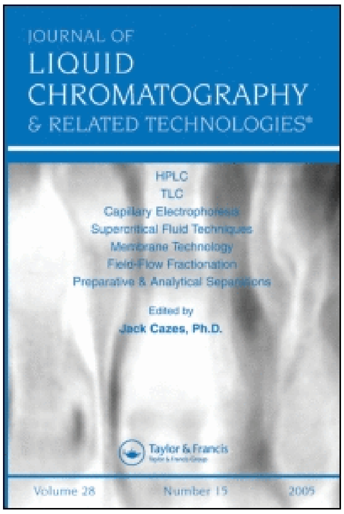

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COMPARISON OF ADSORPTION COEFFICIENT (K_{OC}) FOR SOILS AND HPLC RETENTION FACTORS OF AROMATIC HYDROCARBONS USING A CHEMICALLY IMMOBILIZED HUMIC ACID COLUMN IN RP-HPLC

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ABSTRACT

The determination of soil adsorption coefficients (K_{OC}) via HPLC capacity factors (k') has been studied, including the effect of column type and mobile phase composition on the correlation between log K_{OC} and log k'. K_{OC} values obtained by procedures other than HPLC correlate well with HPLC capacity factors determined on a chemically immobilized humic acid stationary phase, and it is suggested that this phase is a better model for the sorption onto soil or sediment than the octadecyl-, phenyl- and ethylsilica phases. By using log k'_W a theoretical capacity factor has been obtained by extrapolation of the retention data in a binary solvent system to pure aqueous eluent. There is a better correlation between log K_{OC} and log k'_W than the correlation between log K_{OC} and log k'.

INTRODUCTION

Many apolar organic contaminants commonly found in surface and subsurface waters are stable hydrophobic substances which readily partition into a variety of environmental compartments (sediments, biota, soils etc.)(1). Models for quantifying and predicting the partitioning processes of the compounds are frequently predicted by using aqueous solubilities (S) and n-octanol/water partition coefficients (K_{OW}). A very important parameter for the prediction of the movement of organic pollutants through the environment is K_{OC}, the ratio of adsorbed chemical per unit weight of organic carbon on the surface of soil or sediment to the concentration of the chemical in aqueous solution.

Although direct methods of measuring K_{OC} are to be preferred, its estimation from other physical properties can also be used (2-6). As values for K_{OW} and K_{OC} are difficult to determine, alternative methods for their determination have been considered. In view of this, it seemed worthwhile to investigate the relationship between soil or sediment partition coefficients and retention on stationary phases used in reverse-phase high-performance liquid chromatography (RP-HPLC) (7,8). From the theory of surface adsorption and the theory of partition it is evident that close parallels might be predicted for adsorption onto natural particulates and retention by lipophilic HPLC phases (9-11). Obviously, the closest prediction of the partitioning of chemical compounds by soil will be obtained from a stationary phase which bears a strong resemblance to soil.

This paper is an account of the evaluation of a new stationary phase, namely, chemically bound humic acid (**CBHA**). The potential of this new phase potential for the prediction of the soil adsorption coefficient K_{OC} has been evaluated by using a series of aromatic hydrocarbons. The K_{OC} values predicted on CBHA have been compared with the values determined on octadecyl- (ODS), phenyl- and ethylsilica stationary phases. A group of alkylbenzenes and polyaromatic hydrocarbons have been used as solutes in this study as they span a wide range of properties associated with the hydrocarbons that are toxic constituents of oil.

MATERIALS AND METHODS

Chromatographic retention data were measured with an LKB 2150 solvent delivery system and an LKB Wavescan Diode-array detector. Sample introduction was via a Rheodyne 7125 injection valve fitted with a 20 μl loop, and chromatograms were recorded on an Olivetti M24 personal computer. The phenyl- and ethyl-silica columns (250 x 4.6 mm) were obtained from Bio-Separation Technologies Co., Budapest, Hungary. The Partisil^R 10 ODS (250 x 4.6 mm) column was obtained from Hichrom Ltd. Reading, England. All other chemicals were obtained from various commercial sources and used as received.

Chromatography

Mobile phases (HPLC grade methanol and water from Hichrom Ltd.) were mixed, volume/volume, freed from dissolved air by helium entrainment and pumped at flow rates of 0.8 ml/min. The test solutes were dissolved in methanol at a concentration of 0.1 mg/ml. Typically 20 μl was injected. A laboratory temperature of 20-23°C was used for all HPLC measurements. The methanol content of the mobile phase was changed thus: (i) from 80% to 60% in 5% steps for the ODS and phenyl columns; (ii) from 60% to 40% in 5% steps for the immobilized humic acid phase; (iii) from 50% to 30% in 5% steps for the ethylsilica phase. Methanol was used for the measurement of the retention time (t_0) of an unretained compound. The relationship:

$$k' = (t_R - t_0)/t_0 \quad \text{[eqn. 1]}$$

was used to calculate the capacity factor k' from the retention time (t_R) of each compound. All capacity factors reported are the mean of at least three measurements. The correlation analysis for all compounds was made by linear regression analysis of log k' versus log K_{oc} and a least squares fit routine was used for curve fitting.

Selection of Log K_{OC} Values

The literature contains a limited number of compounds for which reliable log K_{OC} values have been reported. In order to have reliable K_{OC} data for the construction of the calibration graph, we have used selection criteria similar to those used by Brooke et al. (12) when they compiled K_{OW} data. These selection criteria are: (i) that the same log K_{OC} value (± 0.1 log K_{OC}) was reported in more than one independent study and (ii) that the procedure was well documented and precautions and checks were included in the study to ensure the validity of the result. In addition, it was required that the log K_{OC} value was obtained after plotting an adsorption isotherm with a soil or sediment in the temperature range of 18-25 ^{O}C. The chemicals having reliable log K_{OC} values are listed in Table 1.

Preparation of Chemically Bound Humic Acid Silica Gel

Dried silica gel (10g) was refluxed with 5% 3-aminopropyltriethoxysilane in anhydrous toluene (13) and the resulting aminopropyl silica gel was removed

TABLE 1. Reference Chemicals with Reliable log K_{OC} Values Obtained from the Literature

Chemicals	Log K_{OC}	Literature
Benzene	1.91	3
Toluene	2.18	12
Ethylbenzene	2.41*	7
Propylbenzene	2.86*	7
Butylbenzene	3.40*	7
o-Xylene	2.34*	7
Naphthalene	3.11	3
Phenanthrene	4.28*	7
Anthracene	4.41	3
Pyrene	4.83*	2

* NOTE: converted from literature log K_{OC} value using the relationship:

$K_{OC} = (K_p \times 100) / \%$ organic carbon by filtration, washed with toluene, methanol and water, washed again with methanol and dried. The reaction product was activated with 10 volumes of 5% aqueous glutaraldehyde for 5 h to produce an activated gel which on isolation was washed with 15 volumes of distilled water. This purified gel was reacted with 100 mL of 1% aqueous solution of humic acid, pH 7.5, for 8 h at ambient temperature. After the chemically bound humic acid silica gel (CBHA) had been washed with 10 volumes of 0.5 M phosphate buffer and distilled water it was treated with 0.1 M buffered ethanolamine, pH 7.5, for 3 h. The reaction product was washed with a large excess of distilled water and dried to yield a dark-brown product. Elemental analysis of this new stationary phase was performed in the Micro Analytical Laboratory of the University of Manchester. This prepared silica gel was packed as a slurry under high pressure in a stainless steel column (250 x 4.6 mm) by Jones Chromatography, Hengoed, Wales.

RESULTS AND DISCUSSION

Elemental analysis of immobilized humic acid revealed a C, H and N composition of 4.7%, 0.7% and 0.5%, respectively

In order to eliminate selective solute-solvent interactions (14,15), we have used log k'_w, the capacity factor obtained by the extrapolation of retention data from binary eluents to 100% water instead of using log k', the capacity factor obtained from binary eluents. Snyder et al. (16) showed that the linear equation

$$\log k' = \log k'_w + S\Phi \quad \text{[eqn. 2]}$$

can be used to describe the relationship between log k' and log k'_w, where Φ is the volume fraction of the organic component in the water-organic compound mixture used as the mobile phase, k'_w represents the capacity factor of a solute with pure water as the mobile phase and S is a constant for a given solute-eluent combination. The log k'_w of 10 organic compounds calculated

TABLE 2. Log K_{oc} Values from the Literature and Log k'_w Values Obtained from Equation [2] on Different HPLC Stationary Phases

Solute	**Log K_{oc}**	**ODS phase log k'_w**	**Phenyl phase log k'_w**	**Ethyl phase log k'_w**	**CBHA phase log k'_w**
Benzene	1.91	1.352	1.756	0.060	0.096
Toluene	2.18	1.934	2.456	0.479	0.514
Ethylbenzene	2.41	2.142	2.892	0.739	0.782
Propylbenzene	2.86	2.786	3.447	1.156	1.107
Butylbenzene	3.40	3.163	3.978	1.577	1.407
o-Xylene	2.34	2.217	2.945	0.759	0.627
Naphthalene	3.11	2.272	2.962	0.934	1.452
Phenanthrene	4.28	3.007	3.723	1.859	2.569
Anthracene	4.41	3.137	3.918	1.961	2.907
Pyrene	4.83	3.531	4.395	2.374	3.212

from equation [2] on the ODS, phenyl, ethyl and CBHA phases are presented in Table 2, along with values of log K_{oc} for these chemicals.

The log K_{oc} versus log k'_w values on the ODS phase calibration curve for the chemicals listed in Table 2 is plotted in Fig. 1 and yields:

$$\log K_{oc} = 1.373 \log k'_w - 0.335 \ [r^2 = 0.794 \quad n=10] \ [\text{eqn } 3]$$

For the same 10 compounds the correlation between log K_{oc} and log k'_w on the phenyl phase is shown in Fig. 1 and gives:

$$\log K_{oc} = 1.149 \log k'_w - 0.560 \ [r^2 = 0.816 \quad n=10] \ [\text{eqn } 4]$$

For these same 10 chemicals listed in Table 2 the correlation between log K_{oc} and log k'_w on the ethyl phase is plotted in Fig. 2 and yields:

$$\log K_{oc} = 1.367 \log k'_w + 1.546 \ [r^2 = 0.949 \quad n=10] \ [\text{eqn } 5]$$

A similar treatment of the data for the humic acid phase (Fig. 2) yields:

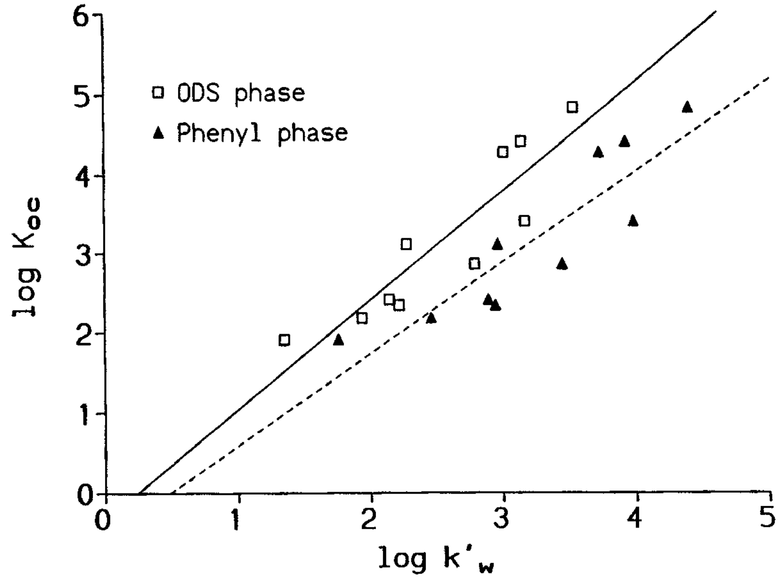

FIGURE 1 Relationship between the soil/water partition coefficient (K_{oc}) and the theoretical capacity factor (k'_w) for ODS and phenylsilica phases.

$$\log K_{oc} = 0.948 \log k'_w + 1.781 \; [r^2 = 0.986 \;\; n=10] \;\; [\text{eqn } 6]$$

From a comparison of equations [3],[4],[5] and [6] it is evident that the best prediction of log K_{oc} from log k'_w arises from data obtained from the CBHA phase. On the basis of correlations of K_{oc} versus log k'_w, it is more accurate to estimate log K_{oc} from k'_w determined from the humic acid phase column than via a single relationship between log K_{oc} and log k'_w on the ODS, phenyl or ethyl phases. The differences for the 10 chemicals listed in Table 1 are small for the humic acid phase, suggesting that its adsorptive properties are similar to those of sediment and soil organic matter. Such similarity might be expected as humic acids represent a large proportion of the organic matter in soil. Thus the following order can be generated:

organic matter on the soil > CBHA > ethyl > phenyl > ODS

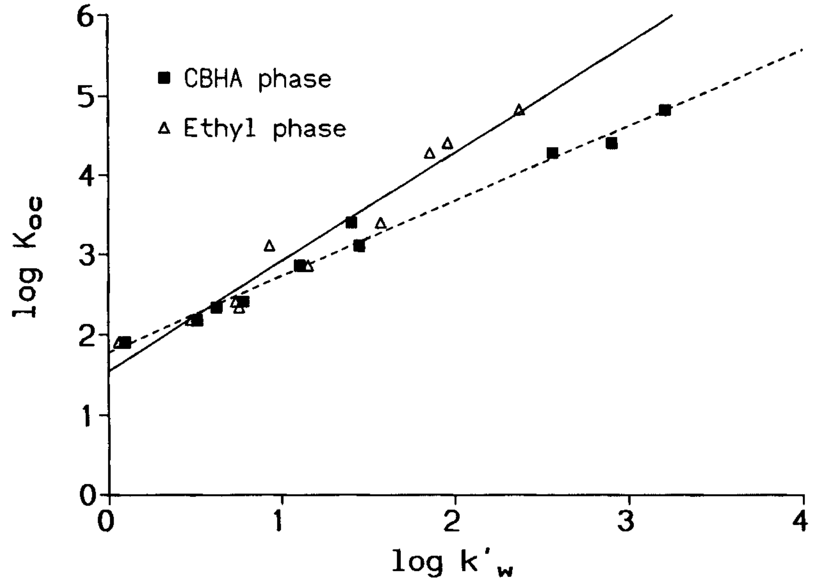

FIGURE 2 Relationship between the soil/water partition coefficient (K_{oc}) and the theoretical capacity factor (k'_w) for ethylsilica and CBHA phases.

This is the order that might be expected on the basis of the polarity of the media. ODS should be the least polar and organic matter of sediment or soil matter should be the most polar due to the presence of carboxyl, phenolic and amino moieties in humic substances.

It was noted that the correlation between log K_{ow} and log k' improves with an increase in the water content of the HPLC mobile phase (7). Harnisch et al. (17) specified a mobile phase water content of at least 30% v/v even for homologues and structurally related compounds. Several groups have demonstrated that an increase in the water content results in superior correlations for log K_{oc} and log k' for the octadecyl and cyanopropyl phases (7,8) and for the ethyl phase (18). In this study we have examined this correlation on the chemically bound humic acid column for mobile phases with varying water contents. The capacity factors determined for a range of water contents are given in Table 3 and the respective correlations are given below.

TABLE 3. Capacity Factors*(log k') Obtained on CBHA Using Different Mobile Phases.

Solute	40 % water	50 % water	60 % water	100 % water
Benzene	-0.744	-0.663	-0.537	0.096
Toluene	-0.705	-0.581	-0.291	0.514
Ethylbenzene	-0.687	-0.358	-0.152	0.782
Propylbenzene	-0.558	-0.287	0.008	1.107
Butylbenzene	-0.423	-0.125	0.204	1.407
o-Xylene	-0.559	-0.380	-0.155	0.627
Naphthalene	-0.222	0.006	0.322	1.452
Phenanthrene	0.221	0.826	1.123	2.569
Anthracene	0.274	0.871	1.293	2.907
Pyrene	0.672	0.999	1.392	3.212

*NOTE: calculated from equation [2]

Mobile phase: 40% water/60% methanol:

$$\log K_{oc} = 2.005 \log k' + 3.721 \quad [r^2 = 0.931]$$

Mobile phase: 50% water/50% methanol:

$$\log K_{oc} = 1.596 \log k' + 3.123 \quad [r^2 = 0.959]$$

Mobile phase: 60% water/40% methanol:

$$\log K_{oc} = 1.448 \log k' + 2.708 \quad [r^2 = 0.972]$$

Calculated results to 100% water:

$$\log K_{oc} = 0.948 \log k' + 1.781 \quad [r^2 = 0.986]$$

From an examination of the above series it is evident that there is an improvement in the correlation on increasing the water content of the mobile phase. Errors in calculating the capacity factor are higher for mobile phases of low water content than they are for high water contents. Reductions in these errors may be contributing to improvements in the correlation values. In addition, the high water content of the mobile phase is more like the conditions which will prevail in environmental processes. We suggest that our use of the calculated log k'_w for correlation is the best way to model the real conditions of soil/water sorption in the environment.

TABLE 4. Log K_{OC} Values Estimated from the CBHA Stationary Phase and Their Differences from Reported Values.

Solutes	**Log K_{OC} from CBHA**	**Reported Log K_{OC}**	**Difference from reported value**
Acenaphthene	3.79		
Acenaphthylene	3.83		
Antracene	4.53	4.41*	-0.12
Benzene	1.87	1.91*	0.04
Butylbenzene	3.15	3.40*	0.25
Chlorobenzene	2.28		
1,3-Dichlorobenzene	2.56		
1,4-Dichlorobenzene	2.56		
1,2-Dichlorobenzene	2.58		
Ethylbenzene	2.52	2.41*	-0.11
Fluoranthene	4.74	4.63$	-0.11
Fluorene	4.15		
9-Methylanthracene	4.78	4.81#	0.03
2-Methylnaphthalene	3.91	3.92#	0.01
Naphthalene	3.15	3.11*	-0.04
Phenanthrene	4.22	4.28*	0.06
Propylbenzene	2.83	2.86*	0.03
Pyrene	4.82	4.83*	0.01
Tetracene	5.77	5.81#	0.04
Toluene	2.26	2.18*	-0.08
1,2,5-Trichlorobenzene	3.45		
o-Xylene	2.37	2.34*	-0.03

* see Table 1 for origin; # reference 6; $ reference 19

By using equation [6] we have determined (Table 4) log K_{OC} values for the 10 chemicals listed in Table 1 by RP-HPLC on CBHA. In addition, we report log K_{OC} values for chlorobenzene, 1,2-, 1,3- and 1,4- dichlorobenzene, 1,2,5-trichlorobenzene, acenaphthene, acenaphthylene, 2-methylnaphthalene, fluorene, fluoranthene, 9-methylanthracene and tetracene. For 4 of this last group of chemicals we subsequently found in the literature log K_{OC} values and, as shown in Table 4, these values reported by others are exceedingly close to the values we have determined by RP-HPLC on CBHA.

CONCLUSION

This investigation has shown that it is possible to determine log K_{oc} values for aromatic hydrocarbons by measuring the HPLC capacity factors on CBHA. This evaluation of the four stationary phases has established that the best correlation between log K_{oc} and log k' was found for the chemically bound humic acid stationary phase. This study indicates that the best way to model the soil/water sorption of aromatics in the environment is to use log k'_w, the capacity factor obtained by extrapolation of retention data from binary eluents to 100% water. The best prediction of log K_{oc} is obtained by using log k'_w measured using binary eluents, instead of log k'.

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REFERENCES

1. Y. P. Chin, W. J. Weber, T. C. Voice, Water Res., 20: 1443-1450 (1986)

2. S. W. Karickhoff, Chemosphere, 10: 833-846 (1981)

3. S. W. Karickhoff, D. S. Brown, T. A. Scott, Water Res., 13: 241-248 (1979)

4. S. M. Lambert, J. Agric. Food Chem., 16(2): 340-343 (1968)

5. C. T. Chiou, L. J. Peters, V. H. Freed, Science, 206: 831-832 (1979)

6. E. E. Kenaga, Ecotoxicol. Environ. Safety, 4: 26-38 (1980)

7. P. D. Vowles, R. F. C. Mantoura, Chemosphere, 16: 109-116 (1987)

8. J. Hodson, N. A. Williams, Chemosphere, 17: 67-77 (1988)

9. R. A. Rapaport, S. J. Eisenreich, Environ. Sci. Technol., 18: 163-170(1984)

10. C. T. Chiou, P. E. Porter, D. W. Schmedding, Environ. Sci. Technol., 17: 227-231 (1983)

11. C. Horvath, W. Melander, I. Molnar, J. Chromatogr., 125: 129-156 (1976)

12. D. N. Brooke, A. J. Dobbs, N. Williams, Ecotoxicol. Environ. Safety, 11: 251-260 (1986)

13. J. M. Hill, J. Chromatogr., 76: 455-458 (1973)

14. Th. Braumann, L. H. Grimme, J. Chromatogr., 206(1): 7-15 (1981)

15. Th. Braumann, G. Weber, L. H. Grimme, J. Chromatogr., 261(3): 329-343 (1983)

16. L. R. Snyder, J. W. Dolan, J. R. Gant, J. Chromatogr., 165(1): 3-30 (1979)

17. M. Harnisch, H. J. Moeckel, G. Schulze, J. Chromatogr., 282: 315-332 (1983)

18. Gy. Szabó, S. L. Prosser and R. A. Bulman, Chemosphere, 21: 495-505 (1990)

19. B. C. Suedel, J. H. Rodgers, Jr., P. A. Clifford, Environ. Toxicol. Chem., 12: 155-165 (1993)

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