

Estimation of soil organic partition coefficients: from retention factors measured by soil column chromatography with water as eluent

Feng Xu^a, Xinmiao Liang^{a,*}, Bingcheng Lin^a, Karl-Werner Schramm^b, Antonius Kettrup^b

^aDalian Institute of Chemical Physics, Chinese Academy of Sciences, 161 Zhongshan Road, Dalian 116011, PR China

^bGSF-National Research Center for Environment and Health, Institute of Ecological Chemistry, Ingolstädter Landstrasse 1, D-85764 Neuherberg, Germany

Received 18 February 2002; received in revised form 17 May 2002; accepted 10 June 2002

Abstract

The retention factors (k) of 104 hydrophobic organic chemicals (HOCs) were measured in soil column chromatography (SCC) over columns filled with three naturally occurring reference soils and eluted with Milli-Q water. A novel method for the estimation of soil organic partition coefficient (K_{oc}) was developed based on correlations with k in soil/water systems. Strong $\log K_{oc}$ versus $\log k$ correlations ($r > 0.96$) were found. The estimated K_{oc} values were in accordance with the literature values with a maximum deviation of less than 0.4 log units. All estimated K_{oc} values from three soils were consistent with each other. The SCC approach is promising for fast screening of a large number of chemicals in their environmental applications.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Partition coefficients; Soil column chromatography; Retention factors; Hydrophobic organic compounds

1. Introduction

Prediction of transport properties is of major importance in assessing the risks associated with the release of chemicals in the environment. Researches dealing with the processes affecting the transport of organic chemicals in soils are needed in order to prevent their contamination of ground-water [1]. The soil organic partition coefficient (K_{oc}) is one of primary parameters in evaluating the movement and persistence of the chemical in soil–water environ-

ment. Although the batch equilibrium method [2] has been widely used for K_{oc} measurements for a long time, it remains labor-intensive, time-consuming and hard to automate. For many existing and new chemicals, measured K_{oc} data are often not available. Variations of K_{oc} in different publications are often encountered, too, due to multiple factors (e.g., soil variety, soil/water ratio, equilibrium time, temperature, concentration range, extraction and determination procedure, etc.) affecting the measurements [3]. Hence, numerous models based on correlations of K_{oc} with physico–chemical properties or structural descriptors have been proposed for decades, e.g., models based on octanol/water partition coefficients [4] and molecular connectivity indices [5]. Some

*Corresponding author. Fax: +86-411-369-8905.

E-mail addresses: liangxm@mail.dlptt.ln.cn (X. Liang), fengxu64@hotmail.com (F. Xu),

RPLC methods using synthetic sorbents, such as octadecyl-, octyl-, cyanopropyl-, and humic acid-silica etc., were also proposed to estimate K_{oc} through correlations with retention factors (k) [6–9]. The RPLC method is successful for compounds with similar structure and that have similar interactions with synthetic stationary phase/mobile phase combinations in both k and K_{oc} measurements [10], but it is not successful for the K_{oc} estimation of chemicals with large structure differences [11].

The soil column chromatographic (SCC) method utilizing a soil filled column is a better means than above conventional RPLC approach, because both soil column experiments and batch K_{oc} measurements can take place in the same soil/water systems [12]. Since soil is not a mechanically rigid material by itself, the soil layer in the column may mobilize under a high flow-rate of water, resulting in possibly blocking the column outlet by small particles that are transported by the fluid. Solving this problem is a key point in achieving reproducible retention factors (k) in SCC [11]. In the present report, we wish to solve the problem by utilizing a soil dryly-packing method for a conventional 10 mm I.D. HPLC column eluted with 1 ml min⁻¹ water to speed up the transport process.

As a liquid chromatography, the SCC method loads lower amount of solutes each time compared to conventional batch methods. Based on a displacement adsorption model [13] in which the solute is distributed between a homogeneous interfacial layer and the bulk water phase, we put forward Eq. (1) previously [11]:

$$\log K_{oc} = \log (n_{2,\text{water}}v_{\text{water}}/n_{2,\text{sorbed}}v_{\text{soil}}) + \log (k\gamma_{1,\text{interface}}^{\infty}/\gamma_{1,\text{soil}}^{\infty}) \quad (1)$$

where subscripts 1 and 2 denote solute and water, respectively. k is the retention factor of the solute on soil, $n_{2,\text{water}}$ (or $n_{2,\text{sorbed}}$) refers to the mole numbers of water in mobile phase (or water sorbed on soil phase), v_{water} (or v_{soil}) corresponds to the molar volumes of the aqueous (or soil) phase, and $\gamma_{1,\text{interface}}^{\infty}$ (or $\gamma_{1,\text{soil}}^{\infty}$) are the infinite dilution activity coefficient of solute in the interface layer (or soil phase), respectively. We have found that $\gamma_{1,\text{soil}}^{\infty}$ and $\gamma_{1,\text{interface}}^{\infty}$ have strong connections with k [11] and determination of parameters in Eq. (1) is burdensome, Eq. (1) may be simplified as a linear equation:

$$\log K_{oc} = A + B \log k \quad (2)$$

The aim of the work reported here is to develop a reliable SCC method for retention factor (k) determination, and K_{oc} estimation from correlations with k . More than one hundred chemicals transported over three naturally occurring reference soils will be examined. The effect of column preconditioning by methanol-water mixtures on k determination will also be preliminarily investigated.

2. Experimental

Carbamates and herbicide phenylureas were synthesized in our institute [14]. All other hydrophobic organic chemicals were obtained from Bayer AG (Bayer Landwirtschaftszentrum, Monheim, Germany), Sigma (St. Louis, MO), and Aldrich (Milwaukee, WI). They were of the highest purity available, and were checked by RPLC on ODS to find that no impurity peaks existing. Water was Milli-Q pure (Millipore, Bedford, MA). Methanol was HPLC grade (Shangdong Yuwang, Jinan, China).

Three reference soils were used as the packing materials. Soils SP 14696 (denoted as Soil I) and SP 20697 (Soil II) were purchased from LUF A, Speyer, Germany, and soil GSE 17201 (Soil III) was from Bayer Landwirtschaftszentrum, Monheim, Germany. Their main characteristics are listed in Table 1. About 14 g of each soil was evenly divided into eleven portions, incrementally packed into a homemade stainless steel column (100 mm × 10 mm I.D.) with the same packing height by a homemade pressurizing device to assure packing homogeneously. The void volume of columns was 2.0 cm³, and the bulk density 1.8 g cm⁻³. A 0.45 μm nylon membrane (Millipore, Bedford, MA) was put in the column output to prevent fine particles from clogging the column. The packed column was flushed at 1 ml min⁻¹ with a (9:1, v/v) methanol-water mixture for 80 min followed by water for 80 min. Consequently, a flat baseline was observed, and the column would keep a stable pressure at about 1 MPa. Then the system was suitable for k measurements.

The SCC system consisted of two Waters 515 pumps (Waters Associates, Milford, MA), a Rheo-

Table 1
Main characteristics of three soils

Soil	pH in 0.01 M CaCl ₂	Organic carbon, OC (%)	Cation-exchange capacity, CEC (mol kg ⁻¹)	Sand %	Silt %	Clay %
I. SP 14696	6.0	0.59	0.04	89.5	8.0	2.5
II. SP 20697	6.1	2.27	0.09	79.7	13.7	6.6
III. GSE 17201	6.3	2.48	0.10	80.5	12.3	7.2

dyne (Berkeley, CA) 7725i 6-port injection valve with a 200 μl loop, a Waters 2487 UV detector, three homemade soil LC columns, and a DL 800 Workstation (Dalian Institute of Chemical Physics, Dalian, China) for data acquisition and processing. The pipes connecting the injection valve and detector were short with negligible extra-column volume. Water was used as an eluent with a flow-rate of 1.0 ml min^{-1} . The column was put in an AT-130 column box (Tianjin Autoscience Co., Tianjin, China) thermostated at 30.0 ± 0.1 °C. The detection was set at the maximum absorption wavelength (λ_{max}) of each compound. By injecting each HOC solution into the soil LC column through a 7725i valve, the retention time was obtained at the apex of the chromatographic peak, similar to the retention measured in conventional RPLC. The injection volume was 0.1 to 200 μl , dependent on the detection sensitivity of the solute. The higher the solute sensitivity, the lower the injection volume. The hold-up time (t_0) of the system was determined with a 1% NaNO_2 solution at 220 nm. To avoid overloading of the column, analytes were dissolved in water (or methanol) at two concentrations (0.1 and 0.01 g ml^{-1}), and both were injected and the corresponding retention times were compared. When they were different, a new solution was prepared from the less concentrated one (10-time dilution) and the experiment was repeated until constant retention was obtained. The lower the solute concentration, the better for facilitating the obtaining of stable and repetitive k values. Hence, the practical solute concentration for k measurements was no higher than 0.01 g ml^{-1} . The retention time (t_R) was based on the average of at least two independent determinations of the solute investigated. The retention factor was calculated according to $k = (t_R - t_0)/t_0$.

3. Results and discussion

3.1. Column preconditioning

Tightly and homogeneously packing a soil column (the bulk density reached 1.8 g cm^{-3}), and preconditioning the column with a methanol–water mixture (9:1, v/v) are two prerequisite conditions in SCC to assure the soil layer physically homogeneous and retention factors reproducible. Fig. 1 demonstrates three chromatograms of atrazine obtained over three independent columns packed with the same soil III. The column-to-column performance is excellent with less than 5.0% RSD for k values (three columns, 6 determinations for each column). If the columns were preconditioned only by water (not methanol),

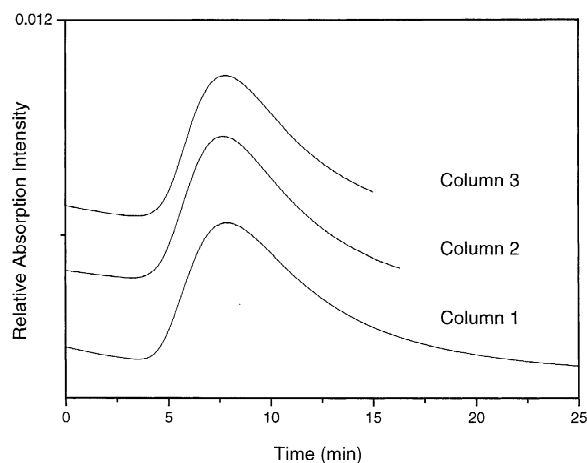


Fig. 1. Comparison of chromatograms of soil column chromatography (SCC) over three independent columns packed with the same soil (Soil III, GSE 17201). Eluent: water; flow-rate: 1 ml min^{-1} ; column temperature: 30 °C; solute: atrazine; injection: 10 ng; detection: 222 nm.

the membrane at the column outlet was easily blocked by small soil particles. Therefore, except for well packed columns by using the dryly-packing technique, preconditioning the column with the methanol–water mixture plays another important role in making the soil phase immobile. Fig. 2 shows the comparison of SCC chromatograms for repetitive injections (from the first to the 1000th injection) of ethyl benzoate over a Soil I-filled column. The column was first preconditioned with 9:1 v/v methanol–water for 80 min, later continuously rinsed with water eluent and the 1000th injection was carried out 3 months after the first injection. The results indicate that the chromatograms have no obvious change. We found the RSD of retention factors was 3.2% ($n = 1000$). Preconditioned soil columns can last for 6000 or more injections (about 1.5 years) until the pressure was higher than the preset instrument pressure limit (e.g., 50 MPa). If some tiny soil particles blocked the 0.45 μm membrane in the column outlet during long experimental periods (normally after more than 600 injections, or continuous runs of 3 months), changing the membrane with a new one could readily rehabilitate the column. When the column was stored and not in use for a long time, it should be sealed in a (9:1, v/v) methanol–water mixture. The column could be easily reconditioned with the same methanol–water mixture, and no retention time alteration

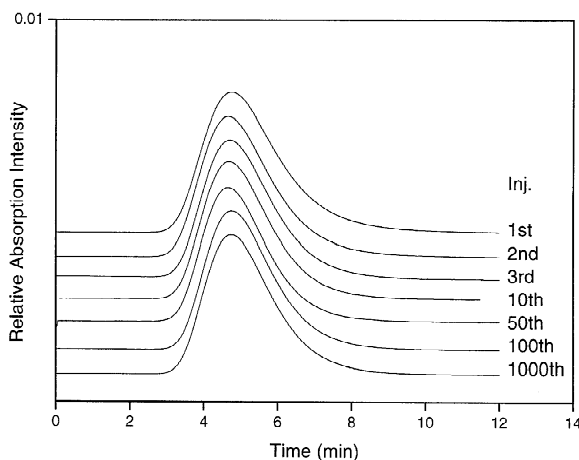


Fig. 2. Comparison of chromatograms of ethyl benzoate over Soil I (SP 14696)-filled column from the first to the 1000th injection. Eluent: water; flow-rate: 1 ml min⁻¹; column temperature: 30 °C; injection amount: 10 ng; detection: 229 nm.

was found, compared with the retention time before storage. For solutes dissolved in a methanol or water solution, there is no difference in retention time and peak shape observed.

As to the surmise that the methanol–water mixture will affect the retention behavior, a comparison was carried out between the retention ($\log k_{\text{cond.}}$) of all HOCs on the column preconditioned by (9:1, v/v) methanol–water mixture, and the retention ($\log k_{\text{uncond.}}$) on the same column but not preconditioned by the methanol–containing solvent (only by the same amount of water). The result is shown in Fig. 3 and Eq. (3):

$$\log k_{\text{cond.}} = 1.06 (\pm 0.01) \log k_{\text{uncond.}} \quad (3)$$

($n = 104, r = 0.975, s = 0.12, F = 1980, P < 0.0001$)

where n is the number of solutes, s is the standard error of the estimate, and F is the significance value (the ratio between regression and residual variances). Data in parenthesis is the confidence interval of the regression coefficient at 95% significant level. Two measured quantities, $k_{\text{cond.}}$ and $k_{\text{uncond.}}$, show statistically similar results. Though methanol has the effect of stabilizing the soil layer in the columns, it has

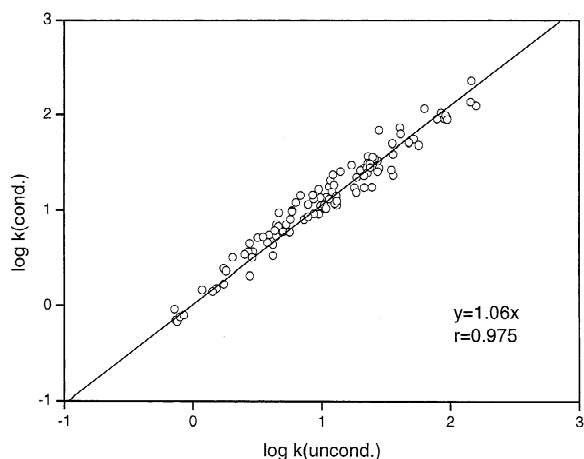


Fig. 3. Comparison between retention factors ($k_{\text{cond.}}$) measured on a Soil III (GSE 17201) filled column preconditioned by the methanol–water mixture (9:1, v/v) and retention factors ($k_{\text{uncond.}}$) measured on another Soil III filled column unconditioned by the methanol–water mixture. Eluent: water; flow-rate: 1 ml min⁻¹; column temperature: 30 °C.

little influence on the retention change of solutes. Brusseau et al. [15] and Bouchard [16] also suggested that the sorption (or transport) behavior over soils was not affected by exposing soil in methanol, though their studies covered only a small set of solutes and were applicable to their solute/soil combinations. The main focus of the following work is to estimate K_{oc} indirectly through correlations with retention factors, so we chose (9:1, v/v) methanol–water for soil column preconditioning. In RPLC, the exponentially modified Gaussian (EMG) model has been widely used to modify the retention time experimentally obtained, especially for tailed peaks [17]. The model could also be employed in SCC for more precisely processing retention data. Due to the asymmetry factor of our data being mainly less than 2.0, and for brevity, we did not process [18] the experimental data using the EMG model again.

3.2. $\log K_{oc}$ versus $\log k$ correlation

The soil columns used in this study were thermostated at 30 °C, because this temperature is easier to control for large amounts of experiments and long time, than 25 °C which is typical to most reported batch experiments.

In order to obtain k and analyze general information about the K_{oc} and k relationship, compounds representing wide hydrophobic classes (polycyclic aromatic hydrocarbons, alkylbenzenes, chlorobenzenes, esters, carbamates, triazines, phenylureas, phenols and other polar HOCs) were chosen, except for acids and nitrogen-containing strong bases which would ionize in the aqueous phase and whose retention factors would not truly reflect the solute retention in molecular (nonionized) form. The HOCs, existing in the aqueous phase in neutral molecular form, were all eligible for the study. The K_{oc} data listed in Table 2 were the medium values of reported batch experiment values [4,9,19,20], and have also been testified by our institute (Institute of Ecological Chemistry, Germany) with the batch methods. Some solutes, whose literature $\log K_{oc}$ values are quite different and difficult to judge the accuracy, were not chosen as reference chemicals. The retention factors of the solutes were feasibly determined on three soil columns, and are also listed in Table 2. UV detection at the λ_{max} of each solute provided satisfactory

sensitivity. For most compounds, a less than 50 ng injection per run is enough for k determination. The gradual dilution injection aforementioned was adopted for the choice of solute concentration until reproducible retention times were obtained for the solute at two concentrations (concentration ratio, 1:10). The maximum RSD of the retention factors from three measurements was less than 3% for strongly retained solutes. Under low injecting concentrations of the HOCs, the retention factors were almost independent of the compound concentration and quite reproducible.

Although some soil factors, such as clay content, cation-exchange capacity, etc., may be of importance for solute sorption, organic carbon (OC) content is recognized as the most important contributor to the sorption of HOCs [21–24]. The effect of OC content on retention is also clearly found in our k values over different soils (see Table 2). Solutes transport fast in Soil I, which possesses lower OC content (0.59%), and slowly in Soil II which are of a higher OC content (2.27%). For example, from the ratio of the retention factors of atrazine over Soil II and Soil I ($k_{(II)}/k_{(I)}=9.75$), the mobility in Soil I is approximately 10-fold greater than that in Soil II. Hence, using the soil with lower OC content could considerably save running time. It is also true that OC content plays a predominant role in solute retention.

Chemicals with larger k values in SCC generally have larger K_{oc} values. Strong correlations between $\log K_{oc}$ and $\log k$ of the reference chemicals from Table 2 are shown in Fig. 4 and Eq. (4).

$$\begin{aligned} \text{For soil I, } \log K_{oc(I)} &= \\ 0.768 (\pm 0.030) \log k_{(I)} + 2.141 (\pm 0.025) & \quad (4a) \\ (n = 44, r = 0.968, s = 0.13, F = 629, P < 0.0001) \end{aligned}$$

$$\begin{aligned} \text{For soil II, } \log K_{oc(II)} &= \\ 0.956 (\pm 0.041) \log k_{(II)} + 1.329 (\pm 0.056) & \quad (4b) \\ (n = 44, r = 0.962, s = 0.14, F = 527, P < 0.0001) \end{aligned}$$

$$\begin{aligned} \text{For soil III, } \log K_{oc(III)} &= \\ 0.914 (\pm 0.033) \log k_{(III)} + 1.422 (\pm 0.044) & \quad (4c) \\ (n = 44, r = 0.973, s = 0.12, F = 733, P < 0.0001) \end{aligned}$$

By using Eqs. (4a), (4b) and (4c), the K_{oc} values for

Table 2
Retention factors (k) measured in three reference soils and soil organic partition coefficients (K_{oc})^a

No.	Compound	$\log k_{(I)}$	$\log k_{(II)}$	$\log k_{(III)}$	$\log K_{oc(lit.)}$ ^b
1	Benzylalcohol	-0.815	0.144	-0.038	1.43
2	<i>p</i> -Nitrophenol	0.091	0.881	0.776	2.37
3	Nitrobenzene	-0.082	0.759	0.638	2.20
4	Methyl benzoate	-0.028	0.843	0.709	2.10
5	Ethyl benzoate	0.182	1.128	0.905	2.30
6	Ametryne	0.687	1.544	1.451	2.59
7	Atrazine	0.013	0.770	0.886	2.17
8	Cyanazine	-0.252	0.846	0.649	2.17
9	Dipropetryne	0.860	1.788	1.725	2.95
10	Prometone	0.372	1.351	1.196	2.54
11	Prometryne	0.691	1.411	1.479	2.66
12	Propazine	0.314	1.186	1.058	2.20
13	Secbumeton	0.684	1.402	1.510	2.64
14	Simazine	-0.050	0.632	0.657	2.02
15	Terbuthylazine	0.538	1.450	1.379	2.51
16	Terbutryne	1.046	1.981	1.865	3.17
17	Trietazine	0.491	1.480	1.298	2.76
18	Phenol	-0.615	0.171	0.166	1.43
19	2,3-Dichlorophenol	0.332	1.377	1.240	2.65
20	Methyl phenylcarbamate	-0.403	0.591	0.532	1.73
21	Ethyl phenylcarbamate	-0.150	0.759	0.752	1.90
22	Isobutyl phenylcarbamate	-0.258	1.078	0.987	2.06
23	Fenuron	-0.883	0.308	0.058	1.40
24	Fluometuron	-0.334	0.805	0.521	2.00
25	Chlorobenzene	0.348	0.897	0.931	2.34
26	1,4-Dichlorobenzene	0.799	1.352	1.396	2.63
27	1,2,3-Trichlorobenzene	1.267	1.965	1.969	3.29
28	1,2,4-Trichlorobenzene	1.257	2.065	1.961	3.15
29	1,3,5-Trichlorobenzene	1.527	2.081	1.992	3.15
30	Bromobenzene	0.480	1.228	1.053	2.49
31	Toluene	0.000	0.720	0.769	2.06
32	<i>o</i> -xylene	0.599	1.060	1.054	2.41
33	<i>m</i> -xylene	0.454	0.986	1.071	2.34
34	<i>p</i> -xylene	0.500	1.100	1.099	2.52
35	1,2,3-Trimethylbenzene	0.819	1.367	1.367	2.80
36	1,2,4-Trimethylbenzene	0.920	1.261	1.495	2.81
37	1,3,5-Trimethylbenzene	0.830	1.312	1.455	2.82
38	1,2,4,5-Tetramethylbenzene	1.327	1.864	1.799	3.12
39	Ethylbenzene	0.480	0.993	1.019	2.32
40	<i>n</i> -Propylbenzene	0.860	1.339	1.411	2.86
41	<i>n</i> -Butylbenzene	1.723	1.980	2.067	3.39
42	Biphenyl	1.512	1.998	1.967	3.27
43	Naphthalene	0.729	1.475	1.425	2.97
44	Fluorene	2.236	2.571	2.622	3.71

^a 100 mm × 10 mm I.D. column packed with Soil I (SP 14696), Soil II (SP 20697), and Soil III (GSE 17201), respectively; eluent: water at 1.0 ml min⁻¹; column temperature: 30 °C.

^b $\log K_{oc(lit.)}$ were the medium values taken from Refs. [4,9,19,20].

60 tested HOCs and 44 reference compounds were estimated from their retention factors measured on the three soils. The results are shown in Table 3. The estimated $\log K_{oc}$ values on the three soils are in

agreement with the published ones with maximum deviation less than 0.4 log-unit of magnitude; at the same time, the estimated $\log K_{oc}$ values of all chemicals were consistent with each other over the

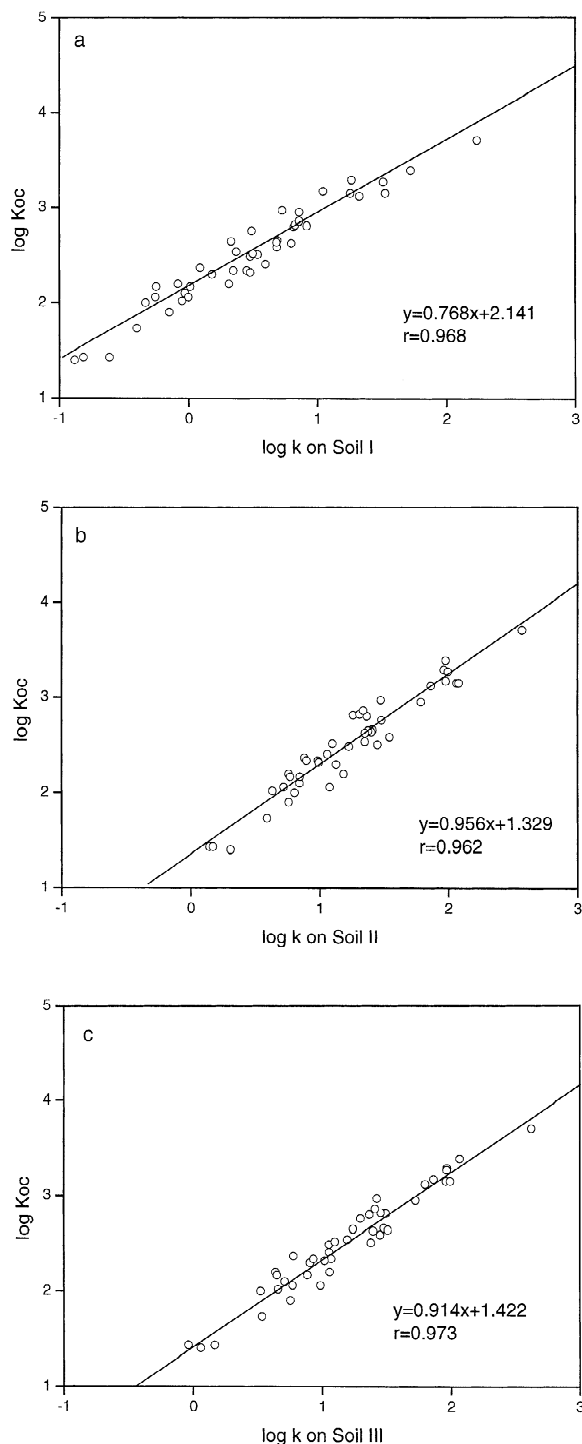


Fig. 4. Correlations of $\log K_{oc}$ with $\log k$ for 44 reference solutes on Soils I, II, and III. Eluent: water; flow-rate: 1 ml min^{-1} ; column temperature: $30 \text{ }^\circ\text{C}$. (A) Soil I (SP 14696); (B) Soil II (SP 20697); (C) Soil III (GSE 17201).

three soils. These results support Eq. (1) which we postulated, and suggest the generality and popularity of correlations between $\log K_{oc}$ and the $\log k$ obtained from different soil columns. The high correlations and the similar K_{oc} estimated values (from three soils) may allow us to speculate that the solute retention in the soil–water system is similar to the solute partition to soil organic matrix. The little difference of the estimated K_{oc} values from different soils may be attributed to the influence of other soil factors (such as clay, pH, cation-exchange capacity, etc.), complicated interactions of solute with the three-dimensional structure of soil organic matter, and experimental deviations, etc. Pertinent studies are being carried out.

There are several advantages of the SCC-based K_{oc} estimation method. First, tedious conditional tests required by batch equilibrium studies are reduced. The injection, transport and detection in SCC are fully automatic in a common HPLC apparatus and user intervention is minimized, which facilitates to obtain reproducible and comparable data from different experiments. Second, except for equilibrium behavior, kinetic transport behavior could also be gleaned, which is not attained in typical batch equilibrium studies. Third, the SCC method needs less soil, chemical and solvent, reducing the amount of waste generated. Fourth, soil columns can be repetitively and consecutively used for thousands of injections. Simple preconditioning and reconditioning procedures facilitate to compare/screen K_{oc} values of a large number of compounds over one soil, or over several soils. Whereas the retention factors of higher K_{oc} (e.g., $\log K_{oc} > 4$) solutes will be too large to measure with water as an eluent. Luckily, the ground-water contamination by chemicals mainly comes from the polar or weak polar compounds whose $\log K_{oc}$ values are commonly less than 4. Further studies in this laboratory will focus on the estimation for much wider solute hydrophobic ranges by utilizing methanol-containing eluents to increase solute mobility, and on improvement of sensitivity by hyphenating SCC with a highly-sensitive fluorescence detector. From the present first-stage results, the SCC method may particularly be helpful for scientists and other regulators who may need such fast estimates in their environmental measurements of chemicals.

Table 3

Logarithmic K_{oc} values estimated from the correlations between $\log K_{oc}$ versus $\log k$ in Soils I, II, and III for 44 reference compounds (Nos. 1–44) and 60 other compounds (Nos. 45–104), and maximum absorption wavelengths^a

No.	Compound	λ_{max} (nm)	$\log K_{oc(I)}$	$\log K_{oc(II)}$	$\log K_{oc(III)}$	$\log K_{oc(III)}$
1	Benzylalcohol	208	1.52	1.47	1.39	1.43
2	<i>p</i> -Nitrophenol	316	2.21	2.17	2.13	2.37
3	Nitrobenzene	262	2.08	2.05	2.00	2.20
4	Methyl benzoate	229	2.12	2.13	2.07	2.10
5	Ethyl benzoate	229	2.28	2.41	2.25	2.30
6	Ametryne	222	2.67	2.81	2.75	2.59
7	Atrazine	222	2.15	2.07	2.23	2.17
8	Cyanazine	220	1.95	2.14	2.01	2.17
9	Dipropetryne	223	2.80	3.04	3.00	2.95
10	Prometone	219	2.43	2.62	2.52	2.54
11	Prometryne	223	2.67	2.68	2.77	2.66
12	Propazine	223	2.38	2.46	2.39	2.20
13	Secbumeton	219	2.67	2.67	2.80	2.64
14	Simazine	223	2.10	1.93	2.02	2.02
15	Terbutylazine	223	2.55	2.72	2.68	2.51
16	Terbutryne	223	2.94	3.22	3.13	3.17
17	Trietazine	227	2.52	2.74	2.61	2.76
18	Phenol	213	1.67	1.49	1.57	1.43
19	2,3-Dichlorophenol	203	2.40	2.65	2.56	2.65
20	Methyl phenylcarbamate	234	1.83	1.89	1.91	1.73
21	Ethyl phenylcarbamate	234	2.03	2.05	2.11	1.90
22	Isobutyl phenylcarbamate	235	1.94	2.36	2.32	2.06
23	Fenuron	239	1.46	1.62	1.48	1.40
24	Fluometuron	243	1.88	2.10	1.90	2.00
25	Chlorobenzene	210	2.41	2.19	2.27	2.34
26	1,4-Dichlorobenzene	213	2.75	2.62	2.70	2.63
27	1,2,3-Trichlorobenzene	206	3.11	3.21	3.22	3.29
28	1,2,4-Trichlorobenzene	205	3.11	3.30	3.21	3.15
29	1,3,5-Trichlorobenzene	205	3.31	3.32	3.24	3.15
30	Bromobenzene	211	2.51	2.50	2.38	2.49
31	Toluene	210	2.14	2.02	2.13	2.06
32	<i>o</i> -xylene	210	2.60	2.34	2.39	2.41
33	<i>m</i> -xylene	210	2.49	2.27	2.40	2.34
34	<i>p</i> -xylene	210	2.53	2.38	2.43	2.52
35	1,2,3-Trimethylbenzene	210	2.77	2.64	2.67	2.80
36	1,2,4-Trimethylbenzene	210	2.85	2.53	2.79	2.81
37	1,3,5-Trimethylbenzene	211	2.78	2.58	2.75	2.82
38	1,2,4,5-Tetramethylbenzene	210	3.16	3.11	3.07	3.12
39	Ethylbenzene	210	2.51	2.28	2.35	2.32
40	<i>n</i> -Propylbenzene	210	2.80	2.61	2.71	2.86
41	<i>n</i> -Butylbenzene	210	3.46	3.22	3.31	3.39
42	Biphenyl	247	3.30	3.24	3.22	3.27
43	Naphthalene	280	2.70	2.74	2.72	2.97
44	Fluorene	262	3.86	3.79	3.82	3.71
45	α -Phenyl-ethyl alcohol	208	1.52	1.51	1.43	
46	α -Phenyl propanol	243	2.12	2.31	2.20	
47	<i>p</i> -Nitrotoluene	278	2.34	2.43	2.30	
48	Anisole	219	2.05	2.03	1.94	
49	Phenetole	220	2.29	2.19	2.20	
50	Benzaldehyde	248	1.90	1.84	1.77	
51	Acetophenone	243	1.94	1.87	1.93	
52	Propiophenone	243	2.11	2.16	2.08	

Table 3. Continued

No.	Compound	λ_{\max} (nm)	$\log K_{oc(I)}$	$\log K_{oc(II)}$	$\log K_{oc(III)}$	$\log K_{oc(lit.)}$
53	<i>n</i> -Propyl phenyl ketone	243	2.39	2.37	2.34	
54	Benzonitrile	221	1.83	1.84	1.75	
55	Propyl benzoate	229	2.64	2.76	2.55	
56	<i>n</i> -Butyl benzoate	229	2.97	3.01	2.86	
57	Isopentyl benzoate	229	3.35	3.38	3.26	
58	Diethyl phthalate	203	2.07	2.20	2.10	
59	Atraton	218	2.61	2.63	2.63	
60	Azidoatrazine	224	2.11	2.32	2.31	
61	Aziprotryne	238	2.24	2.49	2.46	
62	Dimethametryne	222	2.88	2.96	3.04	
63	Methoprotryne	222	2.54	2.57	2.63	
64	Sebuthylazine	223	2.44	2.67	2.33	
65	Simazine-hydroxy	223	2.08	1.95	2.08	
66	Simeton	218	2.74	2.80	2.75	
67	Simetryne	222	2.76	2.83	2.91	
68	Terbumeton	212	2.83	2.88	3.09	
69	Terbutylazine-hydroxy	224	3.39	3.53	3.51	
70	Desmetryn	221	2.72	2.73	2.71	
71	3-Chlorophenol	203	2.21	2.15	2.18	
72	4-Chlorophenol	227	2.14	2.14	2.13	
73	Methiocarb	205	2.51	2.68	2.56	
74	phNHCOO(CH ₂) ₃ CH ₃	235	2.46	2.47	2.52	
75	phNHCOOCH ₂ CH(CH ₃) ₂	234	2.40	2.35	2.38	
76	phNHCOO(CH ₂) ₄ CH ₃	235	3.07	3.24	3.27	
77	phNHCOOCH ₂ CH=C(CH ₃) ₂	235	2.60	2.53	2.72	
78	phNHCOOCH ₂ ph	235	2.62	2.87	2.78	
79	(phNH) ₂ CO	255	2.84	2.66	2.88	
80	(phCH ₂ NH) ₂ CO	203	2.44	2.38	2.54	
81	(2-CH ₃ phNH) ₂ CO	205	2.32	2.36	2.45	
82	<i>N</i> -(phenylcarbamy)morpholine	240	1.53	1.64	1.50	
83	phNHCONHCH(CH ₃) ₂	240	1.70	1.80	1.73	
84	phNHCONH(CH ₂) ₃ CH ₃	240	1.99	2.10	2.14	
85	phNHCONHCH ₂ CH(CH ₃) ₂	243	1.79	1.79	1.86	
86	phNHCONHCH ₂ ph	240	2.44	2.63	2.47	
87	<i>N</i> -cyclohexyl- <i>N'</i> -phenylurea	240	2.32	2.34	2.39	
88	phNHCON(C ₂ H ₅) ₂	240	1.46	1.36	1.64	
89	phNHCON(CH ₂ CH ₂ CH ₃) ₂	240	1.77	1.79	2.00	
90	phNHCON(CH ₂ CH ₂ CH ₂ CH ₃) ₂	240	2.32	2.41	2.58	
91	<i>N</i> -(phenylcarbamy)piperidine	241	1.80	1.70	1.81	
92	<i>N</i> -(4-methylcarbamy)piperidine	242	2.02	1.98	2.06	
93	<i>N</i> -(2-methylcarbamy)piperidine	206	1.63	1.72	1.67	
94	<i>N</i> -(4-chlorophenylcarbamy)piperidine	249	2.32	2.31	2.48	
95	<i>N</i> -(4-bromophenylcarbamy)piperidine	217	2.34	2.57	2.58	
96	1,2-Dichlorobenzene	217	2.78	2.71	2.74	
97	1,3-Dichlorobenzene	212	2.79	2.55	2.74	
98	Iodobenzene	226	2.72	2.73	2.65	
99	1,2,3,5-Tetramethylbenzene	211	3.13	2.89	3.02	
100	Pentamethylbenzene	210	3.40	3.20	3.21	
101	<i>i</i> -Propylbenzene	210	2.91	2.70	2.65	
102	Diphenylmethane	202	3.37	3.24	3.21	
103	Acenaphthylene	229	3.19	3.25	3.34	
104	Acenaphthene	224	3.29	3.33	3.28	

^a Soil I (SP 14696): $\log K_{oc(I)} = 0.768 \log k_{(I)} + 2.141$; Soil II (SP 20697): $\log K_{oc(II)} = 0.956 \log k_{(II)} + 1.329$; Soil III (GSE 17201): $\log K_{oc(III)} = 0.914 \log k_{(III)} + 1.422$.

4. Conclusions

Results obtained in the present work show that preconditioning by methanol–water mixture (9:1, v/v) has little influence on the retention behavior of solutes on soil columns. The retention factors of 104 hydrophobic organic chemicals on three soil columns eluted with water have been obtained. The retention factors were used to test the robustness of the correlations between $\log K_{oc}$ and $\log k$ with satisfactory results. Such correlations are simply an easy way to perform the experiments of estimating and screening K_{oc} values for existing and new chemicals, even over different soils. Compared to the soil with higher organic carbon content, the soil with lower organic carbon content can be used to shorten the experimental time.

Acknowledgements

The authors are grateful to Fan Su, Ying Yang, Qing Zhang, and Mianshen Bao for donating reagents and technical assistance in experiments.

References

- [1] W.A. Jury, W.F. Spencer, W.J. Farmer, *J. Environ. Qual.* 12 (1983) 558.
- [2] OECD, OECD Guidelines for Testing of Chemicals, Proposal for Updating Guideline 106 Adsorption/Desorption using a Batch Equilibrium Methods, OECD, Paris, France, 1996.
- [3] G. Singh, W.F. Spencer, M.M. Cliath, M.Th. van Genuthen, *J. Environ. Qual.* 19 (1990) 520.
- [4] A. Sabljic, H. Güsten, H. Verhaar, J. Hermens, *Chemosphere* 31 (1995) 4489.
- [5] J.R. Baker, J.R. Mihelcic, A. Sabljic, *Chemosphere* 45 (2001) 213.
- [6] J. Hodson, N.A. Williams, *Chemosphere* 17 (1988) 67.
- [7] W. Kördel, J. Stutte, G. Kothhoff, *Chemosphere* 27 (1993) 2341.
- [8] G. Szabó, J. Guzzi, R.A. Bulman, *Chemosphere* 30 (1995) 1717.
- [9] A. Kaune, R. Brüggemann, M. Sharma, A. Kettrup, *J. Agric. Food Chem.* 46 (1998) 335.
- [10] T. Braumann, *J. Chromatogr.* 373 (1986) 191.
- [11] F. Xu, X.-M. Liang, B.-C. Lin, F. Su, K.-W. Schramm, A. Kettrup, *J. Environ. Qual.* 30 (2001) 1618.
- [12] P.S.C. Rao, A.G. Hornsby, D.P. Kilcrease, P. Nkedi-Kizza, *J. Environ. Qual.* 14 (1985) 376.
- [13] W.E. Hammers, G.J. Meurs, C.L. De Ligny, *J. Chromatogr.* 246 (1982) 169.
- [14] Y. Yang, S.-W. Lu, *Tetrahedron Lett.* 40 (1999) 4845.
- [15] M.L. Brusseau, A.L. Wood, P.S.C. Rao, *Environ. Sci. Technol.* 25 (1991) 903.
- [16] D.C. Bouchard, *Chemosphere* 36 (1998) 1883.
- [17] J.P. Foley, J.G. Dorsey, *Anal. Chem.* 55 (1983) 730.
- [18] P.-Z. Lu, Y.-Z. Zhang, X.-M. Liang, *High Performance Liquid Chromatography and Expert System*, Liaoning Science and Technology Publishing House, Shenyang, 1991.
- [19] E.E. Kenega, *Ecotox. Environ. Safety* 4 (1980) 26.
- [20] J.-B. Liu, C.-F. Qian, *Chemosphere* 31 (1995) 3951.
- [21] C.T. Chiou, L.J. Peters, V.H. Freed, *Science* 206 (1979) 831.
- [22] M.A. Locke, *J. Environ. Qual.* 21 (1992) 558.
- [23] D.A. Laird, P.Y. Yen, W.C. Koskinen, T.R. Steinheimer, R.H. Dowdy, *Environ. Sci. Technol.* 28 (1994) 1054.
- [24] C.A. Seybold, W. Mersie, *J. Environ. Qual.* 25 (1996) 1179.