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Adsorption and Mobility of Acetochlor and Butachlor on Soil

H. Zheng, C. Ye

Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, Post Office Box 2871, Beijing 100085, People's Republic of China

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In soil-water systems, surfactant-pesticide interactions are very complex processes, and surfactant sorption as well as pesticide sorption needs to be considered. Numerous studies have dealt with the influence of surfactants on the solubilization and sorption of poorly soluble contaminants on soil, and mobilization of strongly sorbed chemicals is often reported (Amonette & O'Connor, 1980; Kile et al., 1990; Haigh, 1996). Surfactants can solubilize hydrophobic compounds to reduce significantly their sorption. On the other hand, surfactants can also be sorbed onto soil. Soils modified with such surfactant as hexadecyltrimethyl-ammonium (HDTMA) bromide exhibit enhanced sorptive capabilities for organic contaminants (Lee et al., 1989; Sheng et al., 1998). The mobility of pesticides is closely related to their sorptive capabilities. The influence of surfactants on pesticide mobility needs to be considered more thoroughly.

Acetochlor (2-chloro-N- (ethoxymethyl) -N- (2-ethyl-6-methylphenyl) acetamide) and butachlor (2-chloro-N-(2,6-diethylphenyl) -N- (butoxymethyl) acetamide) are two of three the most widely used herbicides in China. The total mass used has been increasing and already is above 1.5×10^7 kg in 1996 (Wang, 1999). Acetochlor was conditionally registered in March 1994 (USEPA, 1994) and has been classified as a B-2 carcinogen by the USEPA. Kolpin et al. (1994) reported results from sampling conducted during 1994. Most of the detectable levels in rain and streams occurred during the spring application period. Maximum concentration found in 1994 were 2.5 μg/L (rain) and 1.2 μg/L (streams). Kalkhoff et al. (1998) reported the median value of the summed concentrations of acetochlor, alachlor, and metochlor was less than 0.05μg/L in groundwater.

Mobility of pesticide can be tested by soil column-leaching or soil thin-layer chromatography (TLC) (Helling et al., 1968) Soil TLC is rapid, reproducible, and inexpensive; requirements for equipment, laboratory space, and soil are modest. A quantitative index of relative pesticide mobility can be based on Soil TLC R_f values. Little research has been reported on mobility of acetochlor and butachlor.

This paper was aimed at (1) determining and comparing the adsorption isotherms

Correspondence to: C. Ye

of acetochlor and butachlor on HDTMA-modified and unmodified Beijing and Hebei soils soils; (2) studying the mobility of acetochlor and butachlor on Beijing and Hebei soils in order to provide basic information for predicting whether acetochlor and butachlor are hazardous to groundwater.

MATERIALS AND METHODS

A LC-6A High Performance Liquid Chromatography was equipped with shimadzu spectro-photometric detector. The stainless steel column (25 cm × 4.6 mm I.D.) was packed with DuPont ODS chemically bonded phase, particle size 10 μm, and was pre-tested by the manufacturer. The detection wavelength of 215 nm was selected in all measurements for both acetochlor and butachlor. The mobile phase was methanol – water (80/20, *v/v*) at a flow rate of 1.0 mL/min. The retention times of acetochlor and butachlor were 6.9 and 11.0 min, respectively.

Acetochlor and butachlor of 99.5% (analytical reference standard) were obtained from Monsanto Company (St. Louis, Mo, USA). All organic solvents were of analytical-reagent grade and purified by redistillation. Dodecylbenzene sulfonic (DDBS) acid sodium salt and HDTMA were purchased from Beijing Chemical Reagents Company (Beijing, China). Experimental river water from Jingmi canal which irrigated Beijing Haidian agricultural area was filtered with a microporous funnel (4G). 30 mg/L of DDBS and HDTMA water solutions were prepared in river water.

Soil samples, from Beijing Haidian agricultural area and Hebei province Baiyangdian Lake area, were air-dried and sieved through 300-μm mesh. The physical and chemical characteristics of the soil samples measured by standard methods are showed in Table 1. The HDTMA-modified soils prepared by adding 50 mL of 60 mg/L HDTMA solution to 100 g soil samples. The slurry was stirred for 10 min to a homogenous mixture, freeze-dried, and stored in bottle for later use.

Adsorption isotherms were obtained by combining 2 g of soil (HDTMA- modified and unmodified Hebei and Beijing soil) with 20 mL of herbicide solutions containing 0.01 M $CaCl_2$ in an intial concentration range from 1 to 20 mg/L. Herbicide solutions were added to 100-mL conical glass bottle with plug. All experiments were duplicated. Equilibration was achieved by shaking for 24 hr at room temperature. The supernatant was then removed by centrifugation at 3000 rmp for 10 min. Acetochlor and butachlor were extracted into petroleum ether and concentrated to about 3 mL under reduced pressure. The concentrated extract was dried under a gentle stream of nitrogen and the residue was dissolved in 1 mL of methanol, then analyzed by HPLC.

A slurry of soil and water was prepared with 13.5 g of soil and 11 mL of water, a

Table 1. The physical and chemical characteristics of the soil samples

Soil sample	PH	Organic carbon (%)	Cation exchang capacity (mmol/100g)	Sand (%)	Silt (%)	Clay (%)
Beijing soil	8.4	1.5	84.0	59	38	3
Hebei soil	7.7	0.8	215.4	73	22	5

conventional TLC coating apparatus was used to coat the soil TLC plates (10×20 cm). The muck soil plates were prepared by moving a glass rod over masking tape along the plate edges to achieve the correct distribution and thickness for the soil-water slurry. The thickness of soil on all the plates was approximately 0.5 mm. The plates were air-dried for 24 hr at room temperature. 50 μL of acetochlor and butachlor standard solutions were spotted, 2 cm from the bottom, and dried with N_2 to volatilize solvent. A spot of acetochlor and a spot of butachlor were spotted to each plate. When the plates were developed for 16 cm with river water or surfactant solution by ascending chromatography, the developed plate was taken out. After the developed plate was air-dried at the room temperature, the developed plate was immediately placed in refrigerator to avoid acetochlor and butachlor volatilizing. The experiments were duplicated. Before acetochlor and butachlor were extracted, the developed plate was taken out and soil was scraped with a razor blade per 2 cm (1-3, 3-5, 5-7, 7-9, and 9-11 cm) into a 10.0-mL centrifugal glass tube. 4 mL of methanol was added to each tube. The mixture was treated with ultrasonic waves for 10 min, then centrifuged 5 min at 3000 rmp. The extraction process was repeated. Supernatants were collected. The combined extract was concentrated to 1mL under reduced pressure, then analyzed by HPLC.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms of acetochlor and butachlor on Hebei and Beijing soils for the whole concentration range investigated (1 to 20 mg/L). Figure 2 shows the adsorption isotherms of acetochlor and butachlor on HDTMA-modified Hebei and Beijing soils. Adsorption of acetochlor and butachlor followed a Freundlich-type isotherm. Nonlinear adsorption isotherms were also reported by Wang et al. (1999) for acetochlor sorption on soils.

$$C_s = K_f C_{eq}^{n} \quad (1)$$

$$\ln C_s = \ln K_f + n \ln C_{eq} \quad (2)$$

Where C_s is mass of acetochlor and butachlor adsorbed per mass soil (mg/kg), C_{eq} is solution equilibrium concentration (mg/L), and K_f ($mg^{1-n} L^n kg^{-1}$) and n are Freundlich constants.

The values of K_f, n and correlation (R^2) are given in Table 2. The results show that the K_f values of acetochlor and butachlor (7.9 and 15.8) on Beijing soil are greater

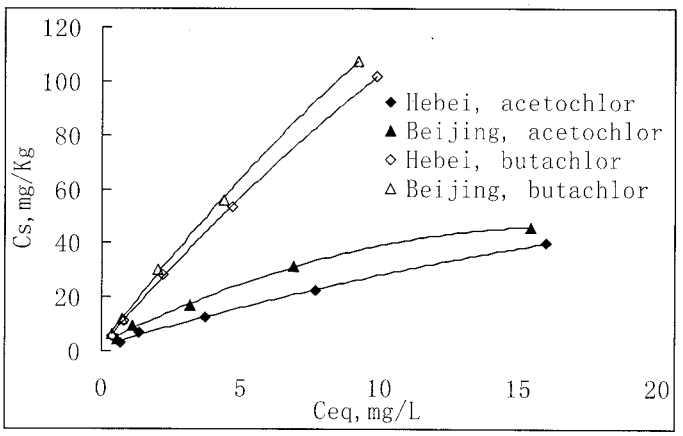

Figure 1. The adsorption isotherms of acetochlor and butachlor on Hebei and Beijing soils

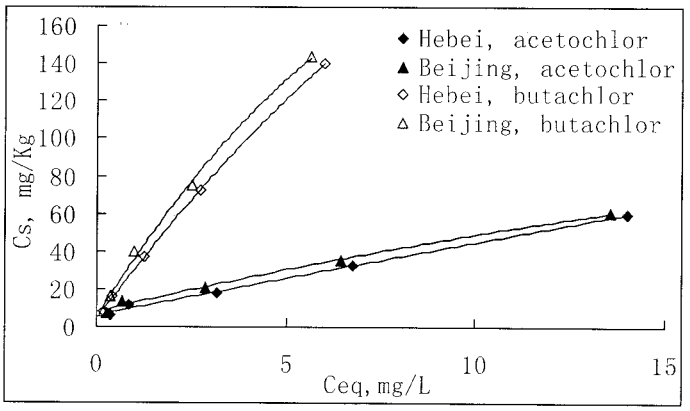

Figure 2. The adsorption isotherms of acetochlor and butachlor on HDTMA-modified soils

than their K_f values (4.8 and 14.0) on Hebei soil. It is usually believed that the adsorption of neutral pesticide is influenced by the organic matter content of the soil. Our experiment is agreed with the previous study. The K_f values on the HDTMA-modified soils are obviously greater than those on the unmodified soils. K_f values of acetochlor and butachlor are 14.8 and 36.8 on the modified Beijing soil, 11.3 and 32.1 on the modified Hebei soil. The increase of the organic matter in soils modified with HDTMA (30 mg/kg HDTMA in soils) is very little comparing to the original organic matter of soils. It indicated that the soil

Table 2. Freundlich constants and correlation coefficients for adsorption of acetochlor and butachlor.

Soil	Acetochlor			Butachlor		
	K_f	n	R^2	K_f	n	R^2
Beijing soil	7.9	0.670	0.989	15.8	0.869	0.999
modified Beijing soil	14.8	0.495	0.981	36.8	0.803	0.997
Hebei soil	4.8	0.764	0.995	14.0	0.872	0.999
modified Hebei soil	11.3	0.582	0.972	32.1	0.815	0.999

Table 3. Soil thin-layer chromatography with river water on soil.

Section	Z_i (cm)	Bejing soil		Hebei soil	
		A* (g)	B¶ (μg)	A (μg)	B (μg)
1~3cm	0.5cm	25.7	80.8	23.3	76.1
3~5cm	2cm	23.5	ND†	18.1	3.7
5~7cm	4cm	9.6	ND	9.8	ND
7~9cm	6cm	3.6	ND	7.9	ND
9~11cm	8cm	ND	ND	2.8	ND
11~13cm	10cm	ND	ND	ND	ND
R_f		0.12	0.03	0.16	0.04

*A: Acetochlor; ¶B: butachlor; †ND: Not detected

adsorbability was effectively enhanced after soils were modified with HDTMA. Although both acetochlor and butachlor belong to chloroacetanilide herbicides, the K_f values of acetochlor are less than the K_f values of butachlor on Beijing and Hebei soil respectively. The reason is their different solubility in water. The adsorption of herbicide on soil is inversely related to its solubility in water.

If the soil TLC R_f values are the ratio of the average moved distance (Z_p) (Sharom, 1976) of herbicides to the solvent front distance (Z_w=16cm), then given

$$Z_p = \frac{\sum_i Z_i M_i}{\sum_i M_i} \tag{3}$$

$$R_f = \frac{Z_p}{Z_w} = \frac{\sum_i Z_i M_i}{Z_w \sum_i M_i} \tag{4}$$

Where i is 1 to 5 for the various 2cm sections, Z_i is the average moved distance (cm) of herbicides on the section i to origin spot; M_i is the content of herbicides (μg) on the section i.

We calculated the TLC R_f values of acetochlor and butachlor on Hebei and Beijing soils through equation 3 and 4, the results are shown in Table 3. Using

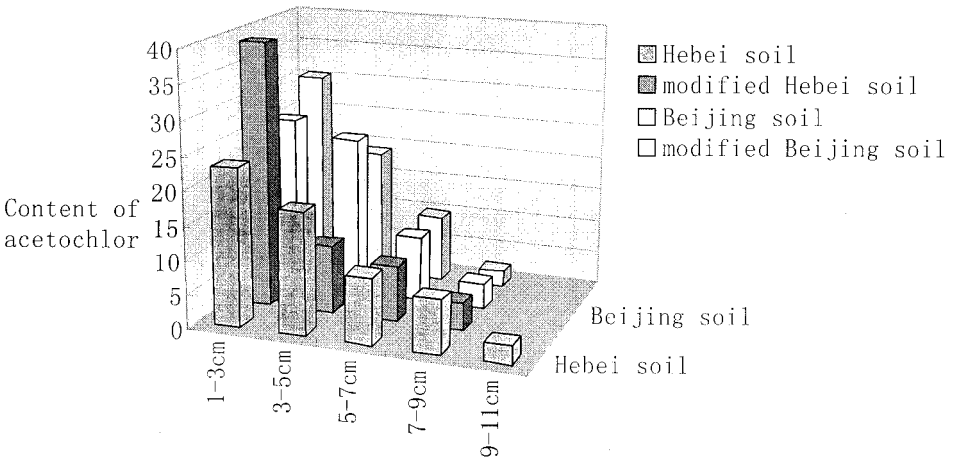

Figure 3. The comparison of acetochlor mobility on soils.

Table 4. The comparison of mobility between acetochlor and butachlor on soils.

Herbicide	K_f on Beijing soil	K_f on Hebei soil	Solubility (mg/L)	R_f of Beijing soil	R_f of Hebei soil	Class
A	7.9	4.8	223	0.12	0.16	2
B	15.8	14.0	20	0.03	0.04	1

river water as the developing solvent, R_f values of acetochlor and butachlor were 0.12 and 0.03 respectively on Beijing soil, and 0.16 and 0.04 respectively on Hebei soil. The mobility of acetochlor and butachlor on soil is different and the former is about 4 times of the latter. Comparing their physical and chemical characteristics (Table 4), can see that the reason is their different solubility in water and adsorption of herbicide on soil. The solubility of herbicide is greater, it is more difficult to be adsorbed and more easily to transfer on soil.

If we apply another method to treat data, R_f' is the ratio of the front distance of pesticide movement to the developing solvent front distance. The R_f' value of aetochlor is about 0.38 on Beijing soil, 0.50 on Hebei soil. It indicates that there is a little possibility for acetochlor to contaminate the groundwater due to use of acetochlor, especially in such areas with sandy soils or shallow water tables. The R_f' value of butachlor is less than 0.06 on Beijing soil because the front of butachlor did not arrived at 3-5cm zone. The R_f' value of butachlor is more than 0.06 and less than 0.19 on Hebei soil since the front of butachlor moved to 3-5cm zone. Butachlor through soil and into groundwater is little possible.

Figure 3 shows the mobility of acetochlor on different soils. River water as the

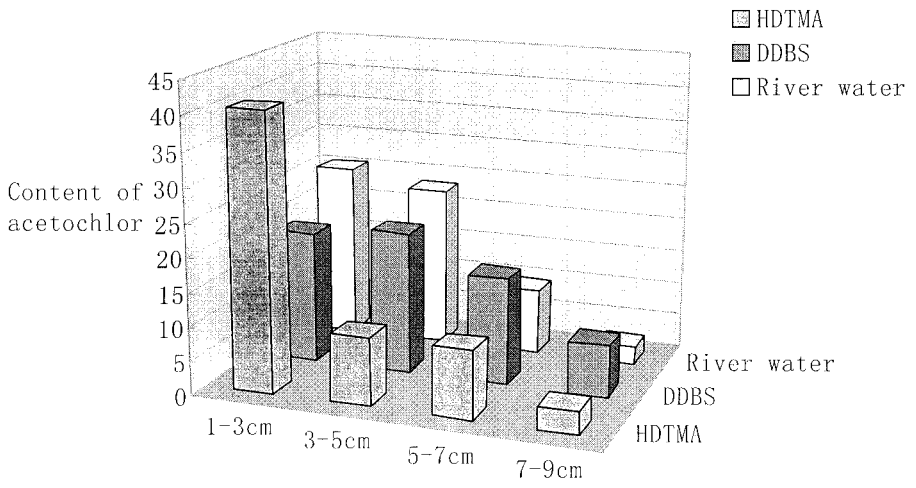

Figure 4. The comparison of acetochlor mobility among river water, DDBS, and HDTMA as the developing solvent on Beijing soil.

developing solvent, the R_f value of aetochlor is 0.11 and 0.12 on HDTMA-modified and unmodified Beijing soil repectively, 0.10 and 0.16 on modified and unmodified Hebei soil. Due to the enhanced sorptive capabilities for acetochlor on HDTMA-modified soils, acetochlor is more difficult to transfer on HDTMA-modified soils. It also indicated that the mobility of acetochlor is related to the adsorption of acetochlor on soils. The greater is the K_f value of acetochlor on soil, the more difficult is acetochlor to transfer on soil.

Although it has been well established that surfactant can enhance the solubility of hydrophobic compounds, it is still not clear whether surfactant can affect mobility of chloroacetanilide herbicides. Sun and Boyd (1993) had reported that surfactants cause decreased sorption of compounds with low water solubility and high sorption coefficients, but cause increased sorption of compounds with higher water solubility and lower sorption coefficients. Soil, subsoils, and aquifer materials modified with cationic surfactants such as HDTMA display enhanced sorptive capabilities for organic contaminants (Boyd et al., 1988a, 1988b; Lee et al., 1989), leading to the suggestion that such materials could be modified via injections of cationic surfactant solutions (Xu et al., 1997) and function as sorbent zones or passive treatment walls to attenuate the mobility of dissolved organic contaminants. Coupling contaminant immobilization with in situ degradation would provide a comprehensive remediable technology to permanently eliminate target contaminants.In our experiment, it also shows that cationic surfactant HDTMA could impede acetochlor to transfer. Anionic surfactant DDBS could accelerate acetochlor to transfer (Figure 4). Using river water, 30 mg/L HDTMA,

and 30 mg/L DDBS as the developing solvent, the R_f value of acetochlor was 0.12, 0.10, and 0.17 on Beijing soil, respectively.

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