Adsorption-desorption behavior of acetochlor to soils in the presence of some environmental substances

YE Chang-ming, LEI Zhi-fang

(Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: yechm@mail.rcees.ac. cn)

Abstract: The behavior of herbicide acetochlor adsorption-desorption to soil in the presence of humic acid (HA), anionic surfactant sodium dodecylbenzene sulfonate (SDBS), cationic surfactant hexadecyltrimethyl-ammonium bromide (HDAB) and NH_4NO_3 as a chemical fertilizer was studied. Observed acetochlor adsorption isotherm were well described using Freundlich isotherm equation, from which the desorption isotherm equation has been deduced. The deduced equation can more directly describe acetochlor desorption process. The results showed that the enhance of acetochlor adsorption capacity by solid HA was greater than by soluble HA. The presence of NH_4NO_3 can slightly enhance acetochlor adsorption to soil by comparison with that measured in NH_4NO_3-free solution. In soil-water system, surfactant-acetochlor interaction is very complex, and the surfactant adsorptions as well as acetochlor adsorption need to be considered. When acetochlor-soil suspensions contained lower concentration SDBS or HDAB (40 mg/L), K_f for acetochlor adsorption was decreased in comparison to that measured in SDBS- or HDAB-free solution. When acetochlor-soil suspensions contained higher concentration SDBS or HDAB (corresponding 1400 mg/L or 200 mg/L), K_f for acetochlor adsorption was increased in comparison to that measured in SDBS- or HDAB-free solution.

Keywords: adsorption-desorption; acetochlor; humic acid; surfactants; ammonium nitrate; soil

Introduction

Although the herbicide acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide] has been used for ten years in China, limited information has been collected to determine its fate and transport in the environment. Formulations are generally sold as emulsifiable concentrates with the active ingredient found in a variety of commercial herbicides. Acetochlor is applied as preemergent to plant growth and, although it is relative soluble in water (223 mg/L at 25 ℃; Jaworski, 1975), it does not have a high being leached potential and is adsorbed by soil colloids.

Adsorption-desorption of herbicides to soil from water is an important factor affecting their fate, biological activity, and persistence in soil (Pigmatallo, 1991). The degree of chemicals adsorption to soil may not only affect a chemical's mobility but may be an important parameter in fate processes such as volatilization, photolysis, hydrolysis, and biodegradation. Better understanding of these processes will permit more effective weed control with minimum residues. The estimation of adsorption behavior of herbicides to soil can be used to explain the nature of processes taking place in variety of different conditions and should provide a potential to predict hazards imposed by the presence of the herbicides in the actual ecosystems (Sabbaan, 1997).

Adsorption of hydrophobic organic chemicals is in most cases modeled as a partitioning process with the organic content of the soil being the primary factor influencing adsorption. The partition conception was extensively utilized to introduce a series of empirical linear free-energy-based relationships correlating various practical aspects of the compounds hydrophobicity, such as aqueous solubility, octanol/water partition, bioaccumulation and soil adsorption, by correlating correspondent partition coefficients (Calvet, 1989; Chiou, 1983; Karickhof, 1979; Leo, 1971; Mailhot, 1988).

More recently, attention has been turned towards the effects of surfactants, co-solvents, and natural organic colloids on the fate and transport of hydrophobic organic chemicals in soils (McCarthy, 1989; Magee, 1991; Dunnivant, 1992; Tostsche, 1997). Natural organic matter comprises the most important

component in soil solution capable of improving the transport of hydrophobic organic chemicals. The association extent of hydrophobic organic chemicals and dissolved organic carbon was found to be enhanced with increasing concentration of dissolved organic carbon and the hydrophobicity of the sorbate.

The Freundlich isotherm for describing adsorption-desorption processes of herbicide can be given in Eq.(1).

$$C_s = K_f C_{eq}^{1/n}. \tag{1}$$

Where C_s is the concentration of herbicide adsorbed on soil (mg/kg); C_{eq} is the herbicide equilibrium concentration in solution (mg/L); K_f(L/kg) and n are the Freundlich constants.

The amount of herbicides adsorbed on soil was calculated by following equation:

$$C_s = (C_0 - C_{eq}) V/m, \tag{2}$$

where C_s is the concentration of herbicide adsorbed on soil (mg/kg), C_0 and C_{eq} are the equilibrium concentration in aqueous phase of herbicides after shaking without soil and with soil (mg/L) respectively; V is the volume of the solution (L) and m is the weight of the soil (kg). At least two replications were carried out for each measurement.

For the desorption experiments, the concentration of herbicides not desorbed in 20h (C_d) was calculated with the equation:

$$C_d = [(C_s m + C_{eq} V_{ent}) - C_{eqd} V_d]/m, \tag{3}$$

where V_{ent} is the volume of solution entrained after the sorption experiment, C_{eqd} is the herbicide concentration in the desorption supernatant solution, and V_d is the volume of entrained solution during the desorption experiment.

Before adsorption reached at equilibrium, the mass of herbicide adsorbed per mass adsorbent is changed with adsorption time and can be described by

$$\frac{\partial S}{\partial t} = k(K_f C^{1/n} - S). \tag{4}$$

The Eq.(4) can be solved analytically as follows

$$S = K_f C^{1/n}(1 - e^{-kt}), \tag{5}$$

in which K_f is the adsorption Freundlich constant; k is a first-order adsorption kinetics rate constant (h^{-1}); S is the mass of herbicide adsorbed per mass adsorbent at time t. The Eq.(5) indicates $S = 0$ when $t = 0$, and $S = K_f C^{1/n}$ when $t \to \infty$ (the adsorption has reached at equilibrium).

The objectives of this study were to (1) obtain the adsorption-desorption distribution coefficients of acetochlor to soils; (2) quantify the kinetics of this herbicide adsorption-desorption to soils; and (3) examine the influence of some environmental substances humic acid, surfactants and $NH_4 NO_3$ on adsorption-desorption behavior of the herbicide to soils.

1   Materials and methods

1.1   Soil

The soil samples were taken from the surface 10 cm layer at the agricultural field of Northwestern Beijing, China that had not received previous application of the studied herbicide. The bulk soil was slightly air-dried, mixed thoroughly, passed through a 0.15 mm sieve. The selected some soil properties were analyzed such as pH, organic carbon content (OC), cation exchange capacity (CEC) and particle-size distribution (Table 1). Soil pH was measured in a 1:1 soil-H_2O suspension with a glass pH electrode at 30 min after mixing. CEC was measured by following the procedure reported by Hendershot and Duquette (Hendershot, 1996). OC and particle-size distribution were determined by potassium dichromate oxidation method and pipette method respectively (NSICAS, 1978).

<div align="center">Table 1   Physical and chemical properties of studied soil</div>

pH	OC, %	CEC, mmol/100g	Silt, %	Sandy, %	Clay, %
8.4	1.5	84.0	59	38	3

1.2   Chemicals

Acetochlor of 99.5% produced by Monsanto Company was used as analytical reference standard. Sodium dodecylbenzene sulfonate (SDBS) of 83% and hexadecyltrimethyl-ammonium bromide (HDAB) of 95% were purchased from Beijing Chemical Regents Company and Shanghai Chemical Regents Company, respectively. All organic solvents were of analytical-reagent grade and purified by redistillation.

1.3   Analytical methods of acetochlor

The concentration of acetochlor in supernatant samples of adsorption-desorption experiments was analyzed directly by HPLC with a Zorbox-ODS stainless steel column ($0.25\text{m} \times 4.6$ mm) and using an UV detector at 215 nm. Methanol:water = 80:20 (v/v) was used as mobile phase with flow rate of 0.7 ml/min. The sample injection volume was $5\mu l$.

1.4   Adsorption-desorption experimental procedures

Distribution coefficients for adsorption and desorption of acetochlor by the soil samples were determined in duplicate using the bach equilibration method. For each determination, amount of soil samples were weighed into 50 ml glass centrifuge jars, and 10 ml of aqueous acetochlor solution of known concentrations (20, 40, 60, 80, and 100 mg/L) was added to each jar. The aqueous acetochlor solutions contained 1‰ NaN_3 as a biocide in experiments. The jars were sealed with Teflon-lined screw caps and mechanically shaken for various lengths of time (usually 21h) at 25℃. After shaking, the solutions were centrifuged for 15 min at 2500 r/min. A 5 ml aliquot of the supernatant was removed, filtered through 0.45 μm micro porous filter membrane, and placed in a glass tube for HPLC analysis of acetochlor.

<div align="center">Table 2   Designed adsorption-desorption experiment systems</div>

No.	Sorbent component	Adsorption solution	Elutriate in desorption	Purpose
1	Soil	OS*	/	Adsorption kinetics
2	Soil	OS	Water contained 1‰ NaN_3	Adsorption-desorption
3	Soil	OS	Water contained 0.01 M $CaCl_2$ and 1‰ NaN_3	Effect of $CaCl_2$ on desorption
4	Soil	OS	Water contained 60 mg/L soluble HA and 1‰ NaN_3	Effect of soluble HA on desorption
5	Soil + 0.1g solid HA	OS	Water contained 1‰ NaN_3	Effect of solid HA on adsorption
6	Soil	OS contained 60 mg/L soluble HA	Water contained 1‰ NaN_3	Effect of soluble HA
7	Soil	OS contained 50 mg/L NH_4NO_3	Water contained 1‰ NaN_3	Effect of NH_4NO_3
8	Soil	OS contained 40 mg/L SDBS	Water contained 1‰ NaN_3	Effect of SDBS
9	Soil	OS contained 1400 mg/L SDBS	Water contained 1‰ NaN_3	Effect of SDBS
10	Soil	OS contained 2240 mg/L SDBS	Water contained 1‰ NaN_3	Effect of SDBS
11	Soil	OS contained 40 mg/L HDAB	Water contained 1‰ NaN_3	Effect of HDAB
12	Soil	OS contained 200 mg/L HDAB	Water contained 1‰ NaN_3	Effect of HDAB

* OS to be composed of water, 1‰ NaN_3 and acetochlor of known concentration (see text)

For the first desorption step the above-mentioned aliquot was replaced with 5 ml of elution solution and the samples shaken for another 21h. Again, a 5 ml aliquot of the supernatant was removed, filtered and stored until analysis. This cycle was repeated two more times to obtain multiple desorption measurements. To obtain our purpose, a series of experiments was designed (Table 2). In order to determine adsorption-desorption equilibrium time and kinetics constant, the variation of concentration of herbicide adsorbed with adsorption time was measured.

2   Results and discussion

2.1   Adsorption equilibrium time and kinetics constant

In Eq. (5) the rate coefficient is an only adjustable parameter, which was estimated by trial and error from the kinetics experimental data (Fig. 1), and found the adsorption kinetics constant k is 0.055 h^{-1} and equilibrium time is about 17h. So the shaking time was selected as 21h in all adsorption-desorption experiments.
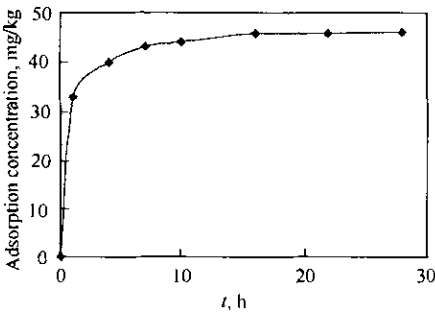

Fig. 1   Curve of adsorption kinetics and equilibrium time of acetochlor to soil

2.2   Adsorption-desorption isotherm

The adsorption-desorption isotherms are shown in Fig. 2—8. The adsorption Freundlich constants for all the system studied were obtained by power regression (nonlinear regression analysis) of adsorption isotherm data (Fig. 2—8). The calculated results are shown in Table 3. For the sake of making Freundlich desorption isotherm parameters more directly express desorption ability of any compound to soil, the Freundlich adsorption equation was alternated into following form

$$C_e = K_{des} Cs'^{1/m}, \qquad (6)$$

in which Cs' is the concentration of herbicide retained on soil during desorption equilibrium (mg/kg); C_e is the herbicide equilibrium concentration (mg/L); K_{des} (kg/L) and m are desorption Freundlich parameters which can be related to adsorption Freundlich parameters K_f and n by $K_{des} = K_f - n$ and $m = 1/n$. The desorption experimental data in Fig. 2—8 were fitted to Eq. (6) using nonlinear curve fitting and to obtain the values of K_{des} and $1/m$ (Table 3).

Table 3   The Freundlich constants describing adsorption-desorption of acetochlor to soils

| No.	Adsorption			First desorption			Second desorption			Third desorption		
	K_f	$1/n$	R^2	K_{des}	$1/m$	R^2	K_{des}	$1/m$	R^2	K_{des}	$1/m$	R^2
2	3.963	0.636	0.982	0.115	0.641	0.950	0.060	1.576	0.949	0.013	1.993	0.973
3	5.241	0.587	0.984	0.034	1.756	0.977	0.092	2.036	0.977	0.003	2.288	0.974
4	3.829	0.685	0.987	0.114	1.462	0.998	0.03	1.754	0.986	0.016	1.845	0.979
5	9.572	0.572	0.996	0.008	1.412	0.959	/	/	/	/	/	/
6	4.405	0.651	0.999	0.028	1.813	0.982	/	/	/	/	/	/
7	4.654	0.58	0.999	0.043	1.775	0.989	/	/	/	/	/	/
8	4.303	0.62	0.989	0.044	1.787	0.977	/	/	/	/	/	/
9	5.353	0.621	0.996	0.118	1.374	0.998	/	/	/	/	/	/
10	5.489	0.789	0.995	0.123	1.063	0.978	/	/	/	/	/	/
11	3.280	0.689	0.976	0.129	1.464	0.974	/	/	/	/	/	/
12	6.491	0.521	0.989	0.043	1.724	0.990	/	/	/	/	/	/
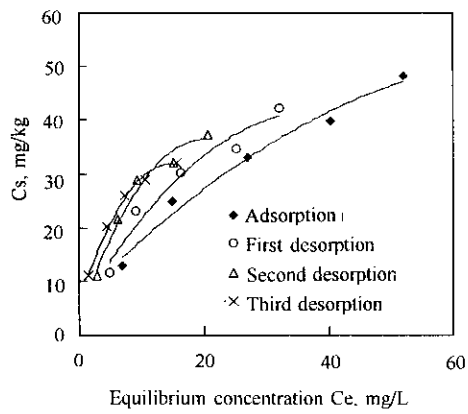
Fig.2   Adsorption-desorption isotherm of acetochlor to soil
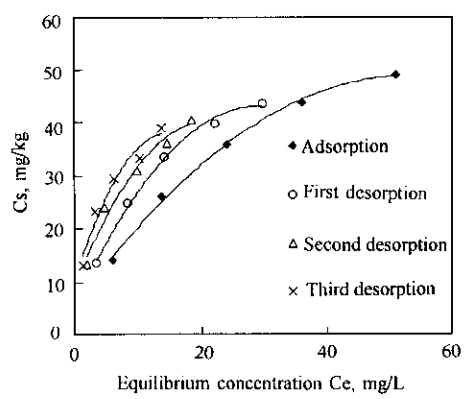

Fig.3   Adsorption-desorption isotherm under $CaCl_2$ effect on desorption of acetochlor to soil
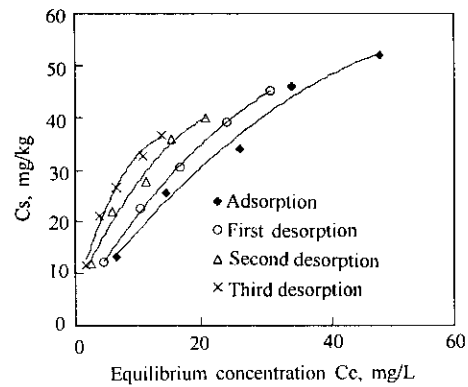

Fig.4   Adsorption-desorption isotherm of influence of soluble HA on desorption of acetochlor to soil
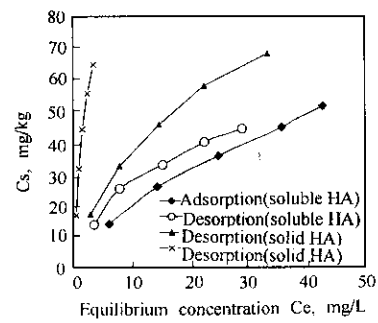

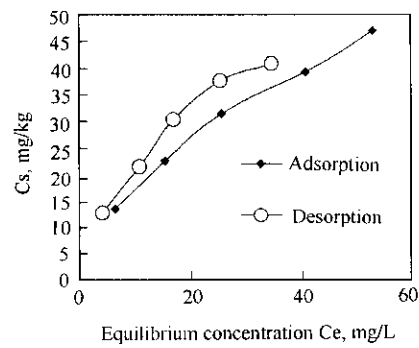Fig.5   Adsorption-desorption isotherm of acetochlor to soil under solid and soluble HA effect

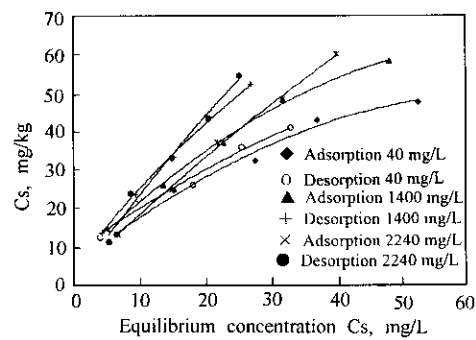Fig.6   Adsorption-desorption isotherm of acetochlor to soil under NH_4NO_3 effect

Fig.7   Adsorption-desorption isotherm of acetochlor to soil under SDBS effect

Under conditions without HA, $CaCl_2$, NH_4NO_3, SBDS and HDAB, the adsorption coefficient K_f mean value of No.2, No.3 and No.4 is 4.339 L/kg which is slightly greater than 4.1 L/kg reported in the literature (Webber, 1982), and less than 6.8 L/kg reported by Ma (Ma, 2000). Through comparison of organic carbon content between our and literature results, we consider the value of 4.339 L/kg is
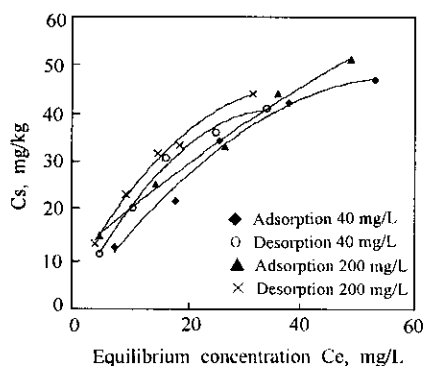
reasonable.

Fig. 8   Adsorption-desorption   isotherm   of acetochlor to soil under HDAB effect

Equilibrium concentration Ce, mg/L.

Legend:
◆ Adsorption 40 mg/L
○ Desorption 40 mg/L
▲ Adsorption 200 mg/L
× Desorption 200 mg/L

2.3   Influence of CaCl$_2$ and soluble HA on desorption

From the results of Nos. 2 – 4 in Table 3, we can find that desorption coefficient K_{des} values decreases with increase of desorption steps. For example, K_{des} of the first desorption step is 1.9 and 8.8 times of the second and third steps in No. 2 respectively. This fact brought to light the explicit physical meaning of K_{des} value that can reflect desorption ability of a system. CaCl$_2$ as a background electrolyte in system can minimize the dissolution-dispersion of organic matter from soil (Werkkeiser, 1996). So that organic matter can be kept in soil texture as possible as it can, thus the desorption ability of acetochlor from soil. For instance, K_{des} values of the first desorption are 0.034, 0.115 and 0.114 of No. 3, No. 2 and No. 4 respectively.

60 mg/L soluble HA has not remarkable influence on desorption of acetochlor from soil, for example K_{des} values of the first and third desorption steps in No. 4 and No. 2 were 0.114, 0.115 and 0.016, 0.013 respectively. However influences of 0.1g solid HA on desorption of acetochlor from soil was very remarkable.

2.4   Influence of HA on adsorption-desorption

In the system of No. 6 in Table 3, soluble HA increased lightly K_f value and decreased K_{des} because the soluble HA was added at beginning of adsorption experiment which is different from No. 4 in which the soluble HA was added only in desorption elutriate. It was found that extent of K_{des} decrease is greater than one of the K_f increase.

The comparison between results of No. 6 and No. 2 in Table 3 found that solid HA has a remarkable effect to adsorption and desorption of acetochlor to soil. The K_f and K_{des} of the first desorption in the system with solid HA are 2.42 and 0.07 times of those without solid HA. Solid HA has such great influence on adsorption-desorption processes of acetochlor to soil because solid HA in soil may be a sorbent itself, and play an important part in adsorption-desorption system of acetochlor.

2.5   Influence of NH$_4$NO$_3$ on adsorption-desorption

In soil water NH$_4$NO$_3$ can be dissociated into NH$_4^+$ and NO$_3^-$, which are common ions in farmland soils. Those ions maybe affect the adsorption-desorption of herbicides to soil. The results of No. 7 system in Table 3 showed that NH$_4$NO$_3$ has to certain effect to adsorption-desorption of acetochlor. When acetochlor-soil suspensions contained the NH$_4$NO$_3$, K_f for acetochlor adsorption was 4.654 L/kg, which is slightly greater than that measured in NH$_4$NO$_3$-free solution (3.936 L/kg). K_{des} value for the former only was 0.374 of the latter. The role of NH$_4$NO$_3$ as an electrolyte here maybe similar to CaCl$_2$.

2.6   Influence of surfactant SDBS and HDAB on adsorption-desorption

As the representative of anionic and cationic surfactants, SDBS and HDAB were used respectively in this study. The results in No. 8 and No. 12 systems found when acetochlor-soil suspensions contained 40 mg/L SDBS and 40 mg/L HDAB, K_f for acetochlor adsorption were 4.303 and 3.28 respectively which are less than that measured in SDBS- and HDAB-free solutions (mean value of 4.339). The results in No. 9 and No. 12 systems found when acetochlor-soil suspensions contained 1400 mg/L SDBS and 200 mg/L HDAB, K_f for acetochlor adsorption were 5.303 and 6.491 which are greater than that measured in SDBS- and HDAB-free solutions respectively.

We also found the higher the concentrations of two surfactants the greater the enhance on acetochlor adsorption. The results showed that surfactants SDBS and HDAB could solubilize acetochlor at lower

concentration, and enhance the adsorption of acetochlor at higher concentration. At higher concentration, the soil surfaces may be completely covered by a monolayer of surfactant, and the additional surfactant monomer may be adsorbed on the monolayer of hydrophobic heads. This would result in a bilayer of surfactant on the soil surface with surfactant hydrophobic tails sticking out in the aqueous phase, which would considerably enhance the adsorption of acetochlor to soil surface as observed. This conclusion is in agreement with results reported by Claude Beigel *et al*. (Claude, 1990) in studying effect of surfactant on sorption of triticonazole fungicide. The above-mentioned results indicted that in soil-water systems, surfactant-herbicide interactions are very complex, and surfactant adsorption as well as herbicide adsorption needs to be considered.

The comparison between No. 8, No. 9 and No. 10 systems also found when the greater the concentration of SDBS contained in suspension solution are, the higher the adsorption capacity of acetochlor to soil is. In No. 11 and No. 12, there was the same rule for HDAB. This may be because systems with SDBS and HDAB could form the more colloid particles, which contribute greatly to the adsorption of acetochlor to soil.

3   Conclusion

Adsorption-desorption processes of acetochlor to soils both without and with some environmental substances (HA, SBDS, HDAB, NH_4NO_3 and $CaCl_2$) are nonlinear, and can be described by Freundlich equation and its conversion form. The square values of correlation coefficient of nonlinear regression analysis range between 0.949 and 0.999.

Our studies have further confirmed that HA can enhance adsorption of organic chemicals (include acetochlor) to soils, especially solid HA which self is a strong adsorbent for many organic substances. Generally speaking, the surfactants can decrease adsorption of organic chemicals to soils above their micelle critical concentration, but this not be universal rule under some conditions, for example, when acetochlor-soil suspensions contained lower concentration SDBS or HDAB, acetochlor adsorption was decreased; higher concentration SDBS or HDAB increase acetochlor adsorption. NH_4NO_3 has certain effect to adsorption of acetochlor. The role of NH_4NO_3 as an electrolyte maybe similar to $CaCl_2$.

References:

Calvet R, 1989. Adsorption of organic chemicals in soils[J]. Environ Health Perspect, 83: 145—177.

Chiou C T, Porter P E, Schmedding D W, 1983. Partition equilibria of non-ionic organic compounds between soil and organic matter and water [J]. Environ Sci Tech, 17: 227—231.

Claude B, Enrique B, Raoul C, 1998. Sorption of low levels of nonionic and anionic surfactants on soil: effects on sorption of triticonazole fungicide[J]. Pest Sci, 54: 52—60.

Dunnivant F M, Jardine P M, Taylor D I et al., 1992. Cotransport of cadmium and hexachlorrobiphenyl by dissolved organic carbon through columns containing aquifer material[J]. Soil Sci Soc Am J, 15: 437—444.

Hendershot W H, Duquette M, 1996. A simple barium chloride method for determining cation exchanger capacity and changeable cation[J]. Soil Soc Am J, 50: 605—608.

Jaworski E C, 1975. Chloroacetamide (P C Kearney, D D Kaufman eds). Herbicides: chemistry, degradation, and mode of action. New York: Marcel Dekker, Inc. 349—376.

Karickhof S W, Brown D S, Scott T, 1979. Sorption of hydrophobic pollutants in natural sediments[J]. Water Res, 13: 241—248.

Leo A, Hansch C, Elkinsd, 1971. Partition coefficients and their uses[J]. Chem Rev, 71: 525—616.

Ma Q L, Patrick T H, Trevor K T et al., 2000. Persistence and leaching of the herbicides acetochlor and terbuthylazine in an allophonic soil: comparison of field results with PRZM-3 prediction[J]. Pest Mang Sci, 56: 159—167.

Magee B R, Lion L W, Lemley A T, 1991. Transport of dissolved organic macromolecules and their effect on the transport of phenanthrene in porous media[J]. Environ Sci Technol, 15: 578—587.

Mailhot H, Peters R H, 1988. Empirical relationships between the 1-octanol/water partition coefficient and nine physicochemical properties [J]. Environ Sci Technol, 22: 1479—1499.

McCarthy J F, Zachara J M, 1989. Subsurface transport of contaminants[J]. Environ Sci Technol, 23: 496—502.

Nanjing Soil Institute of Chinese Academy of Sciences(NSICAS), 1978. Physical and chemical analysis of soil[M], Shanghai: Shanghai Science and Technology Press. 132—141; 469—480.

Pigmatallo J J, Huang L Q, 1991. Sorptive reversibility of atrazine and metolachlor residues in field soil samples[J]. J Environ Qual, 20: 222—228.

Sabban 1, Rebbun M, 1997. Adsorption-desorption of trichlorophenol in water-soil system[J]. Water Environ Res, 69: 1032—1038.

Tostsche K U, Kogel-Knabner I, Danzer J, 1997. Dissolved organic matter-enhanced retention of polycyclic aromatic hydrocarbons in soil miscible displacement experiments[J]. J Environ Qual, 26: 1090—1100.

Webber J B, Peter C J, 1982. Adsorption, bioactivity and evaluation of soil tests for alachlor, acetochlor and metolachlor[J]. Weed Sci, 30: 14—20.

Werkkeiser W O, Anderson S J, 1996. Effect of soil properties and surfactant on primisulfuron sorption[J]. J Environ Qual, 25: 809—814.