

# Transport and Environmental Risks of Propachlor Within the Soil–Plant–Water Phase as Affected by Dissolved Organic Matter as a Nonionic Surfactant

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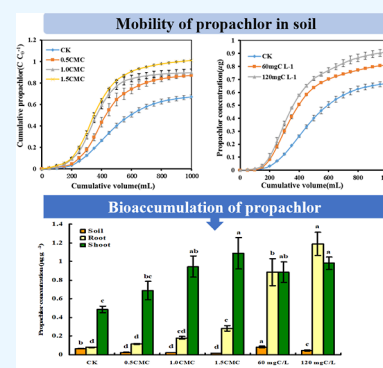
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**ABSTRACT:** Propachlor is a widely used acylaniline herbicide for weeding annual gramineous and dicot plants in farmland. As a toxic agricultural chemical, it is overused in crop production and has become one of the most serious environmental pollutants. Yet, understanding the impact of environmental factors on its behavior in farmland soils is critically important for healthy crop production and food safety. In this study, we characterized the effect of dissolved organic matter (DOM) extracted from rice straw on the mobility behavior of propachlor in farmland soil using comprehensive approaches such as the batch equilibrium experiment, soil thin-layer chromatography, soil column leaching, and wheat bioaccumulation with Triton X-100 (TX-100) as a reference surfactant. The application of DOM at 60 and 120 mg DOC L<sup>-1</sup> and TX-100 at 96, 192, and 288 mg L<sup>-1</sup> reduced the sorption and increased the desorption of propachlor in soil. Freundlich constant  $K_f$  values (sorption) of propachlor declined with the expansion of DOM and TX-100 concentrations. The addition of DOM and TX-100 increased the mobility of propachlor and the total concentration of propachlor in the leachate of soil columns. The retention factors ( $R_f$ ) were evaluated in the soil thin-layer chromatography as 0.741 and 0.772 (for DOM) and 0.731, 0.763, and 0.791 (for TX-100), all of which were greater than the control (0.710) under the treatment. The application of DOM or TX-100 reduced root growth (biomass) and increased bioaccumulation of propachlor in the roots and shoots of wheat. The outcome of the study can provide important references for the rational use of propachlor and help agronomic management to minimize pesticide contamination in realistic crop production.



## INTRODUCTION

Pesticides (herbicides) are widely used in farmland for crop growth and reproductivity. As agricultural chemicals, most of the pesticides remain in the soil after use and can be toxic to many organisms in ecosystems.<sup>1–4</sup> The remaining pesticides may reach out to the non-targets through leaching, surface runoff, wind drift, or other means, posing high risks to crop production and human health through food chains.<sup>5,6</sup> Although some pesticides have been restricted or even forbidden for many years, their residues are still detected in surface and underground water.<sup>7,8</sup> For this reason, exploring the environmental behavior of pesticides in soils and understanding the impacts of environmental factors on their behavior will help formulate precise management strategies to remove the potential hazmats. Propachlor, 2-chloro-*N*-(1-methylethyl)-*N*-phenylacetamide, is a widely used acylanilide herbicide for weed control in farmland for crop production.<sup>9</sup> Propachlor is persistent in neutral and basic aqueous media but unstable under acidic environmental conditions.<sup>10</sup> Thus far, most studies on propachlor fate have focused on degradation and bioremediation,<sup>11–13</sup> while its environmental behavior in different types of soil with inputs of massive organic carbons as straw after crop harvest is less understood.

The environmental behaviors of herbicides depend on many natural factors such as the inherent properties of soil chemicals, the timing of organic matter decay, soil properties, and so forth. The nonionic surfactants are widely used for household applications like laundry, shampoo, paints, coatings, and food emulsifiers because of their low critical micelle concentration (CMC), electrical neutrality, and surface tension value over the ionic surfactants.<sup>14</sup> They are also useful in mixed surfactant systems due to electrical neutrality.<sup>15</sup> Triton X-100 (TX-100) is a kind of commonly used nonionic surfactant with the chemical formula of R–C<sub>6</sub>H<sub>4</sub>–(OC<sub>2</sub>H<sub>4</sub>)<sub>p</sub>–OH, where R is a branched octyl group and p is the average number of oxyethylene groups ( $p \approx 9.5$ ).<sup>16</sup> It was found that the TX-100 supply in the subsurface of the soil elevated the level of residual contaminants, resulting in the delayed goal of clean-up.<sup>17,18</sup> On the other hand, the addition of nonionic surfactants into the soil can facilitate the biodegradation of

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Table 1. Freundlich Coefficients ( $\lg C_s = \lg K_f + 1/n \lg C_e$ ) for Propachlor Sorption and Desorption in Soils

treatment	sorption			desorption		
	$K_f$	$1/n$	$R^2$	$K_f$	$1/n$	$R^2$
control	$1.692 \pm 0.406$	$0.546 \pm 0.090$	0.935	$3.728 \pm 0.049$	$1.139 \pm 0.040$	0.967
0.5 CMC	$0.727 \pm 0.344$	$0.692 \pm 0.189$	0.893	$1.921 \pm 0.283$	$1.934 \pm 0.097$	0.951
1.0 CMC	$0.687 \pm 0.117$	$0.647 \pm 0.028$	0.859	$1.353 \pm 0.356$	$2.132 \pm 0.412$	0.904
60 mgC L <sup>-1</sup>	$1.467 \pm 0.124$	$0.507 \pm 0.017$	0.961	$2.001 \pm 0.139$	$1.183 \pm 0.202$	0.969
120 mgC L <sup>-1</sup>	$1.510 \pm 0.502$	$0.478 \pm 0.114$	0.960	$1.817 \pm 0.167$	$1.292 \pm 0.223$	0.919

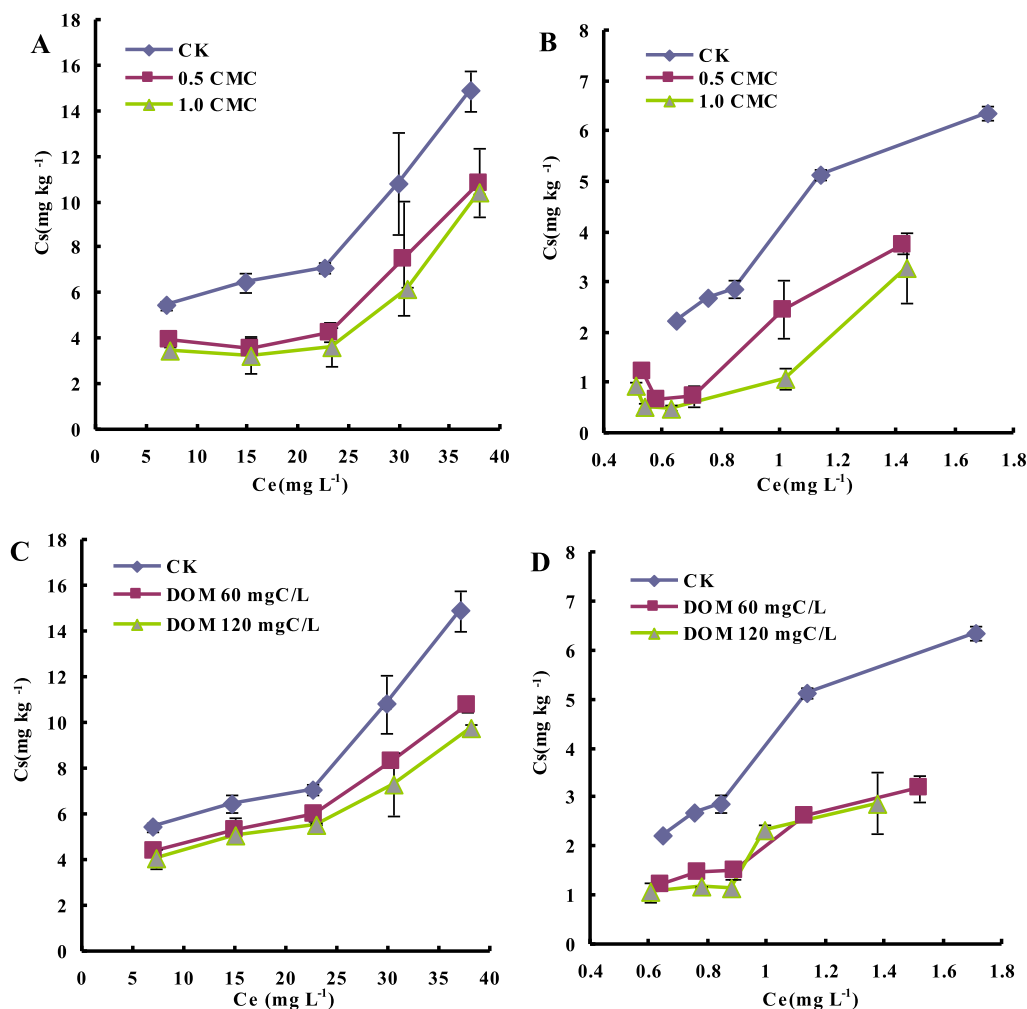


Figure 1. Effects of TX-100 and DOM on the sorption (A,C) and desorption (B,D) isotherms of propachlor in soil. The data are the mean of three replications.

contaminants.<sup>14,19</sup> Dissolved organic matter is a mixture of natural organic compounds, usually generated by well-decayed crop straw in farmland soil. The DOM complex is composed of carbohydrates, proteins, lignin, organic acids, and many other uncharacterized compounds and has some functional similarities to nonionic surfactants.<sup>5</sup> One of the major features of DOM is that it is shown to affect the composition and quantity of nutrient and non-nutrient compounds in soils and further functionally alter the crop growth and physiological processes.<sup>20–22</sup> In the aquatic environment, for example, DOM combines with hydrophobic organic contaminants and affects their mobility.<sup>23,24</sup>

Despite the fact that a growing number of investigations have been made on the behaviors of pesticides affected by DOM,<sup>18,25,26</sup> research on the interaction of DOM with

propachlor in soil–water systems is still lacking. In this study, the batch equilibrium, thin-layer chromatography, column leaching, and bioaccumulation approaches were adopted to study the effect of DOM on the mobility of propachlor in the profile of soil–water–plant systems. The resultant data were carefully analyzed to evidence the role of DOM during the course of propachlor absorption, desorption, and accumulation in wheat crops. The outcome of the study will help understand the propachlor migration process in the presence of DOM and utilize DOM as a valuable natural source to develop an effective strategy to limit pesticide contamination in soil, crops, and water systems.

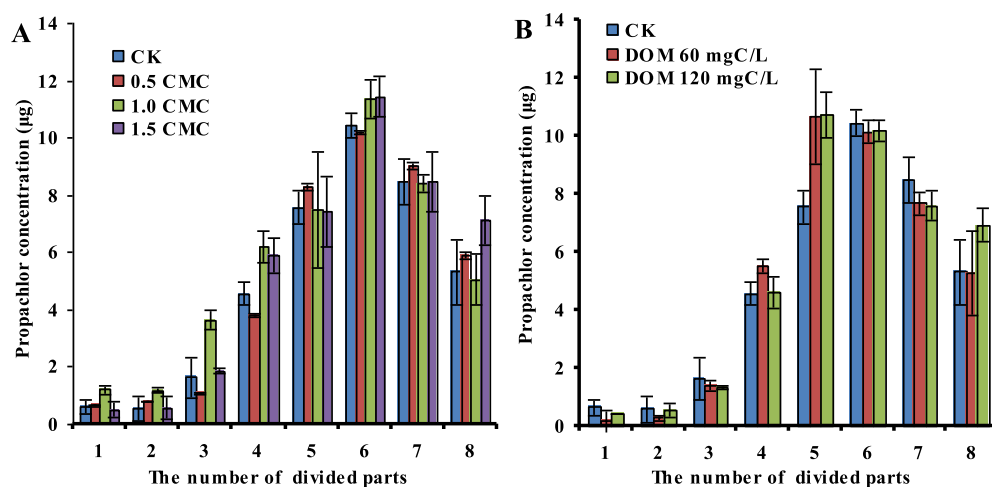


Figure 2. Distribution of propachlor on the soil plates using TX-100 (A) and DOM (B) solutions as developing solvents.

Table 2.  $R_f$  of Propachlor on the Soil Plates Using Different Solutions as Developing Solvents

developing solvent	distilled water	0.5 CMC	1.0 CMC	1.5 CMC	60 mgC L <sup>-1</sup>	120 mgC L <sup>-1</sup>
$R_f$	0.710 ± 0.078	0.731 ± 0.010	0.763 ± 0.084	0.791 ± 0.121	0.741 ± 0.085	0.772 ± 0.053

## RESULTS AND DISCUSSION

**Effects of TX-100 and DOM on Sorption and Desorption of Propachlor.** To investigate the effect of TX-100 and DOM on the transport of propachlor in soil, the sorption and desorption trials were carried out in the first place. The data of the sorption and desorption were calculated using the Freundlich equation. Values of correlation coefficients for all cases were shown to be high ( $0.859 < R^2 < 0.969$ ), suggesting that the Freundlich equation was appropriate to describe the results of propachlor adsorption and desorption in the soil (Table 1). The addition of surfactants TX-100 and DOM could decrease the sorption of propachlor on the soil. The value of  $C_s$  for control was higher than that for TX-100 and DOM treatment (Figure 1A). The  $K_f$  values for propachlor sorption with TX-100 and DOM treatment were on the decline. The sorption constant  $K_f$  is an important index to measure the pesticide sorption ability. In general, the high value of  $K_f$  is associated with the strong ability of pesticide sorption and weak mobility of the pesticide in soil.  $K_f$  values in the presence of TX-100 and DOM were much lower than those of the control, which indicated that both TX-100 and DOM can decrease the sorption of propachlor on soil. The maximum value of  $K_f$  was 1.692 (control), which was 2.46 folds higher than the treatment with 1.0 CMC (0.687). This is mainly because TX-100 and DOM may compete with the pesticide on the sorption site on the soil particle surface.<sup>5,18,25,29</sup> Besides, it is much easier for pesticides to combine with TX-100 or DOM than with soil.<sup>24</sup> Due to the hydrophobic nature of TX-100 and DOM, they may interact with pesticides to form stable composites, which may decrease the sorption of pesticides in soil.<sup>28,34</sup> Alternatively, both TX-100 and DOM could improve the mobility of propachlor in soil–water systems (Figure 1). Because TX-100 is a micelle and DOM was extracted from rice straw, they may present in the form of colloids. In this regard, it is much easier for pesticides to combine with TX-100 or DOM than with soil, and large amounts of propachlor would adsorb on the colloidal TX-100 and DOM. Colloid transport may facilitate the mobility of propachlor, in addition to the solubilized effect.

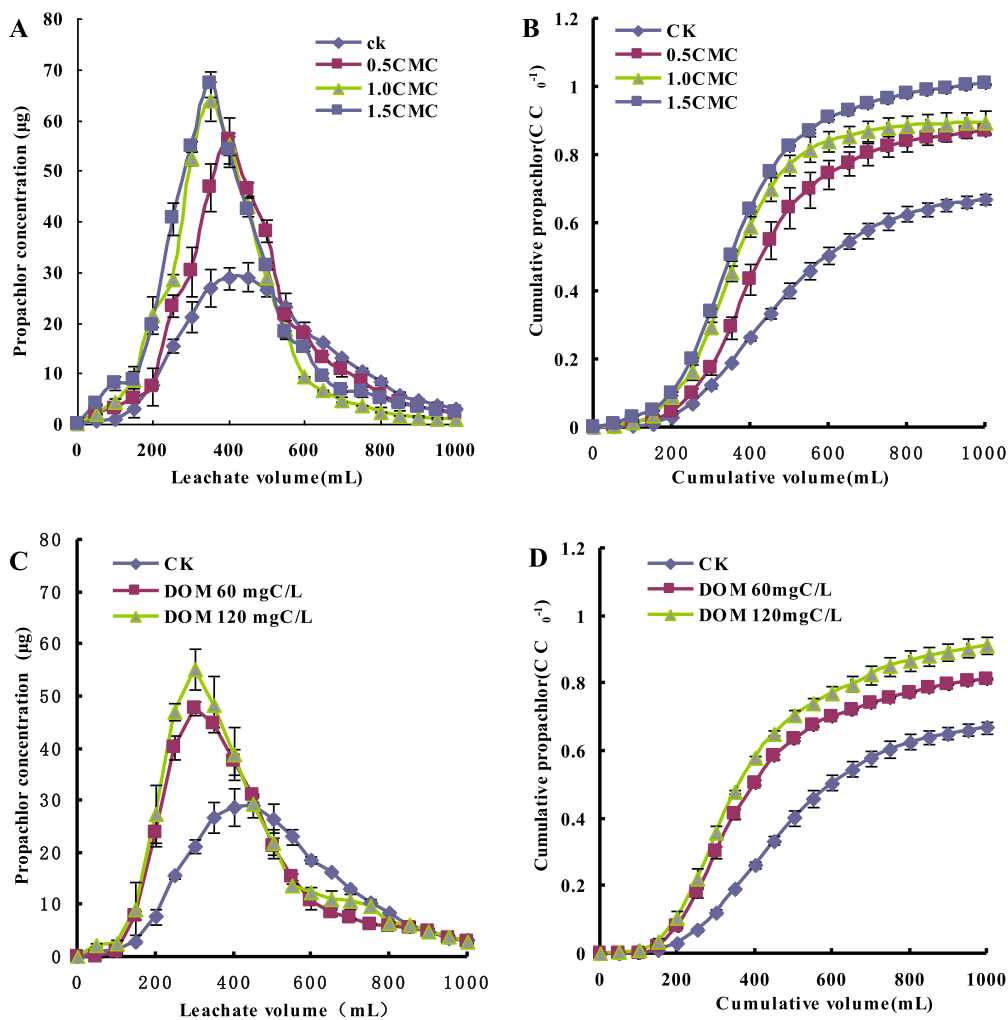
TX-100 appeared more effective in reducing propachlor sorption and promoting propachlor desorption than DOM. Since TX-100 is a nonionic surfactant, it could disperse in water and promote pesticide dissolution.<sup>16</sup> When the degree of hydrophilicity was increased, the adsorbing capacity of soil for TX-100 would be expected to decrease.<sup>15</sup> DOM is a heterogeneous mixture of carbohydrates, proteins, lignin, organic acids, and other uncharacterized compounds.<sup>5</sup> The low sorption may be attributed to the complex formation of DOM with organic chemicals (e.g., pesticides) or competition for sorption sites. Although the declining trend of isopropachlor adsorption was similar after the addition of TX-100 and DOM, the reduced adsorption capacity of isopropachlor was different due to the variations in the structure and addition units of TX-100 and DOM. The propachlor desorption in soil was positively correlated with the increased contents of TX-100 and DOM (Figure 1B,D and Table 1). The more desorption of TX-100 and DOM than the control may be attributed to the less adsorption on soil surfaces.

**Effects of TX-100 and DOM on the Mobility of Propachlor in Soil Microstructure.** The experiment of soil thin-layer chromatography was conducted to illustrate the mobility of propachlor within soil microstructure. The content of propachlor in each segment of a soil thin-layer plate was different using, respectively, distilled water (control), TX-100, and DOM solutions as developing solvents. Compared with the control, the migration of propachlor in soil was enhanced with TX-100 or DOM as developing solvents, especially in the last four segments (Figure 2). The maximum concentration of propachlor was found in the sixth segment (Figure 2), ranging from 10.442  $\mu\text{g}$  (CK) to 11.451  $\mu\text{g}$  (1.5 CMC). When the concentration of the surfactant reached its CMC, the propachlor molecule might be taken into the surfactant micelle–water interface and dissolved in the aqueous phases. The addition of TX-100 could improve propachlor mobility in the soil layer, especially when the concentration of TX-100 is more than its CMC.

The  $R_f$  values (within 0.710 and 0.791) were calculated quantitatively to indicate the mobility of propachlor in soils

**Table 3. Peak Amount of Propachlor and the Corresponding Volume in Column Leaching Using Different Concentrations of TX-100 and DOM**

treatment	CK	0.5 CMC	1.0 CMC	1.5 CMC	60 mgC L <sup>-1</sup>	120 mgC L <sup>-1</sup>
peak amount (μg)	29.002	55.993	63.724	67.081	47.543	55.107
volume (mL)	450	400	350	350	300	300

**Figure 3.** Propachlor breakthrough curves (A,C) and cumulative curves (B,D) using 0.01 M CaCl<sub>2</sub> solution with TX-100 (A,B) and DOM (C,D) to elute from soil columns. The data are the mean of three replications.

using different developing solvents. The  $R_f$  values using TX-100 and DOM solutions were higher than those of the control (0.710), with a rising order being control < 0.5 CMC < 60 mgC L<sup>-1</sup> < 1.0 CMC < 120 mgC L<sup>-1</sup> < 1.5 CMC (Table 2). Because DOM has some similar functional groups as the surfactant, DOM facilitated the mobility of propachlor in the soil layer through the DOM–pesticide interaction. Besides, it was possible that the DOM might occupy the sorption sites on the soil and increase the solubility of propachlor in the aqueous phase. This result is consistent with the previous reports in which the addition of the surfactant increased the mobility of herbicide prometryne, and DOM enhanced the desorption capacity of pesticide imidacloprid.<sup>22,28,30</sup> Due to the different structures and addition units of TX-100 and DOM, the amount of migration in the soil was different. But the migration of pesticide was increased in the presence of TX-100 and DOM.

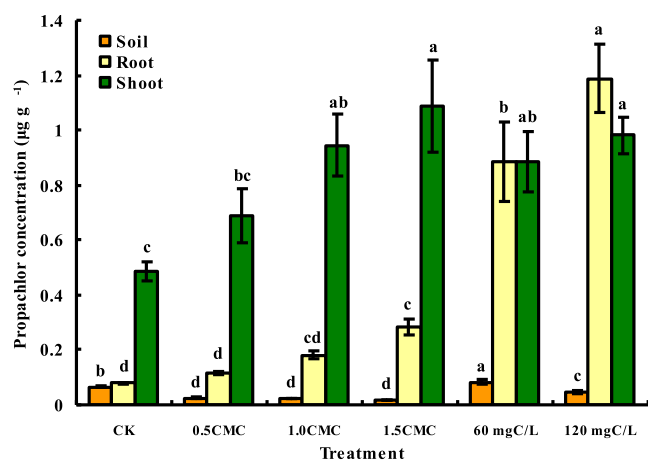
**Effects of TX-100 and DOM on Leaching of Propachlor.** Experiments of the soil column were performed to measure the ability of propachlor to move downward in soil affected by TX-100 and DOM. The addition of TX-100 and DOM into percolating solutions enhanced the peak concentration of propachlor in the leachate, and the total volume of the percolating solution in the peak concentration was decreased (Table 3, Figure 3). When 1.5 CMC was used as the leaching solution, the peak concentration of propachlor was 67.081 μg, which was 231.3% over that of the control (29.002 μg). When the peak concentration of propachlor appeared, the minimum total volume was 300 mL (60 and 120 mgC L<sup>-1</sup>) used as the percolating solution, which saved 150 mL of volume compared with the control (450 mL).

Besides, the percolating solutions added with TX-100 and DOM also increased the total amounts of propachlor leached from the soil columns (Figure 3B,D). The total concentration ratio ( $C/C_0$ ) of propachlor using 0.01 M CaCl<sub>2</sub> (CK), 0.5



CMC, 1.0 CMC, 1.5 CMC, 60 mgC L<sup>-1</sup>, and 120 mgC L<sup>-1</sup> as percolating solutions was 0.67, 0.87, 0.907, 1.00, 0.81, and 0.91, respectively. When the percentage of TX-100 and DOM in percolating solutions became larger, the cumulative concentrations ( $C/C_0$ ) of propachlor were approaching 1.00. These results signified that adding TX-100 and DOM in the percolating solution could reduce propachlor retention in the soil and enhance the downward mobility of propachlor in the soil column, which fit well with the results of soil sorption/desorption and thin-layer chromatography. The hydrophilic groups of TX-100 and DOM increased the solubility of propachlor in the percolating solution.<sup>10,27</sup> Propachlor could be adsorbed less on soil, so it may move downward.<sup>29</sup> Competition of sorption sites between the pesticide and TX-100/DOM with the soil might also contribute to this enhancement.<sup>31</sup>

**Effects of TX-100 and DOM on the Growth and Bioaccumulation of Propachlor.** To investigate the effect of DOM and TX-100 on the bioaccumulation of propachlor in wheat plants, concentrations of propachlor in wheat seedlings and soil were determined by high-performance liquid chromatography (HPLC). The content of propachlor in soil decreased significantly after irrigation of TX-100 and DOM solutions (Figure 4). The minimal concentration in the soil



**Figure 4.** Effects of TX-100 and DOM on accumulation of propachlor in wheat tissues and soil exposed to propachlor. Values are the mean  $\pm$  SD ( $n = 3$ ). Different letters indicate the significant differences between the treatment and control ( $p < 0.05$ ).

was only 0.016  $\mu\text{g g}^{-1}$  (1.5 CMC) and 24.6% of the control (irrigation with water). The concentration of propachlor in roots increased significantly after addition of TX-100 and DOM (Figure 4). The maximal concentration of propachlor in roots reached 1.189  $\mu\text{g g FW}^{-1}$  (DOM 120 mgC L<sup>-1</sup>), almost 15 times that of the control. Notably, DOM had a stronger effect on the bioaccumulation of propachlor in roots than TX-100 because the binding substance of prochloraz-DOM is more easily absorbed and is more soluble. Compared with the control, the shoots had a slightly increased concentration of propachlor after the addition of TX-100 and DOM in the soil. The concentration of propachlor in shoots of wheat seedlings changed in the order: 1.5 CMC > DOM 120 mgC L<sup>-1</sup> > 1.0 CMC > DOM 60 mgC L<sup>-1</sup> > 0.5 CMC > control. These results suggest that the DOM-enhanced solubility of propachlor in the soil medium should be responsible for the

better translocation of propachlor in wheat and the increased uptake of propachlor by wheat plants.

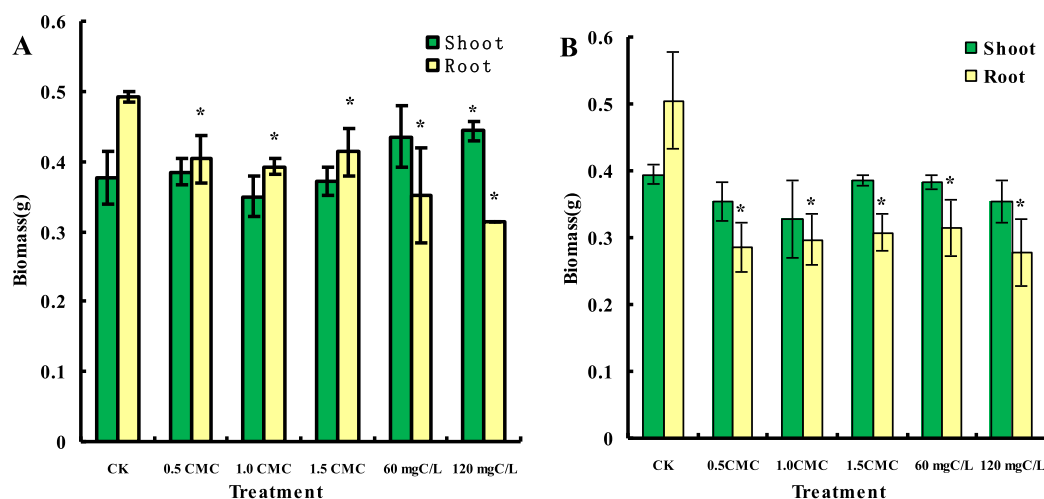
The addition of TX-100 and DOM also affected the bioconcentration factor (BCF) and translocation factor (TF) values (Table 4). BCF refers to the ratio of the propachlor

**Table 4.** BCFs and TFs for Propachlor in the Wheat Shoot and Root

<!--Col Count:4-->treatment	BCF <sub>root</sub>	BCF <sub>shoot</sub>	TF
CK	1.222 $\pm$ 0.046	7.518 $\pm$ 0.561	6.153 $\pm$ 0.422
0.5 CMC	4.907 $\pm$ 0.831	27.501 $\pm$ 3.738	5.780 $\pm$ 1.569
1.0 CMC	8.120 $\pm$ 0.474	42.301 $\pm$ 6.848	5.222 $\pm$ 0.931
1.5 CMC	17.668 $\pm$ 3.508	66.894 $\pm$ 7.983	3.855 $\pm$ 0.706
60 mgC L <sup>-1</sup>	10.831 $\pm$ 0.414	10.573 $\pm$ 0.731	1.005 $\pm$ 0.061
120 mgC L <sup>-1</sup>	25.730 $\pm$ 1.044	21.580 $\pm$ 4.326	0.836 $\pm$ 0.145

concentration in the plant to the soil, while TF refers to the ratio of shoot BCF to root BCF. Compared with the control, the BCFs of roots and shoots became higher with the expansion of TX-100 and DOM. Under the application of TX-100, the BCFs of roots ranged from 1.222 (control) to 17.668 (1.5 CMC), and the BCFs of shoots rose from 7.518 (control) to 66.894 (1.5 CMC). The TF value decreased from 6.153 (control) to 3.855 with TX-100 irrigation, and the minimal TF was about 62.7% of the control. The addition of DOM had the same trend in effects on BCFs and TFs as TX-100. The BCF<sub>root</sub> and BCF<sub>shoot</sub> increased by 21 and 2.87 times, respectively, in the presence of DOM over the control. However, DOM had a stronger influence on the bioaccumulation of propachlor in shoots and roots than TX-100. The TF value was reduced to 16.3% (60 mgC L<sup>-1</sup>) and 13.6% (120 mgC L<sup>-1</sup>) of the control.

Environmental pollutants such as heavy metals and organic contaminants evoke physiological changes and oxidative stress in plants.<sup>21,22,32,33</sup> To identify whether the toxic effect of propachlor on wheat was affected by DOM or TX-100, we measured the biomass of wheat roots and shoots (the above-ground). Under the control condition (without propachlor), treatment with DOM or TX-100 affected the root growth, resulting in a decrease in by which the root biomass, but the shoot biomass stayed unchanged with either DOM or TX-100 (Figure 5A). This suggests that the application of DOM or TX-100 can inhibit the growth of wheat roots, possibly due to the direct contact of roots with the increased propachlor because TX-100 and DOM accelerated the desorption of propachlor into the soil medium and consequently increased the toxicity to roots. It cannot exclude the possibility that DOM or TX-100 might negatively affect the growth of roots in soil. When the plants were treated with 1 mg kg<sup>-1</sup> of propachlor along with DOM and TX-100 for 10 d, the root growth was drastically repressed (Figure 5B), as compared with the root growth without propachlor (Figure 5A). The additional reduction of root biomass should be the result of the enhanced toxic propachlor because treatments with DOM and TX-100 allowed more soil propachlor access to wheat roots. However, in both cases (with or without propachlor), the addition of DOM and TX-100 did not obviously affect the growth of wheat shoots. The current mechanism is unknown and remains to be investigated.



**Figure 5.** Wheat growth (expressed as root and shoot biomass) growing in the soil with ( $1 \text{ mg kg}^{-1}$ ) or without propachlor ( $0 \text{ mg kg}^{-1}$ ) in the presence or absence of TX-100 or DOM for 10 days. (A) Wheat grew without propachlor, TX-100, or DOM as a control. (B) Wheat grew with  $1 \text{ mg kg}^{-1}$  of propachlor, TX-100, or DOM as a treatment. Values are mean  $\pm$  SD ( $n = 3$ ). Asterisks indicate the significant difference between the treatment and the control ( $p < 0.05$ ).

## CONCLUSIONS

The surfactant DOM was able to reduce the propachlor sorption and increase the desorption capacity of propachlor in soil, which facilitated the propachlor migration in soil. The greater uptake of propachlor by wheat plants through the soil–water system with DOM also supports the conclusion that DOM is critical to enhancing the mobility of propachlor in soil. The outcome of the study may allow us to figure out that the application of both TX-100 and DOM would increase the pesticide’s percolation to groundwater and its availability to plants. It can serve as a guide for farmers on when and how to spray pesticide on farmland. Overall, our studies provide theoretical evidence and a practical record for establishing a good soil amendment strategy against contamination and the poisoning effect of the residual pesticide.

## MATERIALS AND METHODS

**Materials.** The herbicide propachlor was obtained from the Academy of Agricultural Science in Jiangsu (AASJ), China, with a purity of 98%. Triton X-100 (TX-100) was provided by Sinopharm Chemical Reagent Co., LTD, China. The critical micelle concentration of TX-100 is  $192 \text{ mg L}^{-1}$ . Uncontaminated soils were collected from the surface layer (0–20 cm deep) at the experimental station of Nanjing Agricultural University (NAU). Soils were sampled, air-dried, gently crumbled, and passed through a 2 mm sieve mesh for experiments as given below: sorption-desorption, column leaching and bioaccumulation, and a  $100 \mu\text{m}$  sieve for soil thin-layer chromatography (TLC). Wheat seeds (Zhenmai 6) were obtained from the Institute of Crop Science, AASJ, China.

**DOM Preparation.** The dissolved organic matter was extracted from rice straw (ST), which was collected from the experimental station, NAU. DOMs were prepared according to the method of Chen et al. with some modification.<sup>5</sup> The straw was air-dried, smashed into pieces, and extracted with Milli-Q water using a solid/water ratio of 1:20 (w/v, dry weight basis) in a reciprocal shaker at 200 rpm and  $20 \text{ }^\circ\text{C}$  for 24 h. The suspensions were centrifuged at  $10,000g$  and  $4 \text{ }^\circ\text{C}$  for 15 min and filtered through a  $0.45 \mu\text{m}$  membrane. The filtrates were

analyzed for total organic carbon (TOC 5000A, Shimadzu, Japan). The DOM extracts were used for the following studies immediately.

**Sorption and Desorption Experiments.** Sorption and desorption isotherms of propachlor affected by DOM and TX-100 were obtained by the standard batch equilibration method.<sup>5</sup> Briefly, 2 g of soil was placed into 25 mL polypropylene centrifuge tubes to which 10 mL of 0.01 M calcium chloride ( $\text{CaCl}_2$ ) solution containing different concentrations of propachlor (8, 16, 24, 32, and  $40 \text{ mg L}^{-1}$ ) was separately added. Each level was made in triplicate. The 24 h equilibrium time of adsorption/desorption was selected based on the method of Zhang et al.<sup>10</sup> The suspensions were shaken at 200 rpm and  $25 \pm 1 \text{ }^\circ\text{C}$  for 24 h and centrifuged at  $7000g$  ( $25 \pm 1 \text{ }^\circ\text{C}$ ) for 10 min. The concentrations of propachlor in the supernatant were measured by HPLC. Desorption experiments were performed immediately after the sorption experiments. The tube was placed in inverse order for 24 h for removing all of the supernatant. Then, 10 mL of fresh  $\text{CaCl}_2$  solution (0.01 M) was added into the above tube. Shaking, subsequent separation of the soil and aqueous phases, and analyses were conducted as described above. The experiments of sorption and desorption were marked as control (CK).

The initial concentrations of TX-100 at 96, 192, and  $288 \text{ mg L}^{-1}$  (0.5 CMC, 1.0 CMC, and 1.5 CMC) and DOM at 60 and  $120 \text{ mg C L}^{-1}$  were prepared with 10 mL of 0.01 M  $\text{CaCl}_2$  solution containing propachlor, respectively. The procedure of propachlor sorption-desorption experiments on soil in the presence of TX-100 and DOM was exactly ranged the same as the method described above.

The sorption data were fitted to the Freundlich adsorption equation:  $\log C_s = \log K_f + 1/n \log C_e$ , where  $C_s$  is the adsorbed concentration ( $\text{mg kg}^{-1}$ ),  $K_f$  ( $[(\text{mg kg}^{-1}) (\text{mg L}^{-1})^{-N}]$ ) is the Freundlich sorption coefficient, representing the amount of propachlor adsorbed at an equilibrium concentration of  $1 \text{ mg L}^{-1}$ ,  $1/n$  is a linearity factor indicating the measure of the intensity of sorption and reflecting the degree to which sorption is a function of pesticide concentration, and  $C_e$  is the concentration in the solution phase ( $\text{mg L}^{-1}$ ). A similar procedure was followed for the desorption isotherms.

**Soil Thin-Layer Chromatography.** The soil sample (15 g) and 10 mL of water were mixed and spread on 20 × 10 cm glass plates. After air-drying, the plates were marked with two horizontal lines at distances of 2 cm (baseline) and 18 cm (foreland) from the base. Then, a 100 μL droplet of 400 mg L<sup>-1</sup> propachlor prepared in acetone was spotted onto the baseline of plate with the aid of a microsyringe.<sup>34</sup> The plate was placed in a closed, individual glass chromatographic chamber. Water solutions with 0.5 CMC, 1.0 CMC, 1.5 CMC, DOM 60 mg DOC L<sup>-1</sup>, DOM 120 mg DOC L<sup>-1</sup>, and distilled water (control) were used as developing solvents. Each treatment had triple replication. After the developing solvent reached the foreland, each plate was taken out from the glass chromatographic chamber and laid flat to dry at room temperature. The soil on the plate was divided into eight equal parts between the baseline and the foreland. Propachlor residue in the soil of each segment was extracted and quantified by HPLC. The mobility factor ( $R_f$ ) of the propachlor was measured by the formulas<sup>35</sup>

$$R_f = \frac{\bar{Z}_p}{Z_w} = \frac{\sum Z_i \times M_i}{Z_w \times \sum M_i}$$

where  $\bar{Z}_p$  is the average moving distance of propachlor from the baseline,  $Z_w$  is the moving distance of the developing solvent from the baseline,  $i$  is the number of segments,  $Z_i$  is the distance of segment  $i$  from the baseline, and  $M_i$  is content of propachlor in segment  $i$ .

**Column Leaching Experiments.** The leaching experiment of propachlor was carried out in a column (30 cm × 4.5 cm i. d.) filled with 500 g soil samples, followed by the method of Jiang et al.<sup>22</sup> The column was pre-saturated with 0.01 M CaCl<sub>2</sub> solution to attain the normal field capacity of soil moisture and allowed us to drain naturally for 24 h before use. Propachlor (400 μg) in 1 mL of acetone was spiked to the column surface and exposed to air for 2 h to evaporate acetone. The top of each column was filled with a layer (1 cm) of acid-washed sand to minimize surface disturbance. Columns were eluted at room temperature and pressure for 20 h with 1000 mL of different percolating solutions as the following: 0.5 CMC (a mixture of 96 mg L<sup>-1</sup> TX-100 and 0.01 M CaCl<sub>2</sub>), 1.0 CMC (a mixture of 192 mg L<sup>-1</sup> TX-100 and 0.01 M CaCl<sub>2</sub>), 1.5 CMC (a mixture of 288 mg L<sup>-1</sup> TX-100 and 0.01 M CaCl<sub>2</sub>), DOM 60 mgC L<sup>-1</sup> (a mixture of 60 mg DOC L<sup>-1</sup> and 0.01 M CaCl<sub>2</sub>), DOM 120 mgC L<sup>-1</sup> (a mixture of 120 mg DOC L<sup>-1</sup> and 0.01 M CaCl<sub>2</sub>), and control (0.01 M CaCl<sub>2</sub>). The leachate fractions were collected, respectively, in 50 mL of one portion and analyzed for the propachlor concentration by HPLC. Each type of column was repeated three times.

**Plant Growth and Bioaccumulation.** Wheat seeds were surface-sterilized with 5% sodium hypochlorite solution, rinsed several times with distilled water, and placed on moist filter paper. After germination, the seeds were sown on soil in plastic pots (1 L) containing 1000 g soil mixed with propachlor at 1 mg kg<sup>-1</sup> and grew at a 25/20 °C (day/night) cycle of 14/10 h under a light intensity of 300 μmol m<sup>-2</sup> s<sup>-1</sup>. Water solution was added to the pots each day to maintain 70% of relative water content in the soil. Different water solutions were set as follows: 0.5 CMC, 1.0 CMC, 1.5 CMC, DOM 60 mgC<sup>-1</sup>, DOM 120 mgC L<sup>-1</sup>, and control (distilled water). Each treatment was repeated in triplicate. After growing for 10 d, the roots and shoots of wheat seedlings were separately harvested. The growth of wheat seedlings and the content of propachlor

in wheat and soil were determined. To evaluate the effects of DOM and TX-100 on the translocation of propachlor in wheat, the BCF and TF values were calculated. While BCF refers to the ratio of the propachlor concentration in the plant to that in the soil, TF refers to the ratio of shoot BCF to root BCF.

**Propachlor Analysis.** The concentrations of propachlor in water, soil, and wheat seedlings were detected according to the methods of Zhang et al.<sup>10</sup> with slight modification. Solid phase extraction (SPE) was used for pre-cleaning and concentration of water samples. The LC-C<sub>18</sub> cartridges containing 300 mg of sorbent (Supelco Park Bellefonte, PA, USA) were conditioned with 5 mL methanol, followed by 5 mL of water. 50 mL of the leaching solution sample was transferred onto the SPE column and allowed to percolate at 2–3 mL min<sup>-1</sup>. The column was dried with a strong stream of air for 10 min. Elutes were discarded. The column was washed with 2 mL of methanol. The washing methanol was collected for HPLC analysis.

Soil sample (20 g) was extracted with 30 mL of mixed acetone–water (3:1, v/v) using a mechanical shaker at 200 rpm for 20 min<sup>-1</sup>, followed by centrifugation at 5000g for 15 min. This step was repeated three times. The supernatant was concentrated to remove acetone in a vacuum rotary evaporator at 40 °C. The residual water was loaded onto an LC-C<sub>18</sub> SPE column. Elutes were discarded, and the column was washed with 2 mL of methanol. The methanol solution was collected for HPLC analysis.

Wheat tissues (4 g) were ground and extracted with 20 mL of mixed acetone–water (3:1, v/v) using a mechanical shaker at 200 rpm for 20 min<sup>-1</sup>, followed by centrifugation at 5000g for 15 min. This step was repeated in triplicate. The supernatant was concentrated to remove acetone at 40 °C in a vacuum rotary evaporator. The residual water was transferred into a funnel and extracted with petroleum ether three times, with each time for 20 mL. The water layer was removed, and the organic phase was gathered to evaporate petroleum ether at 40 °C to dry in a vacuum rotary evaporator. The residue was re-dissolved by adding 20 mL solution of methanol and distilled water (1:40, v/v). The mixture was eluted through an LC-C<sub>18</sub> SPE column. Elutes were discarded, and the column was washed with 2 mL of methanol. The methanol solution was collected for HPLC analysis. Propachlor was determined using HPLC under conditions as follows: a Waters 515 pump with a 2487 dual k absorbance detector at 235 nm; a hypersil ODS column (250 × 4.6 mm ID, 5 μm); mobile phase methanol/water (75/25, v/v) at a flow rate of 0.6 mL min<sup>-1</sup>. The spiked recoveries of propachlor in water, soil, and wheat seedlings are summarized in Table S1.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c06561>.

Spiked recoveries of propachlor from soil and wheat (shoot and root) at different fortified concentrations ( $n = 3$ ) (PDF)

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## Notes

The authors declare no competing financial interest.

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