Mobility of Prometryne in Soil As Affected by Dissolved Organic Matter

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Incorporation of organic fertilizers/amendments in soils has been, and will continue to be, a popular strategy for improving the quality of arable soils. However, the mechanism by which the dissolved organic matters (DOMs) affect soil properties or interact with other substances in soils is largely unknown. In this study, a batch equilibrium experiment was performed to evaluate the effect of two types of DOMs on the behavior of prometryne (a herbicide) in soils. Two sorts of DOMs were derived from lakebed sludge (SL) and rice straw (ST), respectively. The results show that sorption capacity in one soil for prometryne was significantly reduced by application of DOMs, whereas desorption of prometryne was promoted by DOM treatments. To understand the mobility behavior of prometryne in soils with DOMs, a column leaching experiment was carried out. It is shown that both DOMs enhanced the solubility and migration of prometryne in soils. To confirm the role of DOMs in regulating the mobility of prometryne in soils, a soil thin-layer chromatography was performed. The migration of prometryne was promoted by DOMs, which were used as a developing solvent or directly incorporated in the soil thin layer. The data indicate that DOM extracts can modify the mobility of prometryne in soil.

KEYWORDS: Prometryne; DOM; solubility; leaching; mobility

INTRODUCTION

Application of herbicides (or pesticides) in agriculture has greatly improved grain and cereal production. However, with the increasing usage of herbicides have arisen growing concerns regarding the adverse effect of herbicides on nontarget organisms including crops and human beings. It has been estimated that only 0.1% of herbicides applied to crops reach their targets, and a large proportion remains in the environment *(1, 2)*. Due to their toxicity, some herbicides, particularly those persistent in soils, constitute a very important category of contaminants. Although these herbicides have been restrictively used or even banned for years, their contamination still can be detected in surface and groundwaters *(3, 4)*.

Prometryne [2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine] is a selective herbicide of the *s*-triazine chemical family and has been extensively used for pre- or postemergence control of annual grasses and broadleaf weeds. The log K_{ow} of prometryne was estimated to be 3.51 ($K_{ow} > 1000$) *(5)*, suggesting that it tends to have low water solubility and may have potential bioavailability to aquatic organisms. Prometryne has been detected in surface or groundwaters and even breast milk

in recent years *(6, 7)*. Because of the potential threat to human health, it is of great importance to estimate the fate of prometryne in the soil−water−plant ecosystem. Before we can understand its fate, it is essential to quantitatively analyze the behavior of prometryne, including interactions with soils and any other environmental factors.

Previous studies have shown that the sorption−desorption capacity of soil herbicides depends on the soil−water solution properties such as pH, ionic strength, and additive substance, of which the organic chemicals have a great effect on the herbicide behavior *(8−12)*. Application of organic carbon in the form of compost, sludge, and crop residues is a common agronomic practice in developing countries. For instance, application of composts led to a substantial amount of dissolved and colloidal organic materials in soil solutions that might have an impact on the herbicide binding or mobility properties *(13−16)*. The enhanced aqueous solubility, decreased sorption, and intensified mobility resulting from the integration of hydrophobic substances with dissolved organic matters (DOMs) have been demonstrated by both batch and column studies *(13, 17)*. Also, several other studies have focused on the effect of surfactants on the herbicide and PAHs sorption−desorption in soils and on the application of surfactants for remediation of herbicide- and PAHs-contaminated soils *(9, 18, 19)*. However, the mechanism by which surfactants (e.g., Triton X-100, TX100) affected the sorption and desorption of prometryne was rather complex. Surfactants may increase the HOCs aqueous phase concentration

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11934   *J. Agric. Food Chem.,* Vol. 56, No. 24, 2008

Jiang et al.

Table 1. Basic Physicochemical Properties of the Test Soil

			texture			
soil type[a]	pH	organic carbon (%)	sand (%)	silt (%)	clay (%)	CEC (cmol kg^{-1})
Eutric gleysols	7.55	1.28	30.83	37.85	31.32	17.26

[a] Soil type classification based on FAO-Unesco system.

Table 2. Properties of Two Dissolved Organic Matters

	elemental content (%)			atomic ratio		ash content (%)	total organic carbon (mg of DOC L^{-1})	pH
DOM type	C	H	N	H/C	N/C			
DOM-SL	17.33	4.731	4.323	0.27	0.25	63.74	508	7.18
DOM-ST	30.81	4.716	4.908	0.15	0.16	48.51	4247	7.09

via micelle solubilization (*20−22*) and the mobilization of HOCs from soils into the aqueous phases (*23, 24*). Also, the target molecules may be adsorbed onto the surfactant micelle−water interface and dissolved in aqueous phases. Like surfactants, dissolved organic matters may have similar properties, acting as a trap for anthropogenic nonpolar organic compounds (e.g., herbicides) and promoting the solubility of poorly water-soluble substances (*25, 26*). The predominant low molecular weight (<10000 Da) fraction of DOMs is highly mobile in soils (*27*), and as such, a potential effect of using organic fertilizers is to enhance the herbicide transport by DOMs. Indeed, DOMs may serve as a carrier in soil solutions, which results in the flow of organic chemicals throughout the soil profiles (*10*).

Despite the fact that a growing number of studies have focused on herbicide behavior in soils, data on the interactions of DOMs with prometryne and other factors in soil−water solutions are still lacking. In this study, standard batch equilibration and column leaching experiments were carried out. The soil thin-layer chromatogram was analyzed to confirm the role of DOMs that affect the mobility of prometryne. Thus, the purposes of this study were to (1) detect the effect of DOMs on the solubility of prometryne in soil solution; (2) obtain the sorption−desorption characteristics of prometryne in the presence of DOMs; and (3) identify the effect of DOMs on the leaching properties of prometryne in soils. These data may increase our understanding of prometryne mobility within the soil−water profile.

MATERIALS AND METHODS

Materials. The test herbicide prometryne was obtained from the Academy of Agricultural Science in Jiangsu (AASJ), China, with a purity of 97.3%. Undistorted soils were collected from the surface layer (0−20 cm) at the Experimental Station of AASJ. The physicochemical features of the soil are listed in **Table 1**. The sampled soils were air-dried, gently crumbled, and passed through a 2 mm (used for sorption−desorption experiments), a 1 mm (for leaching experiments), and a 100 μm sieve (for soil thin-layer chromatogram), respectively.

DOM Preparation. Two sorts of dissolved organic matters were used. One was extracted from lakebed sludge (SL) and the other from rice straw (ST). The sludge and straw were collected from Taihu Lake, Wuxi, Jiangsu. DOMs were prepared according to the method of Zhou and Wang (*28*). Briefly, the sludge and straw were extracted with Milli-Q water using a solid/water ratio of 1:10 (w/v, dry weight basis) in a reciprocal shaker at 200*g* and 4 °C for 16 h. The suspensions were centrifuged at 10000*g* and 4 °C for 15 min and then filtered through a 0.45 μm sterilized membrane (GN-6 Mctrice, Gelman Sciences, Ann Arbor, MI). The filtrates were analyzed for pH and total organic carbon (TOC-5000A, Shimadzu). The freeze-dried filtrates were ashed at 750 °C for 4 h, and then the ash was quantified. Elemental analysis of freeze-dried DOM samples was performed using a Vario Elemental Analyzer III (Elementar Co., Germany). The major properties are shown in **Table 2**.

Prometryne Solubility. DOM extracts (10 mL) were diluted to various concentrations ranging from 80 to 560 mg of dissolved organic carbon (DOC) L^{-1} and were incubated with 10 mg of prometryne under stirring for 24 h at room temperature. The excess prometryne that could not be dissolved in the DOM solutions was removed by centrifugation (12000*g*, 30 min). The amount of prometryne dissolved in DOM

solutions was determined by HPLC. The samples were first diluted in HPLC mobile phase methanol/water (80:20, v/v) mixture. Then, prometryne was determined under the following conditions: Waters 515 pump, 2487 dual k absorbance detector at 254 nm; Hypersil ODS column (250 × 4.6 mm i.d., 5 μm); mobile phase methanol/water (80: 20, v/v) at a flow rate of 1 mL min^{-1}. We also determined the prometryne solubility as affected by one of the surfactants, Triton X-100 (TX100), with the same procedure described above.

Prometryne Sorption and Desorption. Sorption and desorption isotherms of prometryne were obtained by the standard batch equilibration method (*29*), with minor modifications. A mixture, consisting of 2 g of soil and 10 mL of 0.01 M calcium chloride solution with different concentrations of prometryne, was placed into 25 mL polypropylene centrifuge tubes. The initial concentrations of prometryne were 3.2, 6.4, 12.8, 19.2, and 25.6 mg L^{-1} (corresponding to prometryne: soil at 16, 32, 64, 96, and 128 mg kg^{-1}, respectively). The suspensions were shaken at 200*g* and 25 ± 1 °C for 24 h and then centrifuged at 7000*g* (25 ± 1 °C) for 10 min. The concentrations of prometryne in the supernatant were measured. Desorption experiments were performed immediately after the sorption experiments. All of the supernatant was thoroughly removed. The tube was centrifuged and stood upside down for 24 h to remove the remaining solution in the tube. Then, 10 mL of fresh calcium chloride solution (0.01 M) was added into the tube. Shaking, subsequent separation of soil and aqueous phase, and analyses were conducted as described above. Quantification of prometryne by HPLC was performed as described above. The sorption and desorption experiments were repeated three times.

The adsorption data were fitted to the Freundlich adsorption equation: log C_s = log K_f + 1/n log C_e, where C_s is the sorbed concentration (mg kg^{-1}), K_f (intercept) is the Freundlich sorption coefficient representing the amount of prometryne adsorbed at an equilibrium concentration of 1 mg L^{-1}, 1/n (slope) is a linearity factor indicating the measure of the intensity of sorption and reflecting the degree to which sorption is a function of herbicide concentration, and C_e is concentration in the solution phase (mg L^{-1}).

Sorption of prometryne on soils in the presence of DOMs was determined according to the method described above. In the tube containing the mixture of soil and DOM solutions, 0.02% NaN$_3$ was added to inhibit microbial activity. The final concentrations of DOMs were set to 80 and 160 mg of DOC L^{-1}, respectively. The soil samples treated with DOMs were subjected to shaking, and the subsequent separation of soil and aqueous phase and analyses were conducted as described above. A desorption experiment with DOMs was performed following the sorption experiment without DOMs. The solution removed at the end of sorption experiment was replaced with 0.01 M CaCl$_2$ solutions containing DOMs. The procedure for desorption was the same as described above.

Column Leaching. PVC columns [300 mm (l) × 48 mm (i.d.)] (in triplicate) were packed with soils. The columns were packed to a bulk density of 1.27 kg L^{-1}. Before the prometryne application, the columns were presaturated with 500 mL of 0.01 M CaCl$_2$ solution to achieve field capacity of soil moisture. The water was allowed to drain naturally. Prometryne (500 μg) in 1 mL of acetone was applied to the column surface in a dropwise manner so as to cover the entire column surface and allowed to air-dry for 2 h. A layer (1 cm) of acid-washed sand was laid on the top of each column to minimize surface disturbance. Columns then were eluted for 20 h with 1000 mL of different percolating solutions as follows: SL1 (80 mg of DOC L^{-1} sludge extract), SL2 (160 mg of DOC L^{-1} sludge extract), ST1 (80 mg of DOC L^{-1} straw extract), ST2 (160 mg of DOC L^{-1} straw extract) and control (0.01 M calcium chloride solution). The soil in the column was saturated with percolating solution, and the leaching was kept as natural

Mobility of Prometryne As Affected by DOM

J. Agric. Food Chem., Vol. 56, No. 24, 2008 **11935**

drainage. The leachate fractions were collected in 50 mL portions and analyzed for prometryne concentration as follows: solid phase extraction (SPE) was used for precleaning of water samples. LC-C$_{18}$ cartridges containing 300 mg of sorbent (Supelco Park, Bellefonte, PA) were conditioned with 5 mL of methanol, followed by 5 mL of water. The water samples were transferred onto the columns and passed though the columns at 2.5 mL min^{-1}. Finally, the column was dried with a strong stream of air for 10 min. The filtrate of the water sample was discarded. The column was washed with 4 mL of methanol. The washing methanol was collected for HPLC analysis as described above.

At the end of the experiment, the column was allowed to drain for 1 day. Then, the column was segmented into 5 cm long sections. The soil in each section was air-dried and analyzed for prometryne content as follows: (1) The sample was transferred to the vessel and acetone was added. The vessel was subjected to ultrasonic wave for 30 min. (2) The extract solution was filtered through a 0.45 μm syringe-driven filter and then evaporated at 40 °C to dryness in a rotary evaporator; after that, 3 mL of acetone was added to dissolve the residue for cleanup process application. (3) The LC-C$_{18}$ column was first conditioned with 10 mL of petroleum ether, and then the above 3 mL of dissolved solutions was transferred onto the column, followed by 5 mL of mixture (petroleum ether/ether = 98:2, v/v) passed through the column at 2.5 mL min^{-1}. After that, the remaining section in the column was eluted with 30 mL of acetone at a flow rate of 1 mL min^{-1}. The solution was collected and evaporated at 40 °C to dry in a rotary evaporator, and (4) 1 mL of methanol was added to dissolve the residue. The quantitative analysis of prometryne was performed by HPLC. The effect of the surfactant TX100 on column leaching was analyzed in the same way as described above, except that soil columns were eluted with percolating solutions of TX100 at concentrations of 1.0 CMC (192 mg L^{-1}) and 2.0 CMC (384 mg L^{-1}).

Soil Thin-Layer Chromatography. Experiments were carried out according to the method described by Ravanel et al. (*30*). Fifteen grams of soil sample and 12 mL of distilled water were evenly mixed and spread onto 20 × 10 cm glass plates with the help of a TLC spreading device. The thickness of the soil layer was within 0.50−0.75 mm. The air-dried plates were marked with two horizontal lines at distances of 2 cm (baseline) and 18 cm (foreland) from the base. A 100 μL droplet of 400 mg L^{-1} prometryne solution prepared in acetone was spotted onto the baseline of plate with the aid of a microsyringe.

The plates were placed in closed individual glass chromatographic chambers. Water solutions with SL1, SL2, ST1, ST2, and control (distilled water) were used as developing solvents. After the developing solvents had migrated to the distance of 16 cm from the baseline, the plates were taken out from glass chromatographic chambers and laid flat to dry at room temperature. Soils on plates were divided into eight equal parts between the baseline and the foreland. Prometryne residue in the soil of each segment was extracted and quantified as described above. The mobility factor (R_f) of the herbicide was calculated by the formulas (*31*)

$$R_f = \frac{\overline{Z_P}}{Z_w} = \frac{\sum Z_i \times M_i}{Z_w \times \sum M_i} \tag{1}$$

$$\overline{Z_P} = \frac{\sum Z_i \times M_i}{\sum M_i} \tag{2}$$

where $\overline{Z_P}$ is the average moving distance of herbicide from the start point, Z_w is the moving distance of developing solvent from the start point, i is the number of segments, Z_i is the distance of segment i from the start point, and M_i is herbicide content in segment i.

To investigate the effect of DOMs on prometryne mobility, we also performed the experiments in which the DOM extracts were mixed with soil samples and spread onto the plate. Soil thin layers with DOMs (extracted from sludge) at 400 and 800 mg of DOC kg^{-1} were prepared by mixing 15 g of soil sample with 12 mL given concentrations of DOM extracts and spread onto 20 × 10 cm glass plates with the help of a TLC spreading device. The treatments were labeled as SL1 + soil and SL2 + soil, respectively. Similarly, in treatments with ST1 + soil
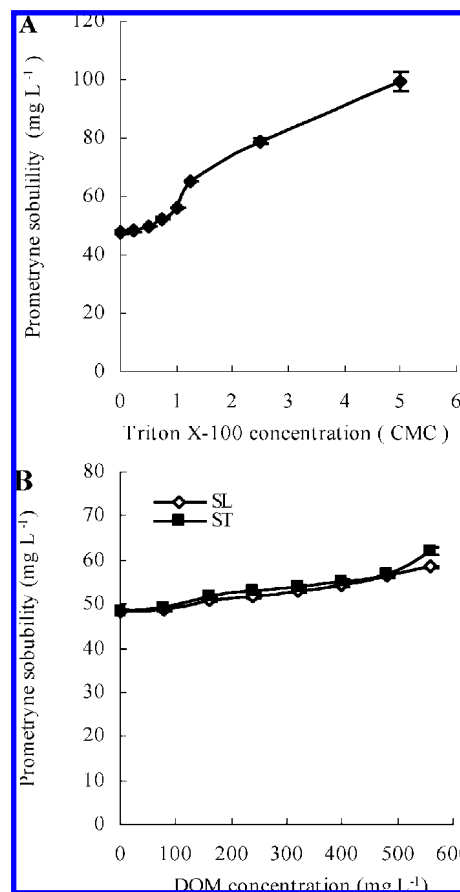

Figure 1. Effect of DOMs and Triton X-100 on prometryne solubility: (**A**) Triton X-100; (**B**) DOMs (SL and ST) at 80, 160, 240, 320, 400, 480, and 560 mg of DOC L^{-1}. Values represent the mean of three replicates, and vertical bars indicate standard deviations.

and ST2 + soil, the concentrations of DOM extracted from straw were 400 and 800 mg of DOC kg^{-1}, respectively. The plates were air-dried, spotted, and developed with distilled water as a spreader. The following process was performed as described above.

RESULTS AND DISCUSSION

Effect of DOMs on Prometryne Solubility. To understand the effect of DOMs on the solubility of prometryne, we used the surfactant Triton X-100 as a reference organic matter. As shown in **Figure 1**, the aqueous solubility of prometryne generally increased with the surfactant concentrations. This was particularly apparent when the concentrations of Triton X-100 were above the CMC (>1). In agreement with Triton X-100, the DOMs show a similar pattern of effect on the solubility of prometryne. This may be attributed to the structural and functional similarity to the surfactant, implying that the DOMs may have the potential capacity to enhance the solubility of prometryne in soil solutions.

Effect of DOMs on Sorption and Desorption of Prometryne. From an environmental viewpoint, the sorption−desorption of herbicides in soils is of great importance because this process is closely related to the mobility, degradation, and bioavailability of herbicides (*32−36*). The sorption−desorption capacity of herbicides depends on the soil−water solution properties such as pH, ionic strength, and additive substance (*10, 37*). In this study, we present the adsorption isotherms that were obtained by plotting the amount of herbicide adsorbed (C_s in mg kg^{-1} soil) with respect to the equilibrium concentration (C_e in mg L^{-1}) (**Figure 2**). A similar procedure was followed for the
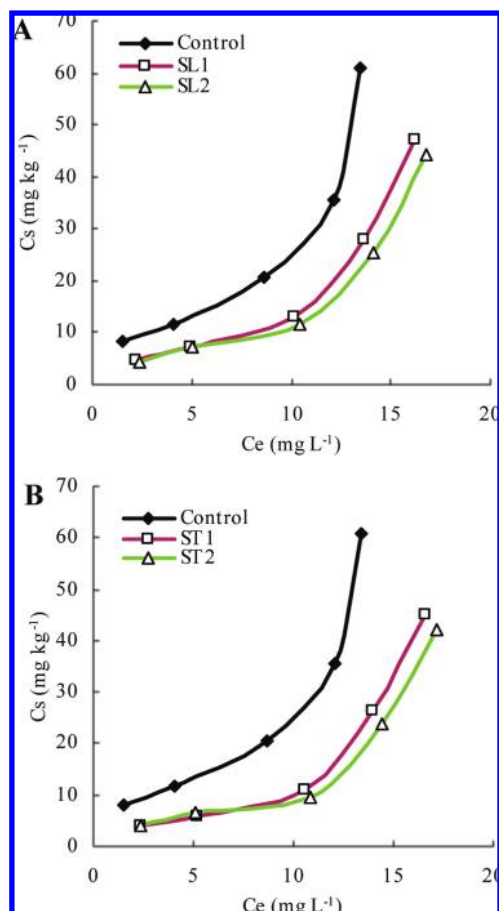
11936 *J. Agric. Food Chem.,* Vol. 56, No. 24, 2008

Jiang et al.

Figure 2. Sorption isotherms of prometryne in soils with DOMs: (**A**) DOMs of sludge extract at 80 mg of DOC L^{-1} (SL1) and 160 mg of DOC L^{-1} (SL2); (**B**) DOMs of straw extract at 80 mg of DOC L^{-1} (ST1) and 160 mg of DOC L^{-1} (ST2). Data are means of three replications.

Figure 3. Desorption isotherms of prometryne in soils with DOMs: (**A**) DOMs of sludge extract at 80 mg of DOC L^{-1} (SL1) and 160 mg of DOC L^{-1} (SL2); (**B**) DOMs of straw extract at 80 mg of DOC L^{-1} (ST1) and 160 mg of DOC L^{-1} (ST2). Data are means of three replications.

desorption isotherms (**Figure 3**). The values of correlation coefficients for all cases were high ($r = 0.922−0.989$) (**Table 3**), indicating that the Freundlich adsorption equation can explain the results of prometryne desorption in soil−water solution with DOMs from sludge (SL1, SL2) and straw (ST1, ST2).

Addition of DOMs from two sources decreased prometryne sorption on soil (**Figure 2**; **Table 3**). Both K_f and $1/n$ are significant for the description of adsorption isotherms, particularly in the case of nonlinear isotherms. Thus, K_f ($1/n$) was selected as the parameter of adsorption (*16, 38*). The K_f ($1/n$) values for prometryne sorption with 0.01 M CaCl$_2$ (control), 0.01 M CaCl$_2$ and 80 mg of DOC L^{-1} sludge extracts (SL1), 0.01 M CaCl$_2$ and 160 mg of DOC L^{-1} sludge extracts (SL2), 0.01 M CaCl$_2$ and 80 mg of DOC L^{-1} straw extracts (ST1), and 0.01 M CaCl$_2$ and 160 mg of DOC L^{-1} straw extracts (ST2) were 4.72, 2.42, 1.37, 2.20, and 1.33, respectively. The prometryne sorption in soil appears to be negatively correlated with the increased DOC content of the soil solutions. Application of DOMs increased the DOC content in the soil solution, which decreased prometryne sorption. The reduced sorption by addition of DOMs to soil solution is ascribed to the following three routes: (1) DOMs may interact with organic pollutants because DOMs have hydrophobic natures (*39*); (2) DOMs compete with organic pollutants for sorption sites in soils (*40−42*); and (3) DOMs may modify the charge on the soils, thus resulting in an unfavorable herbicides−soil interaction. However, the mechanism of DOM facilitation of the reduced prometryne sorption on soils remains elusive. It is shown that both DOMs (sludge and straw) differentially influenced prometryne sorption (**Figure**
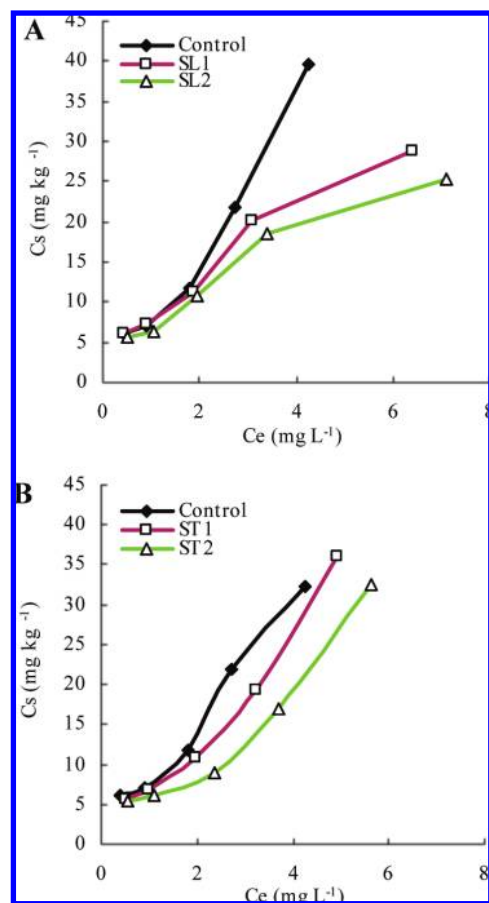
2; **Table 3**). At the identical DOC concentration, application of the DOM-ST resulted in lower sorption capacity than the DOM-SL (**Table 3**).

The amount of DOM-desorbed prometryne during the single desorption step was estimated. The K_f value for the control was 9.73 (**Table 3**). When DOM-ST extracts at 160 mg of DOC L^{-1} were used for prometryne desorption, the K_f value was 6.63, indicating the great desorption of prometryne. K_f values for the other treatments varied within 9.73 and 6.63, suggesting that the addition of DOMs to soil solution decreased the amount of soil-sorbed prometryne. The possible reason may be explained by the hypothesis that DOMs bind to the sorbed prometryne and form the stable DOM−herbicide complex, which is more stable than the prometryne−soil union.

Effect of DOMs on Column Leaching of Prometryne. Adsorption and desorption are the determining processes for the distribution of herbicides in soils and sediment systems. Also, mobility of herbicides in real environments is highly dependent on the solution movement (*43, 44*). To investigate the mobility of herbicide in soils, the soil column leaching experiment was performed. **Figure 4** shows the percolation (breakthrough and cumulative) curves of prometryne in soil columns using 0.01 M CaCl$_2$ (as control), 80 mg of DOC L^{-1} (SL1), and 160 mg of DOC L^{-1} (SL2) DOMs. Addition of DOM-SL to percolating solutions enhanced the downward movement of prometryne in the column and modified the breakthrough time and the maximum concentration of prometryne in the leachate. However, the peak content of prometryne, which occurred at the same time, was different, in the following

Mobility of Prometryne As Affected by DOM

J. Agric. Food Chem., Vol. 56, No. 24, 2008 **11937**

Table 3. Freundlich Coefficients for Prometryne Sorption and Desorption in the Soil[a]

treatment	sorption			desorption		
	K_f	$1/n$	r	K_f	$1/n$	r
control	4.72 ± 0.05	0.827 ± 0.02	0.926	9.73 ± 0.09	0.999 ± 0.01	0.989
80 mg of DOC L^{-1} DOM-SL (SL1)	2.42 ± 0.12	0.952 ± 0.02	0.942	8.84 ± 0.13	0.633 ± 0.01	0.979
160 mg of DOC L^{-1} DOM-SL (SL2)	1.37 ± 0.02	1.100 ± 0.02	0.946	7.88 ± 0.16	0.625 ± 0.01	0.974
80 mg of DOC L^{-1} DOM-ST (ST1)	2.20 ± 0.02	0.934 ± 0.02	0.941	8.01 ± 0.03	0.803 ± 0.01	0.962
160 mg of DOC L^{-1} DOM-ST (ST2)	1.33 ± 0.18	1.066 ± 0.01	0.922	6.63 ± 0.12	0.753 ± 0.01	0.937

[a] Means ($\pm$ standard errors). Freundlich K_f, $1/n$, and r parameters are obtained from three replicates.
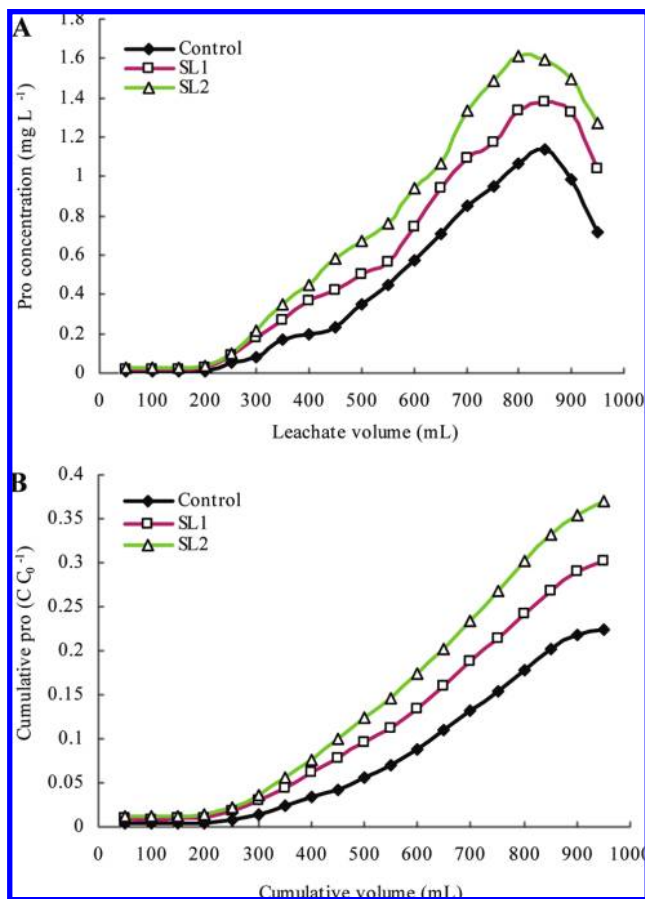

Figure 4. Prometryne breakthrough (**A**) and cumulative (**B**) curves using DOMs of sludge extract (SL) to elute soil columns. Eluants: 0.01 mol L^{-1} CaCl$_2$ (control), 80 mg of DOC L^{-1} (SL1), and 160 mg of DOC L^{-1} (SL2). C_0 is the initial amount of prometryne applied; C is the concentration of prometryne in the leachate.

Figure 5. Prometryne (Pro) breakthrough (**A**) and cumulative (**B**) curves using DOMs of straw extract (ST) to elute soil columns. Eluants: 0.01 mol L^{-1} CaCl$_2$ (control), 80 mg of DOC L^{-1} (ST1), and 160 mg of DOC L^{-1} (ST2). C_0 is the initial amount of prometryne applied; C is the concentration of prometryne in the leachate.

order: SL2 (1.610 mg L^{-1}) > SL1 (1.383 mg L^{-1}) > control (1.135 mg L^{-1}), indicating that the addition of DOM-SL to percolating solution resulted in the enhanced mobility of prometryne in the soil profile. The total prometryne concentrations (C/C_0) of the three treatments ranged as SL2 (0.369) > SL1 (0.302) > control (0.225). This result is in agreement with the batch experiment.

Figure 5 represents the percolation curves of prometryne in soil columns leached by DOM-ST. Application of DOM-ST extracts to percolating solution drastically increased the concentration of prometryne in leachates from 1.135 mg L^{-1} (control) to 1.599 mg L^{-1} (ST1) and 2.039 mg L^{-1} (ST2). Also, it shifted the occurrence of the maximum concentration from 850 mL (control) to 600 mL (ST1 and ST2), indicating rapid downward mobility of prometryne in the column. Compared to the total prometryne concentration of the control (0.225), the
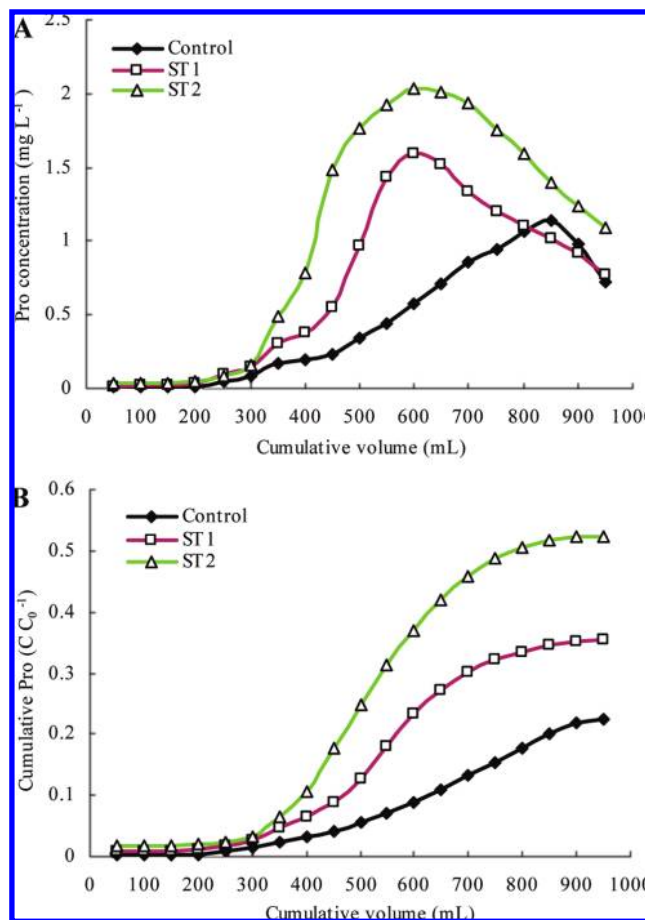
total concentrations of ST1 and ST2 were increased to 0.354 and 0.525, respectively.

After leaching, the columns were dissected into 5 cm sections. The amount of prometryne left in soil was determined. Prometryne leached down to a 25 cm depth in all columns, but its distribution patterns in columns eluted by non-DOM (control) and DOM solutions varied considerably (**Figure 6A,B**). The prometryne contents in the top four sections are shown in the following order: control > SL1 > SL2 > ST1 > ST2. However, in the bottom sections, the pattern was slightly changed to the order control > ST1 > SL1 > SL2 > ST2.

We also analyzed the effect of TX100 on the leaching of prometryne in soil columns to confirm the results obtained above. As shown in **Figure 7**, application of TX100 at 1.0 and 2.0 CMC to percolating solution greatly enhanced the prom-
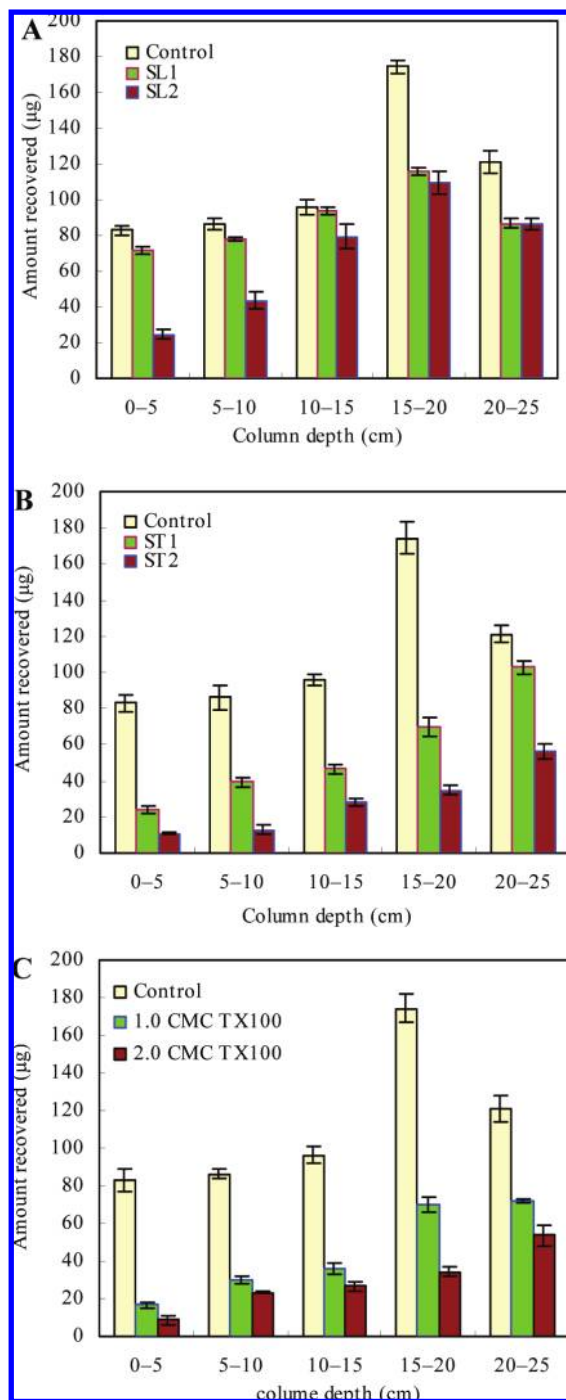
11938 *J. Agric. Food Chem.,* Vol. 56, No. 24, 2008

Jiang et al.

Figure 6. Prometryne recovered from soil column after using different eluants to elute soil columns: (**A**) DOMs of sludge extract at 80 mg of DOC L^{-1} and 160 mg of DOC L^{-1} as eluants; (**B**) DOMs of straw extract at 80 mg of DOC L^{-1} and 160 mg of DOC L^{-1} as eluants; (**C**) TX100 at 1.0 CMC and 2.0 CMC as eluants. Values represent the mean of three replicates, and vertical bars indicate standard deviations.

Figure 7. Prometryne breakthrough (**A**) and cumulative (**B**) curves using TX100 to elute soil columns. Eluants: 0.01 mol L^{-1} CaCl$_2$ (control), TX100 at 1.0 CMC and 2.0 CMC. C_0 is the initial amount of prometryne applied; C is the concentration of prometryne in the leachate.

Table 4. Effect of DOM on R_f Values of Prometryne

developing solvent	R_f
distilled water (control)	0.1757
80 mg of DOC L^{-1} DOM-SL (SL1)	0.2334
160 mg of DOC L^{-1} DOM-SL (SL2)	0.2920
80 mg of DOC L^{-1} DOM-ST (ST1)	0.2765
160 mg of DOC L^{-1} DOM-ST (ST2)	0.3125
distilled water (SL1 + soil)	0.2752
distilled water (SL2 + soil)	0.3024
distilled water (ST1 + soil)	0.2809
distilled water (ST2 + soil)	0.3251

etryne downward mobility in soil columns, and this effect is also concentration-dependent. The promotion is also shown to be concentration-dependent. The result was confirmed by the reduced prometryne retention capacity in the soil column with TX100 (**Figure 6C**), suggesting that the presence of TX100 enhances the mobility of the herbicide. Taken together, the results presented here indicate that addition of DOM reduces the prometryne retention in the soils, suggesting that the presence of DOM would enhance the mobility of the herbicide. Competition between the herbicide and DOMs for sorption sites may
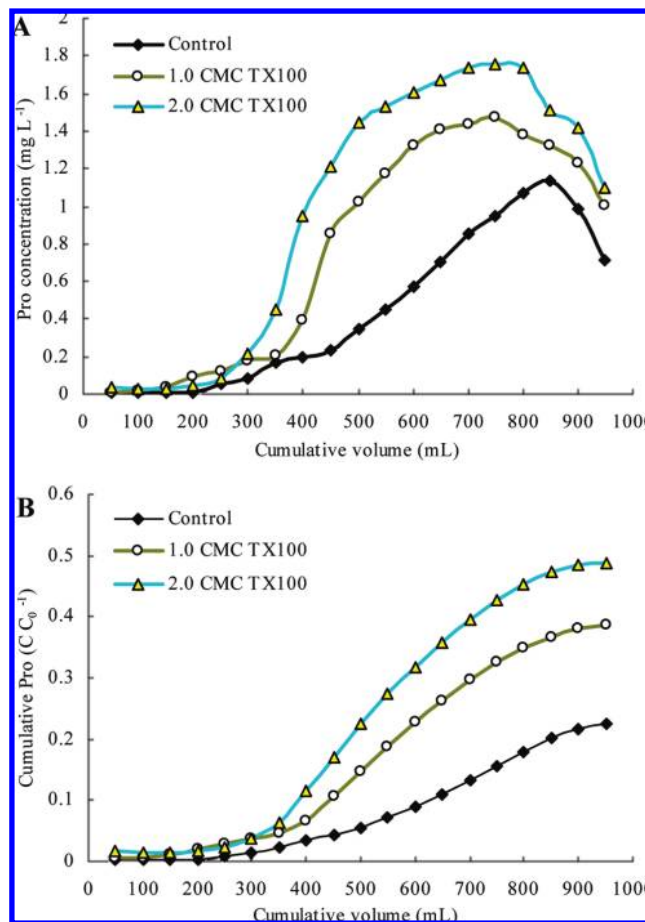
also contribute to this enhancement (*45*). Along with the increasing DOM concentration, the desorption rate was progressively promoted, resulting in greater leaching. Thus, it could be concluded that the leaching or mobility of prometryne might stick to the DOM-controlled sorption/desorption of the herbicide in the soils.

Effect of DOMs on Prometryne Mobility in Soil Microstructures. To investigate the mobility of prometryne within soil microstructures, a soil thin layer coated on a glass plate was utilized. DOMs (SL and ST) were used as developing solvents or directly incorporated in the soil layer. It is shown that the R_f values for prometryne mobility in soils are different within the control (distilled water) and various treatments, in the declining order of control < SL1 < SL1 + soil < ST1 < ST1 + soil < SL2 < SL2 + soil < ST2 < ST2 + soil (**Table 4**). The distance between the baseline and foreland was covered
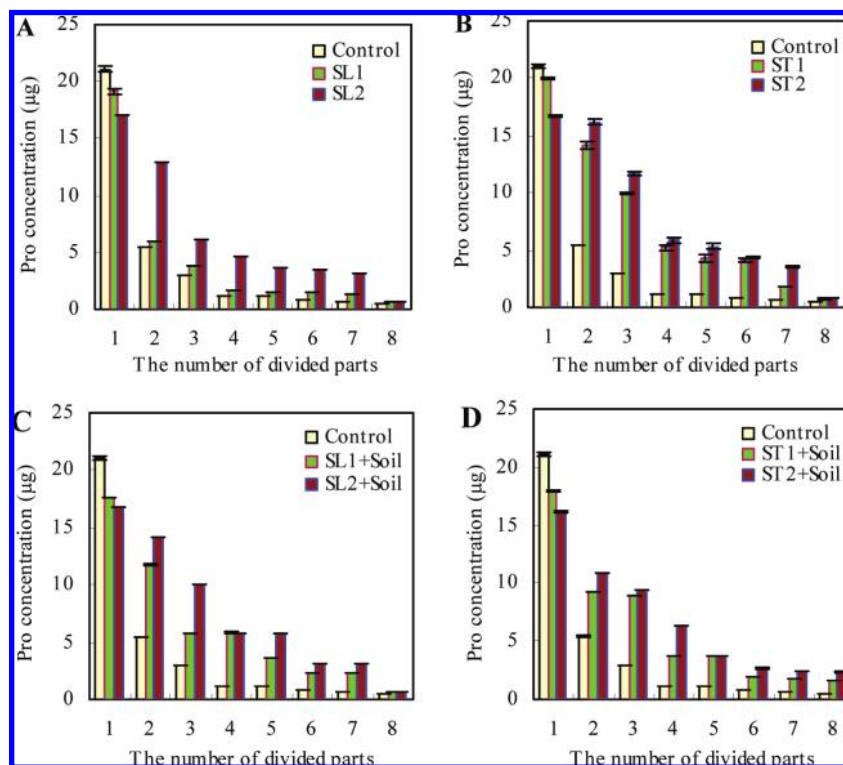
Mobility of Prometryne As Affected by DOM

J. Agric. Food Chem., Vol. 56, No. 24, 2008 **11939**

Figure 8. Distribution of prometryne on the soil plates: (**A**) DOMs of SL at 80 mg of DOC L^{-1} (SL1) and 160 mg of DOC L^{-1} (SL2) as developing solvents; (**B**) DOMs of ST at 80 mg of DOC L^{-1} (ST1) and 160 mg of DOC L^{-1} (ST2) as developing solvents. Distilled water was used as developing solvent, and the soil plates were prepared with DOMs from sludge extract (**C**) and straw extract (**D**), respectively. Values represent the mean of three replicates, and vertical bars indicate standard deviations.

by prometryne on the soil plate, and the maximal prometryne concentration was found in the first segment (**Figure 8**), suggesting that prometryne possesses moderate mobility in the soil. However, the prometryne contents in each segment with distilled water (control) and DOM (SL and ST) as developing solvents were different. Compared with distilled water, the migration of prometryne was enhanced with DOMs (SL and ST). This result was consistent with that of the soil column experiment. A similar situation was described previously for prometryne on soil TLC using a surfactant as developing solvent, in which the mobility of prometryne was enhanced by TX100 at concentrations above the CMC (*19*). The prometryne molecules might be adsorbed onto the surfactant micelle−water interface and dissolved in aqueous phases. Because some functional groups in DOMs might be similar to those of surfactants, DOMs enhanced the solubility of poorly water-soluble compounds through DOM−herbicide interaction (*20, 41, 46*). When DOMs (SL and ST) were incorporated in the soil layer, the promoted prometryne mobility also could be detected. The possible reasons might be related to the facts that the DOMs absorbed onto the soil may occupy the sorbing sites and, when developed with distilled water, a portion of DOMs dissolved into water may increase the solubility of prometryne in aqueous phase.

Conclusions. The present studies have demonstrated that the DOMs used were able to decrease the sorption of prometryne and to increase desorption in the soil. Like the surfactant Triton X-100, DOMs can promote prometryne solubility and migration in soils, as demonstrated by the column and plate experiments. However, compared to DOM-SL, DOM-ST appears to have a greater effect on the solubility and mobility of the herbicide. The outcome of the study may be useful because it may explain that application of the DOMs increases the herbicide percolating to groundwater and availability to plants. To establish a good

soil amendment strategy against herbicide residues, more large-scale experiments will be required to elucidate the role DOMs play in agricultural soils.

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11940 *J. Agric. Food Chem.,* Vol. 56, No. 24, 2008

Jiang et al.

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