		0.26		4.27	4.45	
9-Methylanthracene	1.595	2.290	1.30		0.26	4.81	5.07		
Phenanthrene	1.454	2.055	1.29		0.26	4.28	4.56		
Fluorene	1.357	1.588	1.03		0.20	6.922	3.70	4.18	6.16
Fluoranthene	1.585	2.377	1.53		0.20		4.62	5.16	
Tetracene	1.823	2.847	1.70		0.32		5.81	5.90	
Pyrene	1.585	2.808	1.71		0.29		4.92	4.88	
Benz[ <i>a</i> ]anthracene	1.823	2.992	1.70		0.33		5.30	5.79	
1,2,5,6-Dibenzanthracene	1.954	4.000	1.93		0.44		6.31	6.50	
Benzo[ <i>a</i> ]pyrene	1.954	3.625	1.98		0.44	5.95	6.06		
Chlorobenzene	0.839	0.718	0.65		0.07	3.657	2.34	2.90	3.16
1,2-Dichlorobenzene	0.961	0.872	0.78		0.04	4.518	2.50	3.43	3.50
1,3-Dichlorobenzene	0.961	0.847	0.73		0.02	4.410	2.48	3.53	3.20
1,4-Dichlorobenzene	0.961	0.825	0.75		0.02	4.435	2.63	3.44	3.37
1,2,3-Trichlorobenzene	1.084	1.030	0.86		0	5.419	3.39	4.14	4.30
1,2,4-Trichlorobenzene	1.084	0.980	0.81		0	5.248	3.15	4.05	3.97
1,3,5-Trichlorobenzene	1.084	0.980	0.73		0	5.045	2.85	4.19	3.42
1,2,3,4-Tetrachlorobenzene	1.206	1.180	0.92		0	6.171	3.84	4.64	4.82
1,2,3,5-Tetrachlorobenzene	1.206	1.160	0.85		0	5.922	3.20	4.66	4.39
Pentachlorobenzene	1.328	1.330	0.96		0		3.50	5.18	
Hexachlorobenzene	1.451	1.490	0.99		0		3.99	5.73	
Bromobenzene	0.891	0.882	0.73		0.09	4.041	2.49	2.99	3.56
Iodobenzene	0.975	1.188	0.82		0.12	4.502	3.10	3.25	4.38
Dichloromethane	0.494	0.387	0.57	0.10	0.05	2.019	1.44	1.25	2.40
Trichloromethane	0.617	0.425	0.49	0.15	0.02	2.480	1.65	1.97	2.44
Tetrachloromethane	0.739	0.458	0.38		0	2.823	1.85	2.83	1.79
Tribromomethane	0.775	0.974	0.68	0.15	0.06	3.784	2.06	2.67	3.62
1,1-Dichloroethane	0.635	0.322	0.49	0.10	0.10	2.316	1.48	1.79	2.10
1,2-Dichloroethane	0.635	0.416	0.64	0.10	0.11	2.573	1.52	1.48	2.83
1,2-Dibromoniethane	0.740	0.747	0.76	0.10	0.17		1.80	1.96	
1,1,1-Trichloroethane	0.758	0.369	0.41		0.09	2.733	1.82	2.49	1.96
1,1,2-Trichloroethane	0.758	0.499	0.68	0.13	0.08	3.290	1.87	1.89	3.33

(continued on next page)

Table 1 (continued)

Solute	Descriptors						Distribution constants		
	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	$\text{Log } L^{16}$	$\text{Log } K_{OC}$	$\text{Log } K_{OW}$	$\text{Log } K_{OCA}$
1,1,2,2-Tetrachloroethane	0.880	0.595	0.76	0.16	0.12	3.803	1.90	2.39	3.71
1,1-Dichloroethene	0.592	0.362	0.34		0.05		1.81	2.13	
Trichloroethene	0.715	0.524	0.40	0.08	0.03	2.997	2.00	2.61	2.32
Tetrachloroethene	0.837	0.639	0.42		0	3.584	2.38	3.40	2.31
1,2-Dichloropropane	0.776	0.371	0.60	0.10	0.11	2.857	1.67	1.99	2.60
Acetanilide	1.113	0.870	1.40	0.50	0.67		1.43	1.16	
3-Methylacetanilide	1.254	0.870	1.40	0.50	0.66		1.45	1.68	
4-Methoxyacetanilide	1.313	0.970	1.63	0.48	0.86		1.40	1.05	
Methanol	0.308	0.278	0.44	0.43	0.47	0.970	0.04	-0.77	4.18
Ethanol	0.449	0.246	0.42	0.37	0.48	1.485	0.20	-0.31	3.87
1-Propanol	0.590	0.236	0.42	0.37	0.48	2.031	0.48	0.25	4.04
1-Butanol	0.731	0.224	0.42	0.37	0.48	2.601	0.50	0.88	3.96
1-Pentanol	0.872	0.219	0.42	0.37	0.48	3.106	0.70	1.56	4.05
1-Hexanol	1.013	0.210	0.42	0.37	0.48	3.610	1.01	2.03	4.24
1-Heptanol	1.154	0.211	0.42	0.37	0.48	4.115	1.14	2.72	4.23
1-Octanol	1.295	0.199	0.42	0.37	0.48	4.619	1.56	3.00	4.56
1-Nonanol	1.435	0.193	0.42	0.37	0.48	5.124	1.89	4.26	4.74
1-Decanol	1.576	0.191	0.42	0.37	0.48	5.628	2.59	4.57	5.26
1-Phenylethanol	1.057	0.784	0.83	0.30	0.66		1.50	1.36	
Benzamide	0.973	0.990	1.50	0.49	0.67	5.767	1.46	0.64	9.53
4-Nitrobenzamide	1.147	1.250	2.17	0.75	0.60		1.93	0.82	
4-Methylbenzamide	1.114	0.990	1.50	0.49	0.65		1.78	1.18	
2-Chlorobenzamide	1.095	1.140	1.60	0.45	0.75		1.51	0.64	
N-Methylbenzamide	1.114	0.950	1.44	0.35	0.73		1.42	0.86	
Trichloroacetamide	0.873	0.710	0.63	0.47	0.56		0.99	1.04	
Diethylacetamide	1.070	0.296	1.30	0.78		1.84	0.34		
Aniline	0.816	0.955	0.94	0.26	0.50		1.41	0.94	
3-Methylaniline	0.957	0.946	0.95	0.23	0.55		1.65	1.40	
4-Methylaniline	0.957	0.923	0.95	0.23	0.52	4.452	1.90	1.39	5.99
4-Chloroaniline	0.939	1.060	1.13	0.30	0.35	4.889	1.96	1.88	6.29
4-Bromoaniline	0.991	1.190	1.19	0.31	0.35		1.96	2.26	
N-Methylaniline	0.957	0.948	0.90	0.17	0.48	4.478	2.28	1.66	5.72
N,N-Dimethylaniline	1.098	0.957	0.84		0.47	4.701	2.26	2.31	4.79
Diphenylaniline	1.424	0.700	0.88	0.60	0.38		2.78	3.50	
Dimethylphthalate	1.180	0.780	1.41		0.88		1.60	1.56	
Diethylphthalate	1.711	0.729	1.40		0.88		1.84	2.47	
Methyl benzoate	1.073	0.733	0.85		0.48	4.704	2.10	2.12	4.98
Ethyl benzoate	1.214	0.689	0.85		0.46	5.075	2.30	2.64	4.97
Phenylbenzoate	1.540	1.330	1.42		0.47		3.16	3.59	
Ethyl 4-nitrobenzoate	1.388	0.950	1.38		0.61		2.48	2.33	
Ethyl 4-hydroxybenzoate	1.272	0.860	1.35	0.69	0.45		2.21	2.47	
Ethyl phenylacetate	1.354	0.660	1.01		0.57		1.89	2.28	
Ethyl pentanoate	1.169	0.049	0.58		0.45	3.769	1.97	2.30	3.80
Ethyl hexanoate	1.310	0.043	0.58		0.45	4.251	2.06	2.83	3.79
Ethyl heptanoate	1.451	0.027	0.58		0.45		2.61	3.36	
Ethyl octanoate	1.592	0.024	0.58		0.45		3.02	3.88	
Nitrobenzene	0.891	0.871	1.11		0.28	4.557	2.20	1.83	5.22
Anisole	0.916	0.708	0.75		0.29		1.63	2.11	
1,2-Dimethoxybenzene	1.116	0.810	1.00		0.47		2.03	1.06	
Diphenylether	1.383	1.216	1.08		0.20		3.29	4.21	

Table 1 (continued)

Solute	Descriptors						Distribution constants		
	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	$\text{Log } L^{16}$	$\text{Log } K_{OC}$	$\text{Log } K_{OW}$	$\text{Log } K_{OCA}$
Benzophenone	1.481	1.447	1.50		0.50		2.63	3.18	
Acetophenone	1.014	0.818	1.01		0.48	4.501	1.54	1.58	4.90
Benzoic acid	0.932	0.730	0.90	0.59	0.40		1.50	1.87	
4-Hydroxybenzoic acid	0.990	0.930	0.92	0.87	0.53		1.43	1.58	
4-Nitrobenzoic acid	1.106	0.990	1.07	0.62	0.54		1.43	1.89	
4-Methylbenzoic acid	1.073	0.730	0.90	0.60	0.40		1.77	2.27	
Acetic acid	0.465	0.265	0.65	0.61	0.45	1.750	0.00	-0.17	4.91
Phenylacetic acid	1.073	0.730	0.95	0.60	0.63		1.45	1.41	
Hexanoic acid	1.028	0.174	0.60	0.60	0.45	3.920	1.46	1.92	6.02
Phenol	0.775	0.805	0.89	0.60	0.30	3.766	1.43	1.46	6.28
4-Methylphenol	0.916	0.820	0.87	0.57	0.31	4.312	2.70	1.94	7.20
3,5-Dimethylphenol	1.057	0.820	0.84	0.57	0.36	4.774	2.83	2.35	7.17
2,3,5-Trimethylphenol	1.198	0.860	0.84	0.52	0.42		3.61	2.92	
2-Chlorophenol	0.898	0.853	0.88	0.32	0.31	4.178	2.60	2.15	5.94
3-Chlorophenol	0.898	0.909	1.06	0.69	0.15		2.54	2.50	
2,3-Dichlorophenol	1.020	0.960	0.94	0.48	0.20		2.65	2.84	
2,4-Dichlorophenol	1.020	0.960	0.84	0.53	0.19		2.75	3.06	
3,4-Dichlorophenol	1.020	1.020	1.14	0.85	0.03		3.09	3.33	
2,4,6-Trichlorophenol	1.142	1.010	1.01	0.82	0.08		3.02	3.69	
Pentachlorophenol	1.389	1.270	0.88	0.97	0		3.73	5.12	
4-Bromophenol	0.950	1.080	1.17	0.67	0.20	5.135	2.41	2.59	7.64
4-Nitrophenol	0.949	1.070	1.72	0.82	0.26	5.876	2.37	1.91	10.18
2-Methoxyphenol	0.975	0.837	0.91	0.22	0.52	4.449	1.56	1.32	5.65
3-Methoxyphenol	0.975	0.879	1.17	0.59	0.39	4.803	1.50	1.58	7.12
2-Hydroxyphenol	0.834	0.970	1.07	0.85	0.52		1.03	0.95	
3-Hydroxyphenol	0.834	0.980	1.00	1.10	0.58		0.98	0.80	
1-Naphthol	1.144	1.520	1.05	0.61	0.37	6.130	2.64	2.84	8.27
Urea	0.465	0.500	1.00	0.50	0.90		0.90	-2.11	
Phenylurea	1.073	1.110	1.40	0.77	0.77		1.35	0.83	
Dimethylamine	0.490	0.189	0.30	0.08	0.66	1.600	2.63	-0.38	5.78
1-Butylamine	0.772	0.224	0.35	0.16	0.61	2.618	1.88	0.97	4.99
1-Aminonaphthalene	1.185	1.670	1.26	0.20	0.57		3.51	2.25	
Azobenzene	1.481	0.680	1.20		0.44		3.03	3.82	
Carbazole	1.315	1.787	1.42	0.47	0.26		3.40		
Acridine	1.413	2.356	1.32		0.58		4.11	3.40	
Dibenzothiophene	1.379	1.959	1.31		0.18		4.00	4.38	

Cross-correlation matrix for solute descriptors ( $r^2$ )

	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\text{Log } L^{16}$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$
$R_2$	0.32					$R_2$	0.51	
$\pi_2^H$	0.32	0.48				$\pi_2^H$	0.43	0.53
$\Sigma\alpha_2^H$	0.05	0.02	0.03			$\Sigma\alpha_2^H$	0.00	0.03
$\Sigma\beta_2^0$	0.05	0.00	0.19	0.12		$\Sigma\beta_2^0$	0.00	0.11

ex = 1.84, pre = 1.02; butylamine: ex = 1.88, pre = 1.04; and, 4-methylphenol: ex = 2.70, pre = 1.95; where 'ex' is the experimental  $\text{log } K_{OC}$  value, and 'pre' is the model prediction for the same compound). After removal of outliers the following model was obtained

$$\begin{aligned} \log K_{OC} = & 0.21 (\pm 0.09) + 2.09 (\pm 0.10)V_x \\ & + 0.74 (\pm 0.04)R_2 - 0.31 (\pm 0.09)\Sigma\alpha_2^H \\ & - 2.27 (\pm 0.11)\Sigma\beta_2^0 \end{aligned} \quad (9)$$

where  $\rho = 0.977$ ,  $S.E. = 0.248$ ,  $F = 655$  and  $n = 131$ .

Given the typical uncertainty in literature  $\log K_{OC}$  values, this model is as good as could be expected, and is quite satisfactory for the prediction of  $\log K_{OC}$  values for compounds of diverse structure as indicated by Fig. 1 for the plot of predicted vs. experimental  $\log K_{OC}$  values. The general range of apparent soil pH is 3–7.5. Within this pH range it is possible that the carboxylic acids, some of the more acidic phenols, and the more basic amines are partially ionized and subject to additional sorption interactions not included in the model, such as electrostatic interactions and ion exclusion. Removing solutes that might be significantly ionized resulted in the following model

$$\begin{aligned} \log K_{OC} = & 0.19 (\pm 0.10) + 2.12 (\pm 0.11)V_X \\ & + 0.72 (\pm 0.05)R_2 - 0.23 (\pm 0.10)\Sigma\alpha_2^H \\ & - 2.33 (\pm 0.12)\Sigma\beta_2^0 \end{aligned} \quad (10)$$

where  $\rho = 0.977$ ,  $S.E. = 0.249$ ,  $F = 585$  and  $n = 119$ . The models described by Eqs. (9) and (10) are identical for all practical purposes, verifying the robustness of the model. Either solute ionization is unimportant for the experimental conditions used to acquire the data or changes in sorption characteristics due to ionization are no greater than the general experimental error for the compiled data.

For verification of the model we selected a further

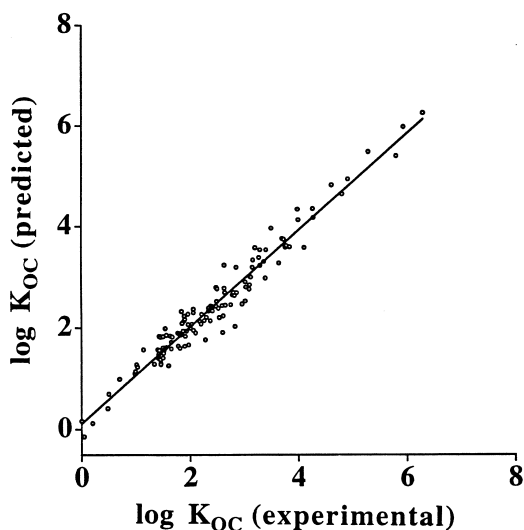


Fig. 1. Plot of predicted vs. experimental  $\log K_{OC}$  values based on Eq. (9) for the data in Table 1.

data base assembled by Borisover and Graber [68] (Table 2). Excluding pyridine ( $ex = 2.48$ ,  $pre = 1.32$ ) and 1-aminonaphthalene ( $ex = 3.50$ ,  $pre = 2.91$ ) from this data set gave

$$\begin{aligned} \log K_{OC} = & -0.02 (\pm 0.21) + 2.58 (\pm 0.28)V_X \\ & + 0.80 (\pm 0.16)R_2 - 0.42 (\pm 0.18)\pi_2^H \\ & - 0.43 (\pm 0.18)\Sigma\alpha_2^H - 2.08 (\pm 0.25)\Sigma\beta_2^0 \end{aligned} \quad (11)$$

where  $\rho = 0.966$ ,  $S.E. = 0.233$ ,  $F = 135$ ,  $n = 55$ . There is good agreement between the two models for the different data sets with only the difference in the  $m$  and  $s$  system constants significant at the 95% confidence level. Table 2 contains 46 solutes out of 57 in common with the data in Table 1, of which only 13 solutes have identical values. The average difference in  $\log K_{OC}$  values is  $\pm 0.20$  log units with the largest difference for the phenols (0–0.93 log units ignoring 4-methylphenol, indicated as an outlier for the model based on Table 1). Thus, the difference between the models represented by Eqs. (9) and (11) is a product of the uncertainty in literature  $\log K_{OC}$  values, particularly for the phenols. If Eq. (9) is used to predict the  $\log K_{OC}$  values in Table 2, reasonable agreement is obtained, as shown in Fig. 2, with a linear regression equation  $\log K_{OC} = 1.08 (\pm 0.05) \log K_{OC} (Eq. (9)) - 0.26 (\pm 0.12)$  and  $r^2 = 0.907$  and  $S.E. = 0.257$ . So, even though Eq. (9) is not the best model that could be obtained to explain the data in Table 2, it is a reasonable model for that purpose, supporting the general use of Eq. (9) for estimating the soil–water distribution constant.

Muller and Kordel [28] have presented a smaller data base of  $\log K_{OC}$  values that differs from the other two data collections in that the distribution constants were determined by the same group, and should be more consistent as to the experimental procedure employed, Table 3. Hexachlorobenzene was removed as an outlier ( $ex = 4.70$ ,  $pre = 4.01$ ) to give

$$\begin{aligned} \log K_{OC} = & 1.20 (\pm 0.22) + 0.64 (\pm 0.24)V_X \\ & + 1.12 (\pm 0.13)R_2 - 0.69 (\pm 0.12)\Sigma\alpha_2^H \\ & - 1.60 (\pm 0.15)\Sigma\beta_2^0 \end{aligned} \quad (12)$$

where  $\rho = 0.964$ ,  $S.E. = 0.191$ ,  $F = 79$  and  $n = 28$ . An



Table 2  
Solute descriptors and soil–water and soil–air distribution constants

Solute	Descriptors						Distribution constants	
	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	$\text{Log } L^{16}$	$\text{Log } K_{OC}$	$\text{Log } K_{OCA}$
Benzene	0.716	0.610	0.52		0.14	2.714	1.90	2.6
Toluene	0.857	0.601	0.52		0.14	3.325	2.06	2.7
Ethylbenzene	0.998	0.613	0.51		0.15	3.778	2.22	2.8
1,3-Dimethylbenzene	0.998	0.623	0.52		0.16	3.839	2.50	3.1
1,4-Dimethylbenzene	0.998	0.613	0.52		0.16	3.839	2.72	3.3
1,3,5-Trimethylbenzene	1.139	0.649	0.52		0.19	4.314	3.00	3.7
1,2,3-Trimethylbenzene	1.139	0.728	0.61		0.19	4.565	3.04	3.9
n-Butylbenzene	1.280	0.600	0.51		0.15	4.730	3.53	3.8
mxx rnyy rnzz rmaa rmtt Naphthalene	1.085	1.340	0.92		0.20	5.161	2.97	4.7
Anthracene	1.454	2.290	1.34		0.26	7.568	4.38	7.3
Phenanthrene	1.454	2.055	1.29		0.26	7.632	4.35	7.2
Pyrene	1.585	2.808	1.71		0.29	8.833	4.85	8.2
Chlorobenzene	0.839	0.718	0.65		0.07	3.657	2.34	3.2
1,2-Dichlorobenzene	0.961	0.872	0.78		0.04	4.518	2.50	3.5
1,3-Dichlorobenzene	0.961	0.847	0.73		0.02	4.410	2.48	3.2
1,4-Dichlorobenzene	0.961	0.825	0.75		0.02	4.435	2.80	3.5
1,2,3-Trichlorobenzene	1.084	1.030	0.86		0	5.419	3.29	4.2
1,2,4-Trichlorobenzene	1.084	0.980	0.81		0	5.248	3.35	4.2
1,3,5-Trichlorobenzene	1.084	0.980	0.73		0	5.045	3.09	3.7
1,2,3,4-Tetrachlorobenzene	1.206	1.180	0.92		0	5.922	3.96	4.9
1,2,3,5-Tetrachlorobenzene	1.206	1.160	0.85		0	5.922	3.38	4.6
Bromobenzene	0.891	0.882	0.73		0.09	4.041	2.55	3.6
Iodobenzene	0.975	1.188	0.82		0.12	4.502	3.10	4.4
Dichloromethane	0.494	0.387	0.57	0.10	0.05	2.019	1.56	2.5
Trichloromethane	0.617	0.425	0.49	0.15	0.02	2.480	1.81	2.6
Tetrachloromethane	0.739	0.458	0.38		0	2.823	1.53	1.5
Tribromomethane	0.775	0.974	0.68	0.15	0.06	3.775	2.10	3.7
1,2-Dichloroethane	0.635	0.416	0.64	0.10	0.11	2.573	1.62	2.9
1,1,1-Trichloroethane	0.758	0.369	0.41		0.09	2.733	1.82	2.0
1,1,2-Trichloroethane	0.758	0.499	0.68	0.13	0.08	3.290	1.99	3.5
1,1,2,2-Tetrachloroethane	0.880	0.595	0.76	0.16	0.12	3.803	1.92	3.7
1,2-Dichloropropane	0.776	0.371	0.60	0.10	0.11	2.857	1.68	2.6
Tetrachloroethene	0.837	0.639	0.42		0	3.584	2.38	2.3
Trichloroethene	0.715	0.524	0.40	0.08	0.03	2.997	2.04	2.4
Benzyl alcohol	0.916	0.803	0.87	0.33	0.56	4.221	1.43	6.3
4-Methylaniline	0.957	0.923	0.95	0.23	0.52	4.452	1.90	6.0
3-Nitroaniline	0.991	1.200	1.71	0.40	0.35	5.880	1.73	8.2
4-Nitroaniline	0.991	1.220	1.91	0.42	0.38	6.343	1.88	9.4
Nitrobenzene	0.891	0.871	1.11		0.28	4.557	2.20	5.2
Anisole	0.916	0.708	0.75		0.29	3.890	1.54	3.3
Acetophenone	1.014	0.818	1.01		0.48	4.501	1.57	4.9
Pyridine	0.675	0.631	0.84		0.47	3.022	2.48	5.9
Quinoline	1.044	1.268	0.97		0.54	5.457	2.84	7.0
Phenol	0.775	0.805	0.89	0.60	0.30	3.766	1.55	6.4
4-Bromophenol	0.950	1.080	1.17	0.67	0.20	5.135	2.41	7.6
2-Nitrophenol	0.949	1.045	1.05	0.05	0.37	4.760	2.01	5.4
3-Nitrophenol	0.949	1.050	1.57	0.79	0.23	5.692	1.68	8.7
4-Nitrophenol	0.949	1.070	1.72	0.82	0.26	5.876	1.70	9.5
2-Chlorophenol	0.898	0.853	0.88	0.32	0.31	4.178	1.67	5.0
3-Chlorophenol	0.898	0.909	1.06	0.69	0.15	4.773	1.78	6.6

(continued on next page)

Table 2 (continued)

Solute	Descriptors						Distribution constants	
	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	$\text{Log } L^{16}$	$\text{Log } K_{OC}$	$\text{Log } K_{OCA}$
4-Chlorophenol	0.898	0.915	1.08	0.67	0.20	4.775	1.80	7.0
2-Methylphenol	0.916	0.840	0.86	0.52	0.30	4.218	1.30	5.6
4-Methylphenol	0.916	0.820	0.87	0.57	0.31	4.312	1.56	6.1
2-Methoxyphenol	0.975	0.837	0.91	0.22	0.52	4.449	1.56	5.7
3-Methoxyphenol	0.975	0.879	1.17	0.59	0.39	4.803	1.50	7.1
1-Aminonaphthalene	1.185	1.670	1.26	0.20	0.57	6.490	3.50	8.8
1-Naphthol	1.144	1.520	1.05	0.61	0.37	6.130	3.07	9.2

Cross-correlation matrix for solute descriptors ( $r^2$ )

	$V_x$	$\text{Log } L^{16}$	$R_2$	$\pi_2^H$		
$R_2$	0.65	0.86				
$\pi_2^H$	0.21	0.61	0.50			
$\Sigma\alpha_2^H$	0.01	0.03	0.00	0.28		
$\Sigma\beta_2^0$	0.04	0.10	0.10	0.26	0.11	

acidic forest soil (Podsol) and an arable soil (Alfisol) were used for the determination of average  $\log K_{OC}$  values [37]. These soils must differ significantly from those used in the other two data sets since the model obtained, although chemically and statistically reasonable, is different from Eqs. (9) and (11). The  $\log K_{OC}$  values for the 25 solutes in common with Table 1, are generally systematically smaller, accounting for at least part of the difference between

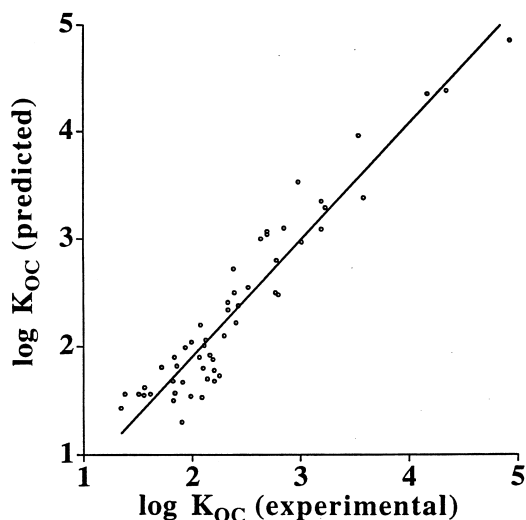


Fig. 2. Plot of predicted vs. experimental  $\log K_{OC}$  values based on Eq. (9) for the data in Table 2.

the models. As indicated by the experimental  $\log K_{OC}$  values for Podsol and Alfisol soils reported by von Open et al. [19] there are large differences in the sorption properties for these soils. Attempts to provide individual models for these soils were unsuccessful. We had solute descriptors for 38 of the solutes in the data set, but a significant number of these (carboxylic acids, alkylamines, and anilines) would be at least partially ionized at the apparent soil pH (Podsol 2.8 and Alfisol 6.7), while others were determined from significantly curved Freundlich isotherms ( $z=0.7-1.7$ ) and could not be relied upon as experimentally invariant values. The model described by Eq. (12) represents either a different group of soil types than Eq. (9) or a local fit for solutes in a mixture of ionization states and with curved isotherms not meeting our selection criteria for the data used to obtain Eq. (9). This can not be decided from the information available, and for the remainder of this paper we will refer to Eq. (9) as the model for the soil–water distribution constants.

#### 4.2. Characteristic properties of the soil–water distribution system

The model described by Eq. (9) provides insight into the sorption mechanism of neutral compounds by soil from water. The driving force for sorption is the lower cohesion of wet soil compared to water

Table 3  
Solute descriptors, soil–water distribution constants and chromatographic retention factors

Solute	Descriptors					Distribution constants and retention factors	
	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	$\text{Log } K_{OC}$	$\text{Log } k^{CN}$
Toluene	0.857	0.601	0.52		0.14	2.12	−0.071
Ethylbenzene	0.998	0.613	0.51		0.15	2.32	0.041
1,4-Dimethylbenzene	0.998	0.613	0.52		0.16	2.37	0.053
Naphthalene	1.085	1.340	0.92		0.20	2.75	0.188
Acenaphthalene	1.259	1.604	1.04		0.20	3.58	0.358
Phenanthrene	1.454	2.055	1.29		0.26	4.09	0.545
1,2,3-Trichlorobenzene	1.084	1.030	0.86		0	3.16	0.274
Hexachlorobenzene	1.451	1.490	0.99		0	4.70	0.640
Aniline	0.816	0.955	0.94	0.26	0.50	2.07	−0.469
4-Methylaniline	0.957	0.923	0.95	0.23	0.52	2.21	−0.357
4-Chloroaniline	0.939	1.060	1.13	0.30	0.35	2.28	−0.187
N-Methylaniline	0.957	0.948	0.90	0.17	0.48	2.28	−0.252
1-Aminonaphthalene	1.185	1.670	1.26	0.20	0.57	2.66	−0.061
Acetanilide	1.113	0.870	1.40	0.50	0.67	1.26	−0.469
Nitrobenzene	0.891	0.871	1.11		0.28	2.20	−0.020
Phenol	0.775	0.805	0.89	0.60	0.30	1.32	−0.456
2-Nitrophenol	0.949	1.045	1.05	0.05	0.37	2.17	−0.260
4-Nitrophenol	0.949	1.070	1.72	0.82	0.26	2.05	−0.292
2,4,6-Trichlorophenol	1.142	1.010	1.01	0.82	0.08	2.59	−0.244
Pentachlorophenol	1.389	1.270	0.88	0.97	0	2.67	−0.174
1-Naphthol	1.144	1.520	1.05	0.61	0.37	2.61	0.017
Benzamide	0.973	0.990	1.50	0.49	0.67	1.46	−0.699
4-Nitrobenzamide	1.147	1.250	2.17	0.75	0.60	1.93	−0.469
2-Chlorobenzamide	1.095	1.140	1.60	0.45	0.75	1.51	−0.678
N-Methylbenzamide	1.114	0.950	1.44	0.35	0.73	1.42	−0.585
N,N-Dimethylbenzamide	1.255	0.950	1.40		0.98	1.52	−0.469
N-Phenylacetamide	1.114	0.950	1.60	0.52	0.79	1.61	
Methyl benzoate	1.073	0.733	0.85		0.48	1.80	−0.181
Phenyl benzoate	1.540	1.330	1.42		0.47	2.87	0.241
Ethyl phenylacetate	1.354	0.660	1.01		0.57	1.89	−0.119

Cross-correlation matrix for solute descriptors ( $r^2$ )

	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$
$R_2$	0.34			
$\pi_2^H$	0.05	0.11		
$\Sigma\alpha_2^H$	0.01	0.31	0.20	
$\Sigma\alpha_2^0$	0.00	0.26	0.37	0.31

and the greater capacity of wet soil for lone-pair electron interactions compared to water (both the  $m$  and  $r$  system constants are positive). Wet soil is as dipolar/polarizable as water ( $s$  system constant is 0) and, therefore, interactions of a dipole-type do not contribute to sorption because of their equality in the two phases. Hydrogen-bonding interactions reduce soil sorption ( $a$  and  $b$  system constants are negative), since wet soil is a slightly weaker hydrogen-bond

base and a significantly weaker hydrogen-bond acid than water. Placed on a general scale, wet soil is quite cohesive and polar with a significant capacity for interactions of a dipole-type as well as for hydrogen-bonding interactions.

The contribution of individual intermolecular interactions to the sorption of organic compounds by soil from water is clearly illustrated by a few representative examples given in Table 4. For all

Table 4

Contribution of different intermolecular interactions to the sorption of some varied solutes by soil from water ( $s=0$ )

Compound	Contribution to $\log K_{OC}$			
	$mV_x$	$rR_2$	$a\Sigma\alpha_2^H$	$b\Sigma\beta_2^O$
Ethylbenzene	2.086	0.454	0	-0.341
1,4-Dichlorobenzene	2.009	0.627	0	-0.045
Hexanol	2.117	0.155	-0.115	-1.090
Benzamide	2.033	0.733	-0.152	-1.521
4-Bromophenol	1.986	0.799	-0.208	-0.454
Phenylacetic acid	2.243	0.540	-0.186	-1.430

compounds the dominant contribution to sorption is the cavity term ( $mV_x$ ) which is significantly larger than the contribution from lone-pair electron interactions ( $rR_2$ ). This is a consequence of the solvophobic tendency of water to expel solutes to the less cohesive water saturated soil organic matter in an attempt to regain its preferred liquid structure. The major factor reducing sorption is solute hydrogen-bond base water hydrogen-bond acid interactions. Water is a strong hydrogen-bond acid and solutes with significant hydrogen-bond base properties are less effectively sorbed by soil, as illustrated by benzamide and phenylacetic acid, which in spite of their strong dipole-type properties and significant hydrogen-bond acidity, it is their hydrogen-bond basicity that is the predominant reason for their weak sorption compared to low polarity solutes of a similar size. The weak hydrogen-bond basicity and favorable electron polarizability of halogenated aromatic compounds, such as 1,4-dichlorobenzene, results in preferential sorption compared to alkyaromatic compounds of a similar size. The greater sorption of aromatic compounds compared to aliphatic compounds of a similar size and polarity is a property of the greater electron polarizability of aromatic compounds.

Models based on the octanol–water distribution constant ( $\log K_{OW}$ ) are not as effective as the solvation parameter model for predicting the sorption properties of soils from water. There is far less scatter around the best fit line representing the predicted values for the solvation parameter model, Fig. 1, compared to the best fit obtained by regressing  $\log K_{OC}$  vs.  $\log K_{OW}$ , Fig. 3. The equation for the fit to a linear model based on the octanol–water distribution constant is  $\log K_{OC} = 0.73 \log K_{OW} +$

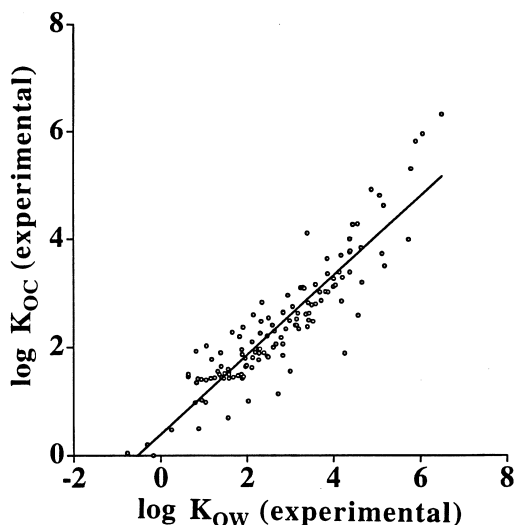


Fig. 3. Plot of experimental  $\log K_{OC}$  values vs.  $\log K_{OW}$  for the compounds in Table 1 with outliers excluded (see text for identification).

0.39 with  $\rho=0.911$  and  $S.E.=0.475$ . The reason for the poor fit can be deduced from the differences in the system constants for the soil–water and octanol–water distribution systems. The system constants for the octanol–water distribution system ( $m=3.84$ ,  $r=0.56$ ,  $s=-1.05$ ,  $a=0.03$ ,  $b=-3.46$ ) are well established [58,60]. Wet octanol is significantly less cohesive and dipolar/polarizable and a weaker hydrogen-bond acid and stronger hydrogen-bond base than wet soil. Wet octanol, therefore, is not a good chemical model for the sorption properties of wet soil, and cannot be expected to represent the sorption properties of wet soil across a varied range of compound types, as is clear from Fig. 3. To be a good model for a distribution process it is not required that the system constants are identical with the process to be modeled; it is sufficient that the ratios of the coefficients (with  $m$  as the preferred basis for normalization) are the same (or nearly the same) for both systems. For the soil–water sorption system  $r/m=0.35$ ,  $s/m=0$ ,  $a/m=-0.15$  and  $b/m=-1.09$ . For the octanol–water system  $r/m=0.15$ ,  $s/m=-0.28$ ,  $a/m=0.01$  and  $b/m=-0.91$ . For a varied group of solutes those with a significant capacity for dipole-type and hydrogen-bond acid interactions will deviate most from the predicted results based on the octanol–water distribution re-

gression model. Aromatic and aliphatic compounds of low polarity and members of a homologous series (because they possess invariant solute descriptors except for  $V_x$ ) will provide acceptable family-dependent models. In general, liquid–liquid distribution systems are not good surrogate models for the soil–water distribution system because organic solvents with the required dipolarity/polarizability and hydrogen-bond properties are miscible with water [58]. The closest useful liquid–liquid distribution system to model the soil–water distribution process would be nitrobenzene–water ( $r/m=0.14$ ,  $s/m=0$ ,  $a/m=-0.55$  and  $b/m=-1.04$ ). For a varied group of compounds poor agreement is likely for compounds with strong hydrogen-bond acid properties due to the difference in the  $a/m$  ratio and for aliphatic and aromatic compounds (particularly polycyclic aromatic compounds with different ring numbers) due to the difference in the  $r/m$  ratio. Because of the analogy between the soil–water distribution process and the chromatographic process, and the greater flexibility and choice of system components afforded by chromatographic systems, it is more likely that a better model for the soil–water distribution system can be found among chromatographic than liquid–liquid distribution systems.

#### 4.3. Chromatographic models for the soil–water distribution system

Using the system constant ratios removes any a priori guesswork from the identification of suitable

chromatographic models for estimating the soil–water distribution constant. The selection of chromatographic models is not restricted to a single technique provided that systems maps are available, which avoids trying to make the technique fit the problem, as is generally the case with empirical approaches. In this instance we used a data bank of system maps for reversed-phase separations obtained by column, thin-layer and micellar electrokinetic chromatography with a variety of mobile and stationary phases to identify a suitable chromatographic model for the soil–water distribution system [56]. Chromatographic systems with favorable system constant ratios to act as suitable models for the soil–water distribution process are summarized in Table 5. The spacer bonded propanediol (DIOL) [69] and cyanopropylsiloxane-bonded [70] sorbents with methanol–water (2:3) as the mobile phase are good chromatographic models for the soil–water distribution system as indicated for a varied group of solutes by the plot of  $\log K_{OC}$  vs.  $\log k$ , Fig. 4. The retention factors and model statistics for the useful chromatographic models are summarized in Table 6. All models show a good correlation with a standard error in the estimate for  $\log K_{OC}$  of 0.18–0.22 log units, which given the established uncertainty in literature  $\log K_{OC}$  values, is as good as could be expected, and verifies the predictive capabilities of the chromatographic models.

Kordel et al. [28,37,38] have developed a chromatographic model using either methanol–water or methanol–buffer (55:45) on a silica-based cyano-

Table 5  
System constant ratios for surrogate chromatographic models for the sorption of neutral organic compounds by soil from water

Sorbent	Mobile phase	System constant ratios			
		$r/m$	$s/m$	$a/m$	$b/m$
Soil	Water	0.35	0	–0.15	–1.09
DIOL <sup>a</sup>	Methanol–water (2:3)	0.29	0	–0.17	–1.09
DIOL <sup>a</sup>	Acetonitrile–water (1:4)	0.20	0	–0.12	–1.02
CN <sup>b</sup>	Methanol–water (1:1)	0.25	0	–0.24	–1.05
CN <sup>b</sup>	Methanol–water (2:3)	0.22	0	–0.22	–1.04
CN <sup>b</sup>	2-Propanol–water (1:4)	0.19	0	–0.17	–1.01
CN <sup>b</sup>	Acetonitrile–water (1:4)	0.19	0	–0.20	–1.00
CN <sup>c</sup>	Methanol–water (3:2)	0.23	0	–0.35	–1.10
CN <sup>c</sup>	Acetone–water (1:9)	0.24	0	0	–1.02

<sup>a</sup> Silica-based spacer-bonded propanediol sorbent [69].

<sup>b</sup> Silica-based cyanopropylsiloxane-bonded sorbent [70].

<sup>c</sup> Silica-based cyanopropylsiloxane-bonded layer [53].

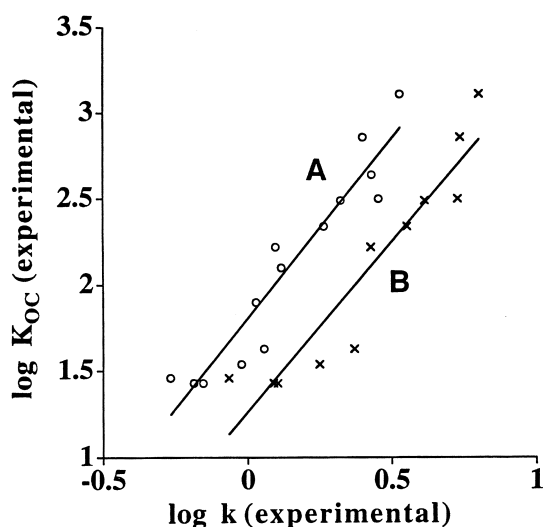


Fig. 4. Plot of experimental  $\log K_{OC}$  values vs. experimental chromatographic  $\log k$  values for a spacer-bonded propanediol sorbent (A) and a cyanopropylsiloxane-bonded sorbent (B) with a mobile phase of methanol–water (2:3).

propylsiloxane-bonded column for the sorption of organic compounds by soil from water. Their selection of  $\log K_{OC}$  values is different to those given in Table 1 and resulted in the model indicated by Eq. (12) in this paper. Using their  $\log k^{CN}$  values, Table 3, for the chromatographic system we obtained the following model after removing 1-naphthol (ex = 0.017, pre = -0.189) as an outlier

$$\begin{aligned} \log k^{CN} = & -0.49 (\pm 0.08) + 0.49 (\pm 0.09)V_x \\ & + 0.26 (\pm 0.05)R_2 - 0.56 (\pm 0.05)\Sigma\alpha_2^H \\ & - 0.85 (\pm 0.06)\Sigma\beta_2^0 \end{aligned} \quad (13)$$

where  $\rho = 0.981$ ,  $S.E. = 0.074$ ,  $F = 146$  and  $n = 28$ . A comparison is now possible between their soil–water distribution constants and the chromatographic model using the system constant ratios, as before. For the soil–water distribution system these are  $r/m = 1.73$ ,  $s/m = 0$ ,  $a/m = 1.08$  and  $b/m = -2.50$  and for the chromatographic system  $r/m = 0.53$ ,  $s/m = 0$ ,  $a/m = 1.14$  and  $b/m = 1.73$ . The data affirms their conclusions that the chromatographic system is a reasonable model for the particular soil properties

with respect to certain compound types. On the other hand, better general models should be possible. Comparing the system constant ratios, compounds with large differences in their hydrogen-bond basicity and capacity for lone-pair electron interactions are expected to result in poor estimates of their soil–water distribution constants.

The majority of studies employing chromatographic models to estimate soil–water distribution constants have employed a restricted number and range of compounds, often limited to alkylbenzenes and polycyclic aromatic hydrocarbons to validate their regression models [32–36,39–45]. These compounds are sorbed by rather non-selective interactions and a wide range of chromatographic systems can be designed to fit the sorption data for these compounds. These models are unlikely to be robust if a more varied group of compounds are considered and are examples of local fits for compounds of restricted properties. Nielsen et al. [40] summarized retention factors for 45 polycyclic aromatic compounds on a silica-based, chemically bonded humic acid column. Many of the compounds in their data set are uncommon and literature  $\log K_{OC}$  values are unavailable. Since the sorption properties of humic acid are of interest for the interpretation of soil–water sorption behavior, we attempted to provide a model for their chromatographic data, but failed because of the high level of cross-correlation among the solute descriptors for compounds with available descriptors and those we could confidently estimate.

#### 4.4. Model for the sorption of neutral organic compounds by wet soil from air

Surface soils are porous structures containing a large volume of air. The sorption of volatile organic compounds by wet soil from air is an important source of soil contamination, and the reverse process, the emission of volatile organic compounds to the air is an important factor affecting the fate of volatile organic compounds bound to soil. From the data in Table 1 for the water saturated soil–air distribution constant,  $\log K_{OCA}$ , the following model was obtained after removing dimethylamine (ex = 5.78, pre = 3.62), *n*-butylamine (ex = 4.99, pre = 4.08) and 4-methylphenol (ex = 7.20, pre = 6.42) as outliers

Table 6

Regression models  $\log K_{OC} = a \log k + b$  for reversed-phase column chromatographic systems identified as surrogate models for the soil–water sorption process ( $\log K_{OC}$  values taken from Table 1)

Mobile phase	Model statistics					
	<i>a</i>	<i>b</i>	<i>r</i> <sup>2</sup>	<i>S.E.</i>	<i>n</i>	<i>F</i>
<i>(i) DIOL sorbent</i>						
Methanol–water (2:3)	2.09 (±0.19)	1.81 (±0.06)	0.907	0.18	14	117
Acetonitrile–water (1:4)	2.37 (±0.23)	1.88 (±0.05)	0.899	0.19	14	107
<i>(ii) CN sorbent</i>						
Methanol–water (1:1)	2.89 (±0.30)	1.38 (±0.10)	0.922	0.18	10	94
Methanol–water (2:3)	1.97 (±0.23)	1.27 (±0.12)	0.887	0.22	11	71
2-Propanol–water (1:4)	1.45 (±0.17)	1.02 (±0.14)	0.886	0.21	12	78
Acetonitrile–water (1:4)	2.00 (±0.21)	0.85 (±0.15)	0.908	0.19	11	89

Retention factors ( $\log k$ ) for regression models

Compound	DIOL sorbent		CN sorbent			
	Methanol–water (2:3)	Acetonitrile–water (1:4)	Methanol–water (1:1)	Methanol–water (2:3)	2-Propanol–water (1:4)	Acetonitrile–water (1:4)
Naphthalene	0.530	0.431	0.525	0.803	1.270	0.983
Benzene	0.029	−0.018				
<i>n</i> -Propylbenzene	0.401	0.391	0.467	0.737	1.186	1.004
Chlorobenzene	0.265	0.207	0.328	0.553	0.992	0.754
Bromobenzene	0.324	0.263	0.386	0.614	0.925	0.804
1,2-Dichlorobenzene	0.455	0.398	0.464	0.728	1.194	0.925
Anisole	0.057	0.009	0.201	0.371	0.631	0.542
Acetophenone	−0.022	−0.061	0.083	0.250	0.521	0.417
Nitrobenzene	0.097	0	0.270	0.428	0.693	0.571
Methyl benzoate	0.117	0.032			0.671	0.671
Phenol	−0.155	−0.168	−0.036	0.090	0.299	0.233
1-Naphthol	0.431	0.299		−0.066	0.127	0.076
Benzamide	−0.268	−0.215			0.127	
Acetanilide	−0.187	−0.168	−0.018	0.104	0.316	0.243

$$\begin{aligned}
 \log K_{OCA} = & -0.46 (\pm 0.11) \\
 & + 0.36 (\pm 0.04) \log L^{16} \\
 & + 0.65 (\pm 0.16) R_2 + 2.40 (\pm 0.20) \pi_2^H \\
 & + 3.39 (\pm 0.17) \Sigma \alpha_2^H \\
 & + 2.57 (\pm 0.22) \Sigma \beta_2^H \quad (14)
 \end{aligned}$$

where  $\rho = 0.991$ ,  $S.E. = 0.238$ ,  $F = 667$  and  $n = 69$ . The model provides a good statistical fit and is chemically sensible. An attempt to analyze the data of Borisover and Graber [68], Table 2, produced a less satisfactory model due to the high level of correlation between the solute descriptors  $\log L^{16}$  and  $R_2$  ( $r^2 = 0.86$ ), and will not be discussed further. The small value for the  $l$  system constant in Eq. (14) indicates that wet soil is cohesive, more cohesive

than most polar organic solvents and many polymeric stationary phases used in gas chromatography, but not as cohesive as water [55,71,72]. Since  $l$  is a measure of the non-selective sorption of compounds by wet soil, and vapors with larger  $\log L^{16}$  values will be more readily sorbed, this results in vapors from less volatile compounds being more strongly retained than those from more volatile compounds, all other things being equal. The other significant characteristic of wet soil is that it is a non-selective polar sorbent with a large capacity for dipole-type and hydrogen-bond interactions. All polar compounds will be significantly retained to a greater extent by wet soil than compounds of low polarity with similar volatility. The contribution of polar interactions to the sorption of organic vapors by wet soil from air is very significant and illustrated by the

Table 7

Contribution of different intermolecular interactions to the sorption of organic compounds by wet soil from air

Compound	Contribution to $\log K_{OCA}$				
	$l \log L^{16}$	$rR_2$	$s\pi_2^H$	$a\Sigma\alpha_2^H$	$b\Sigma\beta_2^H$
Ethylbenzene	1.348	0.398	1.223	0	0.386
1,4-Dichlorobenzene	1.582	0.536	1.799	0	0.051
Trichloromethane	0.885	0.276	1.175	0.509	0.051
Tetrachloromethane	1.007	0.298	0.911	0	0
Hexanol	1.288	0.136	1.007	1.255	1.235
Hexanoic acid	1.398	0.113	1.439	2.035	1.158
Nitrobenzene	1.626	0.566	2.662	0	0.721
Benzamide	2.057	0.643	3.597	1.662	1.724
4-Methylaniline	1.588	0.600	2.278	0.780	1.107
4-Bromophenol	1.832	0.702	2.806	2.272	0.515

data for some representative compounds in Table 7. Even for compounds of relatively low polarity such as ethylbenzene, 1,4-dichlorobenzene, and carbon tetrachloride, more than half their sorption free energy is accounted for by polar interactions. For polar compounds such as phenols, anilines, and amides, etc., by far the largest contribution to their sorption free energy is from polar interactions. Thus, wet soil is a strong sorbent for polar volatile organic compounds, and will retain these compounds tenaciously.

Finding a gas chromatographic model for wet soil is difficult because no other characterized solvent or adsorbent provides a similar range of non-selective polar interactions [55]. By comparing system constant ratios several liquid organic salts {e.g., tetraethylammonium 4-toluenesulfonate, tetrabutylammonium 3-[tris(hydroxymethyl)methyl]amino-2-hydroxy-1-propanesulfonate} are a good match for the dipolarity and hydrogen-bond basicity of wet soil but are weak hydrogen-bond acids in their useful temperature operating range [73]. The cavity/dispersion term for porous polymers is generally too large for these to be useful as chromatographic models for wet soil [50,74]. Most common polymeric liquids used as gas chromatographic stationary phases lack sufficient hydrogen-bond acidity and the correct ratio of hydrogen-bond acidity to dipolarity/polarizability to be good models for the sorption properties of wet soil [55,71,73]. However, the solvation parameter model provides the necessary information for the design of a specific stationary phase (or mixture of stationary

phases) that would provide an effective model for the sorption of organic compounds from air by wet soil.

#### 4.5. Models for the interfacial adsorption of neutral organic compounds from air by water

The interfacial adsorption of organic compounds from air is largely inconsequential when water is present as a large volume reservoir. The absorption of organic vapors by water from the gas phase is well understood and a suitable model for this process has been presented by Abraham et al. [62,72] for which the system constants are  $l = -0.21$ ,  $r = 0.82$ ,  $s = 2.74$ ,  $a = 3.90$  and  $b = 4.81$ . Primarily, polar interactions strongly favor absorption of organic vapors by water which is resisted by the unfavorable cavity formation process (included in this term are favorable dispersion interactions, but for water these do not compensate for the free energy required for cavity formation, a feature so far unique to water among common solvents). For nonpolar compounds absorption by water is very limited and declines with increasing solute size. Interfacial sorption of organic compounds is expected to be more important when film water is present and during aeration processes where micro air bubbles are generated, for example, when gases escape from ocean bottoms or river beds, or in wastewater treatment processes and in mist scrubber systems, where interfacial sorption processes play a significant role in the transport of organic compounds.

The following model was obtained for the ad-



sorption of neutral organic compounds at the air–water interface,  $\log K_{AW}$ , for the data assembled in Table 8

$$\begin{aligned} \log K_{AW} = & -0.65 (\pm 0.11) + 0.76 (\pm 0.02) \log L^{16} \\ & + 0.64 (\pm 0.17) R_2 + 2.99 (\pm 0.19) \pi_2^H \\ & + 4.18 (\pm 0.13) \Sigma \alpha_2^H + 4.39 (\pm 0.18) \Sigma \beta_2^H \end{aligned} \quad (15)$$

where  $\rho=0.999$ ,  $S.E.=0.105$ ,  $F=2101$  and  $n=35$ . Compared to absorption, the adsorption of organic vapors at the air–water interface is favored by the cavity and dispersion interaction term as well as by polar interactions. Surface and bulk polar interactions are very similar in magnitude and the dominant difference for the two processes is the contribution of the cavity and dispersion interactions to location in the surface interfacial volume compared to absorption.

The preferential distribution of organic compounds to the interfacial surface volume from bulk water is important for estimating the efficiency of aeration devices in stripping organic contaminants from water. For the data in Table 8 [65] for  $\log K_S$  the following model was obtained after removing 2-methylhexane (ex=5.868, pre=5.396), cycloheptane (ex=3.908, pre=4.315), cyclooctane (ex=4.236, pre=4.655) and decanoic acid (ex=6.322, pre=5.968) as outliers

$$\begin{aligned} \log K_S = & 1.64 (\pm 0.08) + 3.41 (\pm 0.08) V_x \\ & - 1.71 (\pm 0.11) R_2 - 0.63 (\pm 0.15) \Sigma \alpha_2^H \\ & - 1.41 (\pm 0.18) \Sigma \beta_2^0 \end{aligned} \quad (16)$$

where  $\rho=0.994$ ,  $S.E.=0.132$ ,  $F=698$  and  $n=37$ . Seven of the compounds in Table 8 are alkanecarboxylic acids that are possibly in a partially ionized form (a wide range of experimental conditions were used for the determination of  $\log K_S$  and the pH of the measurements is not always stated in the original literature). Eliminating the alkanecarboxylic acids resulted in the following model

$$\begin{aligned} \log K_S = & 1.79 (\pm 0.07) + 3.25 (\pm 0.06) V_x \\ & - 1.31 (\pm 0.17) R_2 - 0.49 (\pm 0.19) \pi_2^H \\ & - 1.29 (\pm 0.19) \Sigma \alpha_2^H - 0.86 (\pm 0.20) \Sigma \beta_2^0 \end{aligned} \quad (17)$$

where  $\rho=0.997$ ,  $S.E.=0.093$ ,  $F=923$  and  $n=30$ . There are significant differences between the two models due to either the influence of ionization of the carboxylic acids or due to the fact that the solutes contained in Table 8 represent a narrow range of properties that are not ideal for modeling purposes. The models are still useful in the qualitative sense for establishing the main factors that are responsible for the surface excess of certain compounds at the air–water interface. Solute size is the parameter that favors distribution to the surface interfacial volume. The interfacial region has similar dipolar/polarizability as bulk water but is less competitive in hydrogen-bond and lone-pair electron interactions, since these have a negative sign in Eq. (16). All other things being equal compounds with a significant capacity for hydrogen-bond interactions will be impoverished in the interfacial region, aromatic and other compounds with easily polarizable electrons will likewise be in reduced abundance, while increasing size will favor enrichment of compounds of all types in the interfacial volume.

## 5. Conclusions

The models described by Eqs. (9) and (14) are suitable for estimating the soil–water and soil–air distribution constants for a wide variety of compounds to a similar accuracy as that anticipated for the general error embedded in the experimental distribution constants. Also, the characteristic compound properties that result in favorable adsorption at the air–water interface are identified and a suitable model for predicting the air–water adsorption distribution constant provided in Eq. (15). Since solute descriptors are available for thousands of compounds as experimental values or by parameter estimates, these models allow access to a wider range of reliable distribution constants for environmental risk assessment than are available as experimental data. Chromatographic models using reversed-phase liquid chromatography on polar bonded phases provide an alternative means of estimating soil–water distribution constants for those compounds for which solute descriptors are unavailable and cannot be reliably estimated at the present time. A suitable chromatographic model for the soil–air distribution process

Table 8  
Solute descriptors and distribution constants for adsorption at the air–water interface

Solute	Descriptors						Distribution constants	
	$V_x$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	$\log L^{16}$	$\log K_s$	$\log K_{AW}$
Methane	0.250	0	0	0	0	-0.323	2.663	1.203
Ethane	0.390	0	0	0	0	0.492	3.161	1.821
Propane	0.531	0	0	0	0	1.050	3.468	2.028
Butane	0.672	0	0	0	0	1.615	3.965	2.445
Pentane	0.813	0	0	0	0	2.162	4.522	2.822
Hexane	0.954	0	0	0	0	2.668	4.949	3.129
Heptane	1.095	0	0	0	0	3.173	5.263	3.303
Octane	1.236	0	0	0	0	3.677	5.383	3.725
Nonane	1.377	0	0	0	0	4.182	6.346	4.046
Decane	1.518	0	0	0	0	4.686	6.818	4.498
Cycloheptane	0.986	0.350	0.10	0	0		3.908	
Cyclooctane	1.127	0.413	0.10	0	0		4.236	
2-Methylhexane	1.095	0	0	0	0	3.001	5.868	3.718
2,2,4-Trimethylpentane	1.236	0	0	0	0	3.106	5.646	3.526
Benzene	0.716	0.610	0.52	0	0.14	2.786	3.004	3.634
Toluene	0.857	0.601	0.52	0	0.14	3.325	3.427	4.077
Ethylbenzene	0.998	0.613	0.51	0	0.15	3.778	3.849	4.429
Fluorobenzene	0.734	0.477	0.57	0	0.10	2.788	3.218	3.808
Chlorobenzene	0.839	0.718	0.65	0	0.07	3.657	3.320	4.140
Dichloromethane	0.494	0.387	0.57	0.10	0.05	2.019	2.398	3.358
Trichloromethane	0.617	0.425	0.49	0.15	0.02	2.480	2.806	3.596
Tetrachloromethane	0.739	0.458	0.38	0	0	2.823	3.324	3.264
1,2-Dichloroethane	0.635	0.416	0.64	0.10	0.11	2.573	2.681	3.991
1-Chlorobutane	0.795	0.210	0.40	0	0.10	2.722	3.669	3.789
1-Bromobutane	0.847	0.360	0.40	0	0.12	3.105	3.639	3.929
Methyl formate	0.465	0.192	0.68	0	0.38	1.285	2.431	4.471
Ethyl formate	0.606	0.146	0.66	0	0.38	1.845	3.053	4.913
Di- <i>n</i> -propyl ether	1.013	0.008	0.25	0	0.45	2.954	4.430	5.280
1-Butanol	0.731	0.224	0.42	0.37	0.48	2.601	2.716	6.176
1-Pentanol	0.872	0.219	0.42	0.37	0.48	3.106	3.225	6.575
1-Hexanol	1.013	0.210	0.42	0.37	0.48	3.610	3.728	6.958
1-Heptanol	1.154	0.211	0.42	0.37	0.48	4.115	4.230	7.320
1-Octanol	1.295	0.199	0.42	0.37	0.48	4.619	4.732	7.732
Propanoic acid	0.606	0.233	0.65	0.60	0.45	2.290	2.079	6.819
Butanoic acid	0.747	0.210	0.62	0.60	0.45	2.830	2.813	7.473
Pentanoic acid	0.886	0.205	0.60	0.60	0.45	3.380	3.380	7.900
Hexanoic acid	1.028	0.174	0.60	0.60	0.45	3.920	3.820	8.380
Heptanoic acid	1.169	0.149	0.60	0.60	0.45		4.415	
Octanoic acid	1.310	0.150	0.60	0.60	0.45		5.079	
Nonanoic acid	1.451	0.132	0.60	0.60	0.45		5.613	

Cross-correlation matrix for solute descriptors ( $r^2$ )

	$V_x$	$\log L^{16}$	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$
$R_2$	0.04	0.04			
$\pi_2^H$	0.03	0.02	0.38		
$\Sigma\alpha_2^H$	0.05	0.07	0.00	0.29	
$\Sigma\beta_2^0$	0.02	0.06	0.00	0.43	0.65

could not be identified, but through the solvation parameter model the necessary requirements for such a model are indicated. The variation of soil distribution constants for individual soils with extreme properties suggests that a further use of the approach presented here would be the characterization of individual soil types to elucidate structural characteristics responsible for different sorption behavior and to provide data suitable for modeling soil properties from different geographical origin with greater reliability than is possible with a general (global) approach.

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