Prediction of Soil Adsorption Coefficients from Retention Parameters on Three Reversed-Phase Liquid Chromatographic Columns

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Reversed-phase high-performance liquid chromatographic (RP-HPLC) retention parameters, which are determined by the intermolecular interactions in retention process, can be considered as the chemical molecular descriptors in linear free energy relationships (LFERs). On the basis of the characterization and comparison of octadecyl-bonded silica gel (ODS), cyano-bonded silica gel (CN), and phenyl-bonded silica gel (Ph) columns with linear solvation energy relationships (LSERs), a new multiple linear regression model using RP-HPLC retention parameters on ODS and CN columns as variables for estimation of soil adsorption coefficients was developed. It was tested on a set of reference substances from various chemical classes. The results showed that the multicolumn method was more promising than a single-column method was for the estimation of soil adsorption coefficients. The accuracy of the suggested model is identical with that of LSERs.

Soil adsorption coefficients can be determined by the batch equilibrium method recommended by OECD,[1] but it is a time-consuming and expensive procedure. Therefore, many estimation methods based on chemical structure or physicochemical properties have been developed.[2,3] Gawlik et al. performed a thorough review of various methods and discussed their advantages and drawbacks.[4] As an alternative estimation method, RP-HPLC is more reliable than those from quantitative structure activity relationship (QSAR) calculations, and it can be used for mixtures. The method was first introduced by Hodson et al.[5] and Vowles et al.[6] Later works of other groups studied its applications to different compound classes, the influences of mobile-phase composition,

and stationary phases.[7–14] Most attempts have been made to discover a suitable column for RP-HPLC screening of soil adsorption coefficients of diverse chemicals. The major works focus on the chemically or physically immobilized humic acids on a SiO_2 or Al_2O_3 support, silica salicylic and silica-8-hydroxyquinoline.[10,15] Comparing with this type of column, commercially available columns are more facile and reproducible. At the actual state-of-the-art, the CN column has been proposed as the most suitable one for the soil adsorption coefficient estimation.[5,6,12,16,17] But for some compounds from different chemical classes, the CN column is not applicable. Recently, Liang et al. developed soil column liquid chromatography (SCLC) to investigate the behavior of pollutants in the soil/water system.[18–21] Although soil adsorption coefficients for pure compounds can be conveniently measured with SCLC, it is almost impossible for mixtures because of its low column efficiency.

In a recent review, Gross and Schwarzenbach[22] compared one-parameter and polyparameter linear free energy relationships (LFERs) from theoretical aspects. They concluded that one-parameter LFERs could not describe the complete compound variability by a single parameter. Polyparameter LFERs are based on a concept that considers all interactions involved in partitioning

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by separate parameters, so it allows the prediction of the complete compound variability by a single equation. The commonly used RP-HPLC methods for the estimation of soil adsorption coefficients also suffer from the principal inherent shortcomings of one-parameter LFERs, which limit their applications only in a narrow chemical range.

As one type of polyparameter LFERs, linear solvation energy relationships (LSERs) have been mainly promoted by the groups of Kamlet, Taft, Abraham, and Poole.[23-27] LSERs have already been successfully applied to the study of QSAR for a wide variety of compounds. The form of the LSER equation is as follows,[25]

$$\log K = c + vV_x + rR_2 + s\pi_2^* + a\sum\alpha_2^H + b\sum\beta_2^H \quad (1)$$

where V_x is the solute molecular volume, R_2 is the solute excess molar refraction, π_2^* is the solute dipolarity/polarizability, and $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ are the solute's effective hydrogen bond donor (HBD) acidity and effective hydrogen bond acceptor (HBA) basicity, respectively. The fitting coefficients v, r, s, a and b measure the corresponding specific interactions. V_x and R_2 can be calculated for any structures, and π_2^*, $\Sigma\alpha_2^H$, and $\Sigma\beta_2^H$ can be measured by experiments, but the process is time-consuming.[26,27] π_2^*, $\Sigma\alpha_2^H$, and $\Sigma\beta_2^H$ can also be estimated through the use of partition coefficients (e.g., water−solvent partition coefficients, GC retention factors).[27] Many past studies have shown the RP-HPLC retention parameters can be accurately correlated with the solvatochromic parameters;[28-31] therefore, the solute's retention factors in several different chromatographic systems can be used to calculate the solute's solvatochromic parameters as the solutions to those simultaneous LSERs equations. Similarly, the retention parameters involving specific molecular interactions can be taken as molecular descriptors to replace the solvatochromic parameters in LSERs. Zhang et al. used the solute's GC retention factors on several columns to predict the K_{OA} values of PCB.[32] For RP-HPLC, ODS, CN and Ph are the routinely used commercial stationary phases, and they have different specific molecular interactions with solutes.[28,33]

In this study, we characterize them with LSERs and take the solute's retention parameters on them as the solute's different molecular descriptors for the multiple linear regression method to estimate soil adsorption coefficients. However, because the soil adsorption coefficient value varies with many complex factors (such as the composition of the soil, temperature, and pH value,

etc.),[34] the data available in the literature lack comparability. Thus, we use the chemicals' retention factors on SCLC to replace the soil adsorption coefficient data to evaluate our method. In fact, it has been proved that the retention factors of chemicals on SCLC were correlated very well with its soil adsorption coefficient values.[16] In this paper, we study the correlation between the retention factors on SCLC and the retention parameters on the three stationary phases of 35 compounds belonging to widely different chemical classes (including alkylbenzenes, halogenated benzenes, phenols, anilines, and pesticides). In addition, we compare our suggested method with LSERs.

Considerations of the Multiple Linear Regression Model of RP-HPLC for the Estimation of Soil Adsorption Coefficients. The multiple linear regression model of retention factors on a soil column (k_{soil}) using the solute's retention factors in different RP-HPLC systems (k_i) as molecular descriptors is as follows,

$$\log k_{soil} = \sum_{i=1}^{n} a_i \log k_i + b \quad (2)$$

where a_i and b are constants and n is the number of the chromatographic systems that have different selectivities. At the same time, the relationship between the solute's retention factor and the composition of the binary mobile phase can be described by[35]

$$\log k_i = \log k_{wi} - S_i\varphi \quad (3)$$

where $\log k_{wi}$ and S_i are constants. Combining eq 3 and eq 2 yields

$$\log k_{soil} = \sum_{i=1}^{n} (a_i \log k_{wi} + c_i S_i) + b \quad (4)$$

where c_i is a constant that reflects the relative contribution of the corresponding retention parameters. We can deduce this equation for an accurate description of interactions for solute adsorption in a soil/water system.

EXPERIMENTAL SECTION

Reagents. The following RP-HPLC columns were employed: Hypersil ODS, 5 μm, 200 mm × 4.0 mm (Dalian Elite Scientific Instruments Co., Ltd.); Hypersil CN, 5 μm, 150 mm × 4.6 mm (Dalian Elite Scientific Instruments Co., Ltd.); and Hypersil Ph, 5 μm, 250 mm × 4.6 mm (Dalian Elite Scientific Instruments Co., Ltd.). Soil GSE 17201 (Bayer, Germany, f_{OC} (%) = 2.48, clay (%) = 7.20, sand (%) = 80.50, and silt (%) = 12.30) were packed into an SCLC column (100 mm × 5 mm) by our laboratory. Methanol (HPLC grade) was from ShanDong YuWang Ltd., and water was prepared with a Milli-Q water purification system (Millipore, Milford, MA). Citrate and all the test substances were A.C. grade and were separately dissolved in methanol.

Apparatus. The instrument consisted of two Waters 515 HPLC pumps, a Waters 2487 Dual λ absorbance detector, and an injection

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Table 1. Chemicals and Experimental Data

chemical no.		log k_{soil}	log k_{wODS}	S_{ODS}	log k_{wCN}	S_{CN}	log k_{wPh}	S_{Ph}
1	benzene	−0.31	2.00	2.67	0.11	0.86	0.96	1.61
2	toluene	−0.13	2.42	2.97	0.43	1.29	1.30	1.96
3	ethylbenzene	0.01	2.96	3.47	0.80	1.83	1.79	2.54
4	*n*-propylbenzene	0.24	3.55	4.00	1.23	2.41	2.08	2.80
5	*n*-butylbenzene	0.51	4.12	4.49	1.84	3.30	2.57	3.34
6	chlorobenzene	0.00	2.51	3.13	0.58	1.51	1.32	1.98
7	bromobenzene	0.09	2.63	3.21	0.68	1.64	1.45	2.12
8	iodobenzene	0.23	2.87	3.41	0.94	2.01	1.66	2.34
9	nitrobenzene	−0.12	1.43	2.20	0.26	1.06	0.86	1.47
10	*m*-dichlorobenzene	0.32	3.19	3.68	1.02	2.13	1.77	2.48
11	biphenyl	0.57	3.62	4.12	1.66	3.04	2.30	3.01
12	naphthalene	0.37	2.96	3.48	1.07	2.19	1.76	2.44
13	anthracene	1.31	4.20	4.56	2.15	3.60	2.68	3.40
14	fluorene	0.95	3.78	4.14	1.73	3.04	2.44	3.13
15	pyrene	1.68	4.43	4.62	2.56	4.11	2.93	3.63
16	phenanthrene	1.32	4.42	4.68	2.53	4.62	2.66	3.25
17	*N,N*-dimethylaniline	0.47	2.03	2.59	0.51	1.45	1.30	1.94
18	benzyl alcohol	−0.72	0.81	1.74	−0.20	0.54	0.29	0.88
19	1-phenylethanol	−0.63	1.23	2.13	0.01	0.86	0.59	1.22
20	phenol	−0.43	0.83	1.76	−0.07	0.75	0.44	1.11
21	*p*-nitrophenol	0.00	0.98	1.99	0.31	1.37	0.73	1.56
22	*p*-chlorophenol	−0.14	1.71	2.59	0.42	1.38	0.94	1.66
23	*p*-methylphenol	−0.38	1.29	2.16	0.18	1.09	0.71	1.39
24	3-chlorophenol	−0.11	1.82	2.72	0.43	1.40	1.04	1.80
25	2,3-dichlorophenol	0.10	2.28	3.19	0.82	1.95	1.29	2.06
26	aniline	0.17	0.41	1.26	−0.19	0.48	0.30	0.90
27	*p*-nitroaniline	0.06	0.44	1.44	0.28	1.17	0.45	1.15
28	*p*-chloroaniline	0.09	1.32	2.20	0.26	1.08	0.79	1.49
29	fenthion	0.51	3.85	4.66	1.92	3.30	2.92	3.69
30	azinphosmethyl	0.30	2.50	3.45	1.47	2.87	2.32	3.07
31	tebuconaz	0.39	3.91	4.76	2.10	3.83	2.82	3.72
32	fuberidzole	0.89	1.36	2.26	0.87	2.10	0.98	1.67
33	methiocarb	0.01	2.60	3.39	1.09	2.37	1.73	2.50
34	triadimenol	−0.21	3.27	4.18	1.52	3.07	2.30	3.17
35	atrazine	−0.36	1.96	2.81	0.70	1.93	1.36	2.06

valve (Rheodyne, 7725i) fitted with a 20-μL sample loop. The chromatographic data processing was achieved on a personal computer equipped with DL 800 work station.

Chromatographic Conditions. All of the RP-HPLC columns and the soil column were thermostated at a temperature of 30 °C; the flow rate was 1.0 mL/min. Citrate buffer having a concentration of 0.01 M and pH of 6 was used for RP-HPLC experiments. The methanol contents (by volume) of mobile phase were changed from 80 to 60% by 10% steps for the ODS column, from 60 to 20% by 20% steps for the CN column, and from 80 to 60% by 10% steps for the Ph column. The retention factors (log k_{soil}) of 35 substances on a soil column were determined using 50% MeOH/50% water as the mobile phase. NaNO$_2$ was used to determine the dead time (t_0) for all of the experiments.

RESULTS AND DISCUSSION

The log k_w and S of 35 organic compounds on ODS, CN, and Ph columns were calculated using eq 3. The calculated log k_w and S are presented in Table 1, along with the experimental log k_{soil} data. For all of the solutes, the squares of the regression correlation coefficients (R^2) of eq 3 were above 0.97.

Characterization of Stationary Phases. Of the 35 chemicals, 28 were used to characterize column interactions. Their solvatochromic parameters are from literature.[36] The solutes' retention parameters (log k_w, and S) on the ODS, CN, and Ph columns were

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Table 2. Results of Retention Parameters of Three Columns on LSERs

LSERs coefficients	log k_{wODS}	S_{ODS}	log k_{wCN}	S_{CN}	log k_{wPh}	S_{Ph}
c	−0.24	0.70	−1.79	−1.89	−0.71	−0.18
v	4.09	3.60	2.88	4.15	2.87	3.10
r	0.46	0.32	0.24	0.27	0.16	0.08
s	−1.22	−1.02	−0.18	−0.24	−0.46	−0.41
a	−0.38	−0.03	−0.10	0.06	−0.29	−0.16
b	−3.47	−3.05	−1.85	−2.49	−2.11	−2.37
R^2	0.99	0.98	0.98	0.96	0.99	0.99

regressed against their solvatochromic parameters using eq 1, and the results are listed in Table 2.

According to the regression results of log k_w, the magnitudes of coefficients *v, r, s, a,* and *b* vary substantially with the type of stationary phases. This indicates that there is an obvious difference in the contributions of the corresponding molecular interactions to log k_w on the ODS, CN, and Ph columns. Comparison of the magnitudes of *v* indicates that the ODS column has the strongest dispersive forces, and the CN and Ph columns have similar dispersive forces. The magnitudes of *r* show that the *n* and *π* electron-involved interactions for the ODS column are more significant than those for the CN and Ph columns. The negative *s, a,* and *b* values for all of the HPLC columns that were used to denote that the corresponding interactions are stronger in the mobile phase than in the stationary phase. The largest negative *s* for the ODS column means that, in comparing it with the CN and
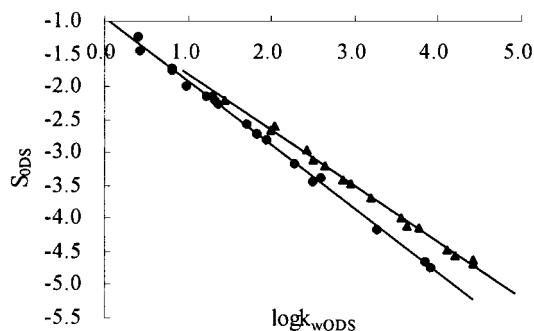
Figure 1. Correlations of log k_w and S on an ODS column for set 1 (▲) and set 2 (●).

Ph columns, its ability to interact with the solute's polarizable functional groups is diminished. The coefficients a and b measure the difference between the stationary and mobile phases in HBA basicity and HBD acidity, respectively. A large negative a and b can be obtained for the less basic and acidic stationary phases, whereas smaller negative constants reveal the increasing column basicity and acidity. Factually, according to the magnitudes of a and b shown in Table 2, it is clear that the CN and Ph columns have a significantly stronger HBD acidity than the ODS column, and the HBA basicity for the CN, Ph, and ODS columns sequentially diminishes. In addition, we found there were some differences in sign and magnitude between log k_w and S. For all three columns, the most apparent difference between log k_w and S is that the HBA basicity involved in S is stronger than that involved in log k_w. The results of LSER indicate that the S parameter involves specific interactions from log k_w and the contribution of each molecular interaction to S is different from log k_w.

We further correlated log k_w with S for the 35 chemicals on the three columns. Their R^2 for the CN, Ph, and ODS columns were 0.989, 0.994, and 0.978, respectively. The obtained results showed that there was an approximately linear relationship between log k_w and S, which agreed with the results obtained by Braumann,[37] and Hafkenscheid and Tomlinson[38] on an ODS column using methanol/water as the mobile phase. Nevertheless, when carefully examined, the data of log k_w and S on ODS column, we found that those experimental data distributed around two separated straight lines on the plot of log k_w against S. One set is for chemicals nos. 1−17 (set 1), and the other is for chemicals nos. 18−35 (set 2) in Table 1. The linear relation of log k_w and S of ODS column for the two sets of chemicals are shown in Figure 1, and the R^2's of set 1 and set 2 are 0.996 and 0.998, respectively. This indicates the S parameter actually involves some specific interactions, according to the chemical structures.

Correlation between log k_{soil} and the Retention Parameters in a Single Chromatographic System. In the past studies, the most commonly used RP-HPLC model for the determination of soil adsorption coefficients has been the so-called "collander-type" equation,[39]

$$\log K = a \log k + b \tag{5}$$

where a and b are constants; K is the partitioning constant, here replaced by k_{soil}; and k is the RP-HPLC retention factor (in some cases, k_w is used).[40]

On the basis of our experimental data, we compared the results of log k_{soil} predicted from log k_w by eq 5 for alkylbenzenes and for the entire chemical set. For the five alkylbenzenes, their k_{soil} and k_w on the three HPLC columns were separately achieved in an accurate correlation with eq 5, and the corresponding R^2 for the ODS, CN, and Ph columns were 0.990, 0.997, and 0.980, respectively. But for the group of tested chemicals, the correlation accuracy largely decreased, and the R^2 of eq 5 for the ODS, CN, and Ph columns were 0.47, 0.66, and 0.50. The plots of the experimental log k_{soil} against the predicted log k_{soil} (from the CN column) are shown in Figure 2 for akylbenzenes and in Figure 3 for the entire chemical set. These results show that the commonly used RP-HPLC method (in the form of eq 5) in the prediction of soil adsorption coefficient is accurate for structurally similar compounds, but for chemicals with diverse structures, its accuracy is too poor to be acceptable.

Combining eq 3 with eq 5, we obtain eq 6,

$$\log k_{soil} = a_1 \log k_w + a_2 S + b_1 \tag{6}$$

where a_1, a_2, and b_1 are constants. The quotient of a_2 and a_1 shows the optimum composition of the binary mobile phase by which the best correlation can be found between log k_{soil} and RP-HPLC retention data. This method has been used for the determination of K_{OW} by Valko.[41] Equation 6 has the best potential of a single RP-HPLC system for the prediction of soil adsorption coefficients by optimizing the solvent/water binary mobile phase. Comparison of the prediction results of log k_{soil} for the 35 chemicals using eq 5 with those results obtained using eq 6, show that the log k_{soil} prediction accuracy of eq 6 (R^2's for the ODS, CN, and Ph columns are 0.53, 0.70, and 0.58, respectively) is better than those of eq 5. But even for the best results of eq 6 (i.e., CN column), shown in Figure 4, the accuracy is still not good enough for application.

The above results show that when data originates from different classes of chemicals, it is practically impossible for ODS, CN, and Ph columns to determine soil adsorption coefficients for them with a single HPLC system. Although with optimum composition of the mobile phase, the correlation accuracy can be in some extent improved, it is still difficult to satisfy the real application. This may be the reason that the solute's molecular interactions with a soil/water system are quite complex and different from those in a single chromatographic system.

Multiple Linear Regression RP-HPLC Model. A systematic examination of various combinations of retention parameters for the prediction of soil adsorption coefficients was performed so as to establish its simple and accurate multiple linear regression HPLC model. The valuable results of multiple linear regressions for the complete data set are summarized in Table 3, and the R^2 of all other results are below 0.87.

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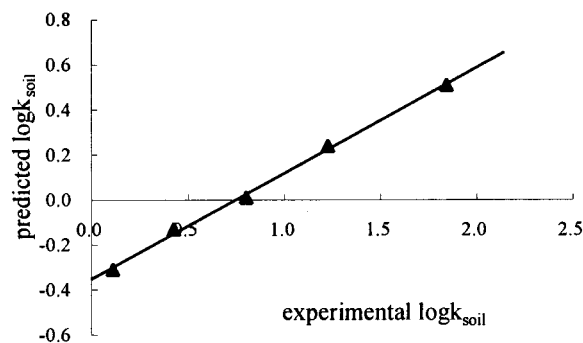(41) Valko, K. J. *Liq. Chromatogr.* **1984**, *7*, 1405−1424.

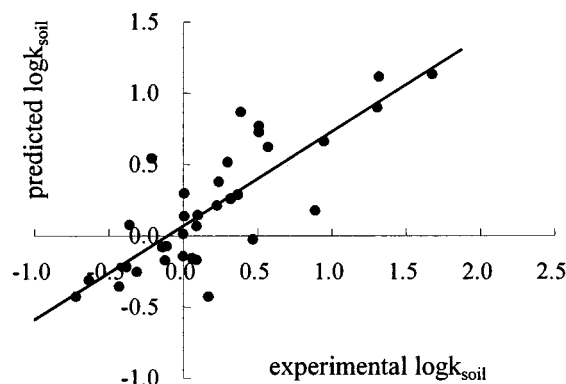**Figure 2.** Experimental vs predicted log k_{soil} (eq 5) of the CN column for five alkylbenzenes.

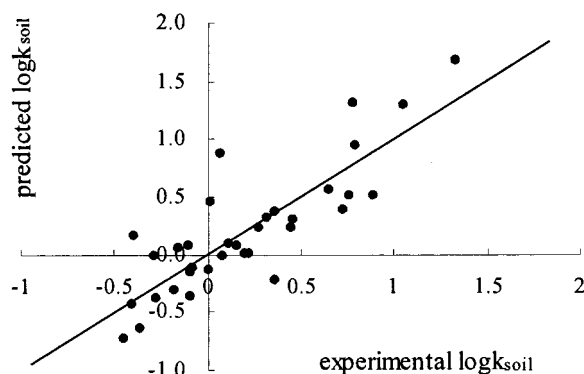**Figure 3.** Experimental vs predicted log k_{soil} (eq 5) of the CN column for the entire set.

Figure 4. Experimental vs predicted log k_{soil} (eq 6) of the CN column for the entire set.

Table 3. Multiple Linear Regression Results of RP-HPLC

independent variables	R^2	S	F	n
log k_{wODS}, S_{ODS}, log k_{wCN}, S_{CN}, log k_{wPh}, S_{Ph}	0.92	0.17	50.64	35
log k_{wODS}, S_{ODS}, log k_{wCN}, S_{CN}	0.91	0.17	76.13	35
log k_{wODS}, S_{ODS}, log k_{wCN}	0.89	0.19	80.59	35

From the results of the multiple linear regressions shown in Table 3, we found that the retention parameters on the Ph column were not very significant in improving the regression results; therefore, we suggest that the four-variable combination of retention parameters (k_w and S) on the CN and ODS columns is suitable for the prediction of soil adsorption coefficients, and its equation is
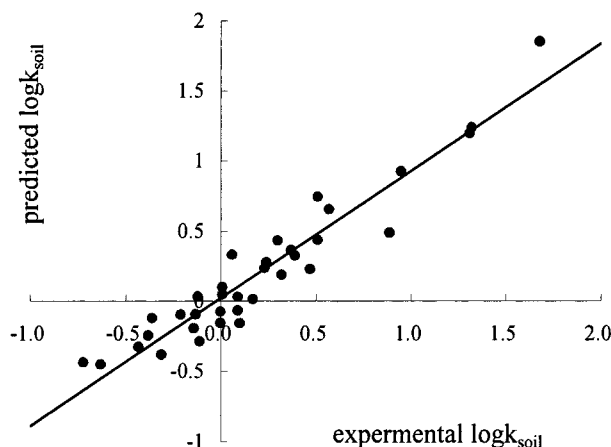

Figure 5. Experimental vs predicted log k_{soil} (eq 7).

$$\log k_{soil} = 2.46 + 0.82 \log k_{wODS} - 1.50 S_{ODS} + 2.46 \log k_{wCN} - 0.87 S_{CN} \quad (7)$$

$$R^2 = 0.91, \quad S = 0.17, \quad F = 76.13, \quad n = 35$$

The plot of the predicted log k_{soil} using eq 7 against the experimental log k_{soil} is shown in Figure 5. Comparison of the results shown in Figure 3 to that in Figure 5 shows that it is clear that the linear regression RP-HPLC model derived from the multicolumn is better than that from the single column for the prediction of soil adsorption coefficients. These results agree with the suggestion of Gross and Schwarzenbach.[22]

Until now, LSERs have been considered to be the most suitable model for the prediction of some important physicochemical parameters of compounds with very different structures. We compared the results of our model with those of LSERs for the same chemicals (nos. 1−28). The regression equation of log k_{soil} on LSERs is

$$\log k_{soil} = -1.27 + 1.12 V_x + 0.44 R_2 + 0.13 \pi_2^* - 0.41 \sum \alpha_2^H - 0.89 \sum \beta_2^H \quad (8)$$

$$R^2 = 0.91, \quad s = 0.19, \quad F = 45.20, \quad n = 28$$

The regression equation of log k_{soil} in the form of eq 7 is

$$\log k_{soil} = 1.97 + 0.68 \log k_{wODS} - 1.25 S_{ODS} + 2.12 \log k_{wCN} - 0.70 S_{CN} \quad (9)$$

$$R^2 = 0.93, \quad s = 0.16, \quad F = 80.64, \quad n = 28$$

From the results of eq 8 and eq 9, it is obvious that the two methods have similar accuracy. We conclude that the four-parameter LFERs based on the retention parameters of the ODS and CN columns can describe the essential molecular interactions involved in the soil adsorption.

Although we also get the same conclusion, that is, that CN is the best stationary phase for the prediction of soil adsorption coefficients by RP-HPLC method, as that reported by other authors, the single CN column is still not sufficient for diverse chemicals with different structural classes. In agreement with

Gross and Schwarzenbach,[22] in the field of environmental partition process, improving the comprehensive polyparameter LFERs are more valuable than trying to refine the existing one-parameter LFERs. In fact, the prediction accuracy of soil adsorption coefficients can be significantly improved by combining the retention parameters of a CN column with those of an ODS column. Meanwhile, using the solute's chromatographic parameters in place of the solvatochromic parameters as the molecular descriptors, it is a convenient way to practically predict the soil adsorption coefficient data.

CONCLUSION

A new approach was suggested to predict the soil adsorption coefficients for diverse chemicals with different structural classes from HPLC retention parameters. In this method, log k_w and S on ODS and CN stationary phases were finally used as molecular descriptors to achieve the correlation of soil adsorption coefficients with them, and the accuracy of our method is similar to that obtained with LSERs. In addition, S is a useful molecular descriptor for some specific interactions in the calculation of LFERs.