

Transformation of Herbicide Propachlor by an Agrochemical Thiourea

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Propachlor and other chloroacetanilide herbicides are frequently detected contaminants of groundwater and surface water in agricultural regions. The purpose of this work was to develop a new approach to remove propachlor residues from the environment via chemical remediation by the nitrification inhibitor thiourea. The transformation processes of propachlor and thiourea mixed in aqueous solution, sand, and soil were elucidated. Analysis of transformation products and reaction kinetics indicated that an S_N2 nucleophilic substitution reaction occurred, in which the chlorine of propachlor was replaced by thiourea, detoxifying the herbicide. It appears that propachlor undergoes a catalytic reaction in sand or soil amended with thiourea, which results in a significantly accelerated transformation rate as compared to the reaction in aqueous solution. The second-order reaction process was examined at different temperatures to investigate the role of the activation energy. The enthalpy of activation (ΔH) for the reaction of propachlor with thiourea was demonstrated to be significantly lower in sand than in aqueous solution, which provides evidence that a catalytic transformation mechanism occurs in thiourea-amended sand. The chemical reaction rate increased proportionally to the amount of thiourea added to the sand. Column experiments further suggested that the remediation strategy could be used to remove propachlor residues from sand or soil to reduce leaching and prevent contamination of surface water and groundwater.

Introduction

Propachlor (2-chloro-*N*-isopropylacetanilide) is one of several chloroacetanilide herbicides that are widely applied in the United States for pre-emergent control of annual grasses and broad-leaved weeds in corn and soybean crops. Owing to their popularity in agricultural applications, chloroacetanilide herbicide residues have been frequently detected in groundwater, surface water, and coastal marine environments (1–4). There is increasing evidence that exposure to

these anthropogenic chemicals via drinking water or agricultural products, even at very low concentration, can have adverse effects on public health and the ecological environment (5). To minimize pesticide residues in agricultural systems and the environment, it is of utmost importance to improve current integrated pest management (IPM) strategies and develop contaminant remediation approaches to manage pesticide residue.

Various treatment strategies have addressed the need to prevent and mitigate pesticide contamination of the natural environment. These technologies involve physical, chemical, microbiological, and integrated practices, including bioremediation (6–9), chemical remediation (10–13), phytoremediation (14–16), and photocatalytic degradation (17). Unfortunately, few currently available practices are both environmentally benign and economically feasible.

Chemical remediation, defined here as the use of nucleophilic chemicals or redox reagents to destroy contaminants in soil and aquatic environments, offers a rapid and economical approach to clean up contaminated sources. To use the technology safely, it is essential to find appropriate remediation reagents. In previous studies, we utilized a chemical remediation strategy to accelerate the transformation of halogenated fumigants on the surface of soil and control their atmospheric emissions (18, 19). Using agrochemicals (e.g., fertilizers and nitrification inhibitors) as remediation reagents provides an innovative approach to remove unwanted agricultural contaminants (such as pesticide residues) with minimal change to the agricultural system. Thiourea, a sulfur-based nitrification inhibitor (20–22), has been discovered to accelerate the degradation of halogenated fumigants in aqueous solution and soil via an S_N2 nucleophilic substitution reaction (18, 23). Furthermore, a catalytic process was found to increase the rate of fumigant dissipation in soils as compared to aqueous systems. This led to the development of a reactive surface barrier (RSB) as an alternative to the use of plastic tarps to reduce halogenated fumigant emissions from the soil surface (23).

In addition to halogenated fumigants, our recent exploration revealed that thiourea may react with many other organic pesticides that have halide substitution on aliphatic carbons, such as chloroacetanilide herbicides. Use of the agrochemical thiourea as a remediation reagent has great potential to decontaminate these compounds via nucleophilic substitution reactions, reducing their adverse effects on the environment. Previous studies implied that propachlor was a more reactive herbicide than other chloroacetanilide herbicides (e.g., alachlor and metolachlor) for nonenzymatic conjugation by glutathione (24) and nucleophilic transformation with thiosulfate (10) and bisulfide (11). Thus, propachlor was selected as a representative of chloroacetanilide herbicides to investigate chemical remediation in the study. The objectives of this work were (i) to systematically investigate the reaction kinetics of propachlor and thiourea in an aquatic environment, sand, and soil; (ii) to characterize the transformation products and elucidate their reaction mechanisms in different environmental media; and (iii) to perform laboratory column experiments to illustrate the potential for thiourea to remediate soils contaminated by propachlor

Experimental Section

Chemicals and Soils. Propachlor (99% purity) and CH_3I (99% purity) were purchased from Chem Service (West Chester, PA). Thiourea (99% purity) was obtained from Aldrich Chemical (Milwaukee, WI). All chemicals were used as

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received. Propachlor stock solutions were prepared in a mixture of methanol (HPLC grade) and water (1:1, v/v) and used for spiking all samples.

Silica sand (90 mesh, pH 8.1) obtained from P. W. Gillibrand Co (Simi Valley, CA) was washed several times with deionized water and then oven-dried at 105 °C. The soil used in this study was an Arlington sandy loam that was collected from the University of California, Riverside Agricultural Experiment Station. The soil had a pH of 7.2 and an organic carbon content of 0.92%.

Experimental Systems. In the first experiment, second-order reaction kinetics of propachlor and thiourea were measured in buffer solutions (pH 6.9) with an initial molar ratio (propachlor:thiourea) of 1:4. Reactions were initiated by combining propachlor stock solution and 100 mL of thiourea solution (1.0 mM) in serum bottles, which were then capped. Samples containing only propachlor were also prepared as untreated controls. All bottles were placed in incubators maintained at 15, 24, 35, 48, and 55 °C (± 0.5 °C). At intervals, 1.0-mL aliquots of solution were withdrawn from triplicate bottles and extracted with 2.0 mL of hexane. Preliminary experiments revealed that the reaction was quenched immediately when hexane was added as an extraction solvent because propachlor was efficiently extracted into the organic phase, while thiourea remained in the aqueous phase. The concentration of propachlor in each extract was analyzed using an Agilent 6890 GC equipped with a microelectron capture detector and a 30 m DB-35MS capillary column (0.25 mm i.d. \times 0.15 μ m, J&W Scientific, Folsom, CA). The analysis conditions were carrier gas flow rate (He), 1.5 mL min⁻¹; inlet temperature, 250 °C; and detector temperature, 280 °C. The initial oven temperature was 70 °C, and the temperature was increased at 50 °C min⁻¹ to 190 °C and held for 7 min. Under these conditions, the retention time of propachlor was 5.1 min.

In the second experiment, the transformation kinetics of propachlor in thiourea-amended sand or soil were studied. Samples of sand or soil were thoroughly premixed with thiourea at 1.0 mmol kg⁻¹. The final moisture content of amended sand or soil was 7% (w/w). Ten grams (dry weight equivalent) of the amended samples was treated with propachlor at 0.25 mmol kg⁻¹ in 20-mL headspace vials. Vials containing soil or sand treated with only propachlor were also prepared and used as controls. All samples were incubated at 28 \pm 0.5 °C in the dark. At regular time intervals, triplicate samples were removed and extracted with 10 mL of hexane and 8.0 g of anhydrous sodium sulfate. After the samples were shaken vigorously for 4 h, an aliquot of each extract was transferred to a GC vial and stored at -20 °C until the end of the experiment. Preliminary experiments demonstrated that hexane was the most efficient solvent to use in the above extraction procedure. The recovery of propachlor ranged from 94 to 106% in the sand and greater than 90% in Arlington sandy loam.

The effect of incubation temperature on the rate of propachlor transformation in thiourea-amended sand was measured. The procedures described above were used to prepare, treat, and analyze the samples. The treated sand samples were incubated at 15, 24, 35, 48, and 55 °C. Variation in temperature was less than 0.5 °C. The influence of the initial thiourea concentration on the propachlor transformation was evaluated in sand treated with thiourea at 0, 0.25, 0.5, 1.0, and 2.0 mmol kg⁻¹. The initial molar ratios of propachlor to thiourea were thus 1:0, 1:1, 1:2, 1:4, and 1:8. These treated samples were incubated at 28 \pm 0.5 °C in the dark and were extracted and analyzed using the procedures described above.

In the third experiment, reaction products were identified using GC-MS. Because the primary transformation product of propachlor with thiourea is a polar ion, three derivative

approaches were used prior to hexane extraction as follows: (i) aliquots of the reaction mixtures were adjusted to pH 10; (ii) aliquots of the reaction mixtures were heated in a water bath at 60 °C for 30 min; and (iii) the transformation product was methylated using CH₃I: a 2-mL aliquot of propachlor:thiourea reaction mixture was treated with excess CH₃I (0.1 M) and then heated in a water bath at 60 °C for 30 min. After being cooled to room temperature, all treated samples were extracted with hexane. Hexane extracts were analyzed using an HP 5890 GC coupled to an HP 5971 quadrupole mass spectrometer equipped with a 30 m HP-5MS capillary column (0.25 mm i.d. \times 0.25 μ m film thickness; Wilmington, DE). Electron impact mass spectra were generated using an electron energy of 70 eV, and data were collected in full-scan mode in the *m/z* range of 50–400.

The chemical reaction between propachlor and thiourea is presumably one of bimolecular substitution, which follows second-order kinetics. A second-order kinetic model (10, 25) was fitted to the transformation data for each matrix (aqueous solution, sand, and soil). To better understand the transformation of propachlor in sand amended with different levels of thiourea, a pseudo-first-order kinetic model was also used to obtain the half-life, for comparison. All statistical analyses were performed at a 0.05 significance level.

Column Experiments. To demonstrate a potential application of thiourea to remediate pesticide contamination, two sets of column experiments were conducted. The first set of experiments was designed to investigate the decontamination of propachlor-polluted sand using thiourea and to demonstrate the feasibility of reducing the mobility of propachlor residues in aquifer sand. Sand was cleaned with flowing deionized water for 4 h prior to use in order to remove loosely attached material that might detach during the experiment. Clean sand (500 g) was packed into acrylic cylinders 5 cm (i.d.) by 31 cm (length). A 1.0-mL aliquot of propachlor stock solution (1.5 mg/mL) was applied to the top of each column, followed by 4 mL of thiourea solution with an applied mass of 4.3, 13.5, and 27 mg. This corresponded to a propachlor to thiourea molar ratio of 1:8, 1:25, and 1:50. Water (145 mL) was delivered to the top of each column to obtain saturation (30% water content). A control column not treated with thiourea was prepared simultaneously. All columns were maintained at 25 °C for 10 d. Then, each column was leached with deionized water at 2.5 mL/min, and the leachate was collected from the bottom end of the column using a fraction collector. After hexane extraction, the concentration of propachlor in each fraction of the leachate was analyzed by GC-ECD.

A second set of experiments was performed to explore the distribution and retention of propachlor residues in a sand column after thiourea remediation. This experiment was conducted in acrylic columns (5 cm i.d.) packed with 500 g of clean sand. Similar amounts of propachlor and thiourea were applied to the top of each column as described above, and then 145 mL of water was applied to the top of the column. All of saturated columns were placed in an incubator maintained at 25 °C in the dark. After the 10-d incubation, these columns were transferred to a -20 °C freezer. Frozen columns were split, and sand samples were sectioned in 1.5-cm increments. The sand samples were transferred into 20-mL headspace vials and analyzed for propachlor by GC-ECD under the conditions given above.

Results and Discussion

Reaction of Propachlor with Thiourea. A subset of experiments was conducted to determine the dissipation of propachlor by thiourea in aqueous solution, sand, and soil systems at a molar ratio (propachlor:thiourea) of 1:4 at 28 °C. The time courses for the transformation of propachlor with thiourea in different media are portrayed in Figure 1. No

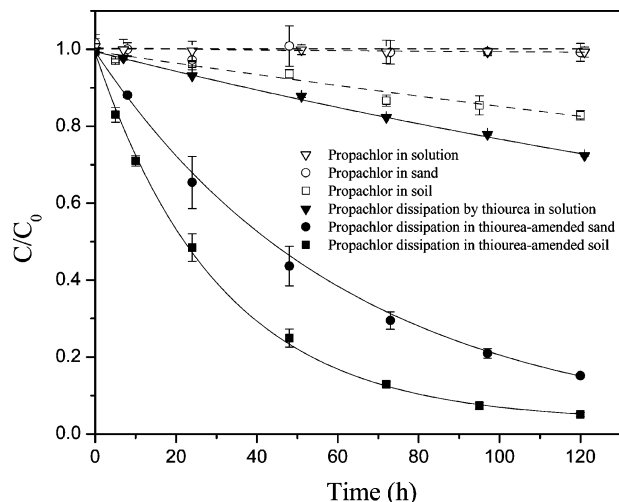


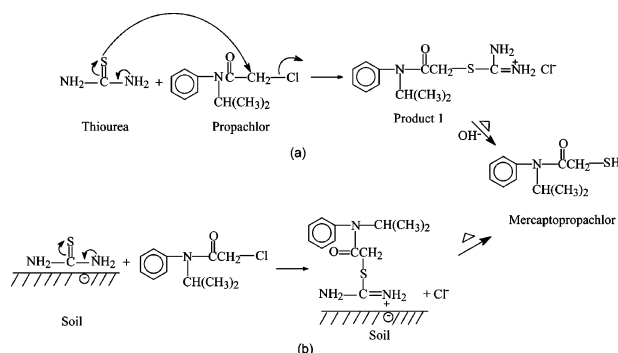
FIGURE 1. Comparison of propachlor dissipation in thiourea solution (1.0 mM) and thiourea-amended soil and sand (1.0 mmol/kg) at $28 \pm 0.5^\circ\text{C}$ (1:4 propachlor:thiourea ratio). C_0 is the initial concentration of propachlor in the solution, sand, and soil. Error bars represent standard deviation of triplicate samples.

discernible propachlor degradation occurred in control experiments conducted in sand and aqueous solution in the absence of thiourea (Figure 1). Although propachlor could undergo transformation in soil, the herbicide degradation progressed remarkably slowly in Arlington sandy loam (half-life, $t_{1/2} = 460$ h) in contrast to the rapid transformation in thiourea-amended soil (Figure 1). These results imply that the dissipation of propachlor in soil containing thiourea is primarily due to abiotic reaction.

Figure 1 also clearly discloses the reactivity trends of propachlor and thiourea across soil, sand, and water systems. The reactivity of propachlor with thiourea in these systems decreases in the following order: Arlington sandy loam > sand > aqueous solution. For example, the transformation half-life of propachlor by thiourea in the Arlington sandy loam, sand, and aqueous solution was approximately 24, 42, and 380 h, respectively. Compared to reaction kinetics in aqueous solution, the transformation rate of propachlor in thiourea-amended soil or sand was significantly higher. This suggests the involvement of a catalytic process that results in a lowering of the activation energy for reaction of propachlor and thiourea in soil or sand.

Propachlor and thiourea reacted in aqueous solution via a bimolecular nucleophilic substitution ($\text{S}_\text{N}2$) reaction, similar to thiourea reaction with halogenated fumigants (18, 23). The electron-donating properties of the amino group may increase the nucleophilic reactivity of the thiono group of thiourea. As a result, the sulfur atom of thiourea as a nucleophilic center may readily attack propachlor to form a thiourea-substituted propachlor salt, liberating a chlorine (Scheme 1a). Some attempts were made to identify the reaction product by GC-MS after derivatization. Prior to the hexane extraction, aliquots of the propachlor and thiourea reaction mixture were alkalinized (pH 10) or heated at 60°C for 30 min. In both cases, mass spectra (Figure S-1a) were consistent with the RSH derivative mercaptopropachlor (2-mercapto-*N*-isopropylacetanilide) (11). Note that the initial reaction product (product 1, Scheme 1a) resulting from nucleophilic substitution was not identified directly by the analytical technique employed in this study because it could not be extracted as a isothiuronium salt by hexane. However, this intermediate can further cleave to mercaptopropachlor under alkaline or pyrogenic conditions (Scheme 1). Identification of the sulfur-substituted intermediate resulting from propachlor reaction with thiourea was further supported by

SCHEME 1



methylation reaction mixtures, followed by extraction into hexane and analysis via GC-MS (EI). The mass spectrum (Figure S-1b) for the derivatized product is consistent with that provided in Loch et al. (11), as an anticipated mercaptomethyl-substituted (RSC_2H_5) derivative.

On the basis of the reaction mechanism of propachlor with thiourea in aqueous solution, we propose that a catalytic process occurs on the soil surface, resulting in a higher rate of propachlor transformation in thiourea-amended soil or sand. The characteristic negative charge at the surface of soil particles induces the delocalization of electrons in thiourea leading to formation of a bond between the thiourea NH_2 group and soil particles. The electron transfer of the amino group enhances the nucleophilic activity of thiourea and leads to the observed catalytic reaction in soil (Scheme 1b).

Previous studies have shown that dehalogenation of halogenated organic compounds is a detoxification process because the biological activity of these compounds is generally associated with the halide substitution (10, 26). Bioremediation of halogenated organic contaminants often seeks and isolates bacteria capable of dehalogenation to mitigate their toxicity (27, 28). Similar to the chemical reaction of propachlor and thiourea in this study, glutathione as a biological nucleophile may conjugate with chloroacetanilide herbicides to finally yield the ethane sulfonic acid (ESA) metabolites (29). Glutathione conjugation has been suggested as an important detoxification pathway carried out by aquatic and terrestrial plants and soil microorganisms. Previous research also revealed that the release of chlorine associated with nucleophilic substitution of propachlor by thiosulfate is an environmentally beneficial process (26). Therefore, the rapid nucleophilic reaction of thiourea with propachlor could potentially control the persistence and fate of propachlor residues in the ecological environment. Since thiourea is much more reactive toward propachlor in soil than in solution (Figure 1), thiourea application to soil as a nitrification inhibitor has great potential to decrease herbicide residues, reducing the risk of environmental contamination associated with the use of chloroacetanilide pesticides.

Activation Energy for Propachlor Reaction with Thiourea. To explore the influence of the activation energy on the reaction process, propachlor dissipation rates were measured over the temperature range of 15.0 – 55.0°C in thiourea-containing buffered solutions (pH 6.9) and thiourea-amended sand. No measurable degradation was observed in the absence of thiourea at these temperatures over comparable time periods in control experiments. As the temperature increased, the transformation rate of propachlor by thiourea consistently increased (Figure 2). This suggests that the reaction of propachlor with thiourea is an endothermic process and that the remediation of herbicide contamination should be more effective during warmer periods.

The second-order reaction rate coefficient at each temperature was plotted to allow estimation of the activation

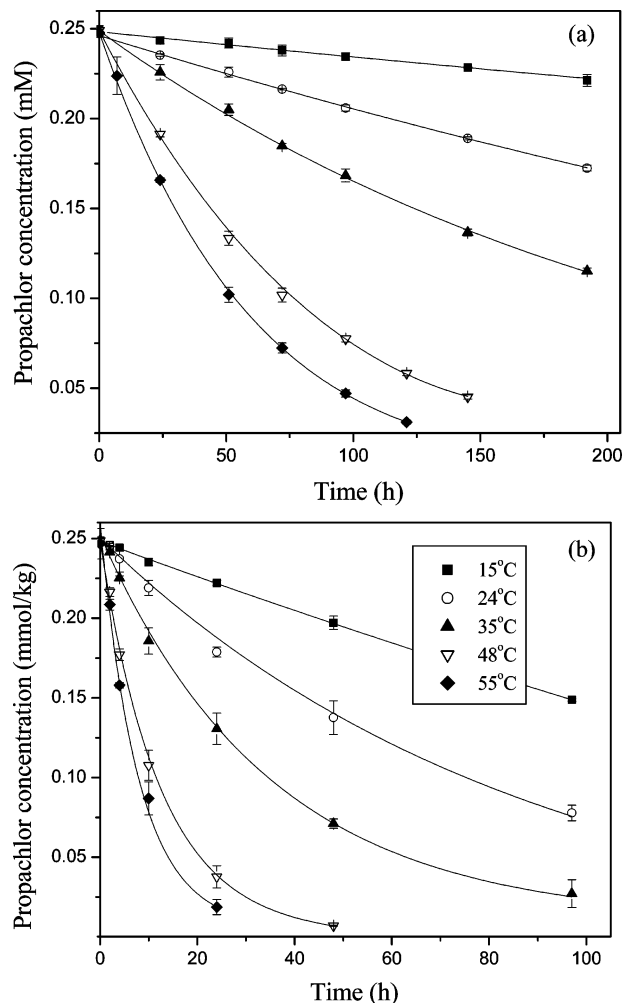


FIGURE 2. Transformation of propachlor by thiourea at different temperatures: (a) in pH 6.9 buffered solution where the initial concentrations of propachlor and thiourea were 0.25 and 1.0 mM, respectively, and (b) in sand where the initial concentrations of propachlor and thiourea were 0.25 and 1.0 mmol/kg, respectively.

energy according to the Arrhenius equation ($\mu = Ae^{-E_a/RT}$). The activation energy (E_a) in aqueous solution was calculated to be 68.6 kJ mol^{-1} with a correlation coefficient (r^2) of 0.992. However, in thiourea-amended sand, the activation energy decreased by approximately 13% to 59.8 kJ mol^{-1} ($r^2 = 0.989$). This indicates that the reaction utilizes less energy in soil systems compared to aqueous systems. The large decrease in the activation energy resulting from the catalytic effect of sand surfaces may account for the significantly accelerated transformation of propachlor in thiourea-amended soil or sand.

On the basis of the Activated Complex Theory (30), the effect of enthalpy or entropy of activation on propachlor reactivity was further demonstrated for the different media. From a molecular point of view, the enthalpy (ΔH) involves both intermolecular forces (i.e., molecule's attractions or attachments to its surroundings) and intramolecular forces (i.e., its internal attractions or bonds). Entropy (ΔS) is associated with the "freedom" or latitude of orientation, configuration, and translation of the molecule (31). The values of ΔH and ΔS were calculated according to linear regression analyses using the following equation (32):

$$\ln(\mu/T) = -\Delta H/RT + \ln(k/h) + \Delta S/R \quad (1)$$

where k is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J/K}$), h is Planck's constant ($6.626 \times 10^{-23} \text{ J s}$), and T is temperature

TABLE 1. Calculated Activation Barriers for Reaction of Propachlor with Thiourea in Aqueous Solution and Sand

reaction media	$\Delta H \text{ (kJ/mol)}^a$	$\Delta S \text{ (J/mol}\cdot\text{K)}$	$\Delta G \text{ (kJ/mol)}^b$
solution	66.04 ± 3.62	-86.43 ± 9.15	91.81 ± 4.53
sand	57.28 ± 3.58	-99.06 ± 11.72	86.81 ± 5.00

^a Indicated a significant difference in different reaction media at the 95% confidence level. ^b Calculated at 298.15 K.

TABLE 2. Kinetics of Propachlor (0.25 mmol/kg) Transformation by Thiourea in Sand at $28 \pm 0.5^\circ \text{C}$ as Indicated by the Pseudo-First-Order Half-Life ($t_{1/2}$, h) and Second-Order 50% Disappearance Time ($T_{1/2}$, h)

initial thiourea concn (mmol/kg)	initial propachlor:thiourea	$t_{1/2}$ (h)	$T_{1/2}$ (h)
0.25	1:1	217.1	259.1
0.5	1:2	85.4	84.1
1.0	1:4	42.1	40.7
2.0	1:8	19.8	20.7

in Kelvin. The slope of a plot of $\ln(\mu/T)$ versus $1/T$ is $-\Delta H/R$, and ΔS can be calculated from the intercept. The overall activation barrier ΔG is attributed to a combined contribution of the enthalpy and entropy:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

The calculated values for these parameters are listed in Table 1. Statistical differences for ΔH and ΔS in different media were compared to distinguish their influence on the reaction mechanism of propachlor and thiourea. The difference of enthalpy of activation in aqueous solution and sand systems was significantly different at the 95% confidence level, suggesting that the reaction is primarily enthalpy (ΔH) driven rather than entropy (ΔS) driven. Also, this substantiates the proposed transformation mechanism, in which changes in the intermolecular attraction (because of the delocalization of electrons) increased the nucleophilic activity of thiourea in soil. Therefore, a decrease in the enthalpy of activation was the most important determinant in increasing the rate of thiourea and propachlor reaction in soil or sand.

Effect of Initial Thiourea Concentration on Propachlor Degradation. Since propachlor degradation by thiourea is chemically based, the rate of transformation depends on the molar ratio of propachlor to thiourea. With a constant initial propachlor concentration of 0.25 mmol/kg, experiments were conducted for different initial molar ratios of propachlor and thiourea in sand. The dissipation of propachlor in thiourea-amended sand was described by second-order and pseudo-first-order kinetics (Table 2). Generally, the second-order reaction model does not provide a true half-life that is independent of initial concentration. The speed of reaction, therefore, can be defined using a 50% propachlor disappearance time ($T_{1/2}$). As the molar ratio of thiourea to propachlor increased, the $t_{1/2}$ (first-order) and $T_{1/2}$ (second-order) proportionally decreased. For example, the 50% disappearance time ($T_{1/2}$) of propachlor decreased by more than a factor of 10 when the molar ratio of thiourea to propachlor increased from 1:1 to 8:1 (Table 2). Owing to the S_N2 nucleophilic reaction mechanism between propachlor and thiourea, the second-order kinetic model is believed to appropriately reflect the reaction characteristics. For experiments conducted using identical initial concentrations, pseudo-first-order kinetics can also satisfactorily describe changes in the rate of the transformation process.

No discernible degradation of propachlor occurred in sand in the absence of thiourea, indicating that enhanced pro-

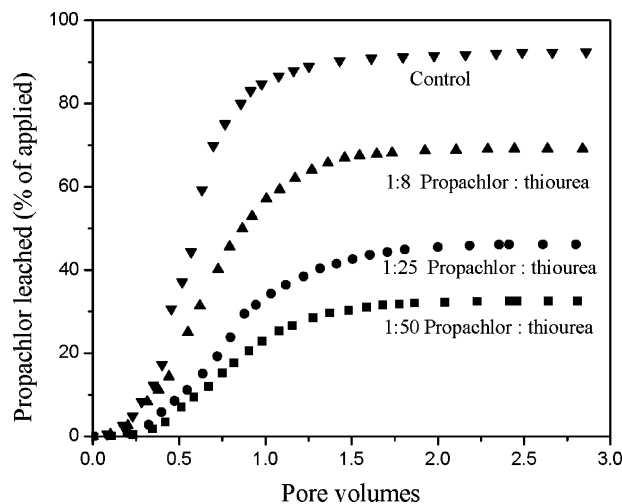


FIGURE 3. Influence of thiourea amendment levels on cumulative propachlor leaching through sand columns.

propachlor degradation by thiourea could significantly reduce herbicide residues in the environment. The concentration dependence of the propachlor transformation rate implies that the effectiveness of the soil remediation process will depend on the thiourea application technology, including the thiourea application rate, application method, and soil conditions. These factors, along with the potential effects of this remediation strategy on the environment, should be further evaluated to optimize the actual use of this technology.

Propachlor Remediation in Saturated Sand Columns. A series of saturated column experiments were conducted to simulate chemical remediation of sandy soils. In the first experiment, the propachlor concentration in the column leachate was determined for different application rates of thiourea. When propachlor application was followed by thiourea, the propachlor concentration in the leachate was significantly reduced at all propachlor:thiourea ratios, and propachlor leaching decreased with increasing thiourea application rate (Figure 3). For example, the total leaching loss of propachlor from the sand columns accounted for approximately 69%, 46%, and 32% of the applied amount, respectively, in columns amended with a 1:8, 1:25, and 1:50 molar ratio of propachlor to thiourea (Figure 3). These results clearly illustrate that thiourea is effective in reducing propachlor residues in soil and provides a strategy to decrease pesticide contamination.

In the second experiment, the distribution of propachlor in saturated sand columns was studied in the presence and absence of thiourea (Figure 4). The transformation of propachlor and thiourea in sand columns decreased propachlor residues in the reaction zone. Higher thiourea rates increased degradation, resulting in lower propachlor concentrations throughout the sand columns (Figure 4). For example, in the absence of thiourea, the maximum concentration of propachlor was approximately 0.030 mmol/kg. In comparison, the maximum concentration of propachlor in sand amended with thiourea at a 1:50 propachlor:thiourea was reduced by 60% relative to the control. Note that in the thiourea-amended columns, the peak concentrations occurred at shallower depths compared to the control columns. The change of profile of the propachlor concentration may be attributed to the integrated results of sorption and reaction of propachlor and thiourea in the columns. These results further indicate that the remediation of thiourea may improve the retention of herbicide contaminants and reduce their leaching to groundwater.

Environmental Significance. Thiourea served as a chemical remediation reagent that could potentially clean up

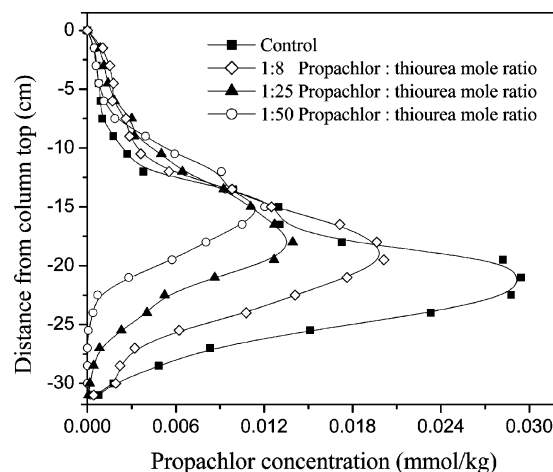


FIGURE 4. Influence of thiourea amendment levels on concentration profiles of propachlor in sand columns.

residues of propachlor in soil and aquatic environments via a nucleophilic substitution reaction. Thiourea was found to be much more reactive in soil than in solution due to a catalytic reaction mechanism, which suggested that thiourea has a higher potential to decontaminate soils polluted by halogenated pesticides. Recently, thiourea has been recommended for agricultural use to inhibit nitrification by retarding the oxidation of $\text{NH}_4^+ -\text{N}$ to $\text{NO}_2^- -\text{N}$ by *Nitrosomonas* sp. (21, 33). Compared to other nonselective chemical remediation reagents, such as ozone and hydrogen peroxide, which might alter the soil-environmental system, thiourea has great potential to detoxify electrophilic contaminants with less effect on the ecosystem. Because typical application rates of nitrification inhibitors are at the milligram per kilogram soil level (22, 34), thiourea is likely to control pesticide residues, which often occur at the microgram per kilogram soil level. Therefore, soil application of thiourea may not only minimize fertilizer N loss but may also reduce some pesticide residues. To better understand and apply this remediation strategy, further research on the application methods and rates should be conducted, especially in field experiments.

The characteristics of the reaction between thiourea and propachlor indicate that many other halogenated organic contaminants may also be degraded via this remediation process. Similar to many reduced sulfur nucleophiles such as thiosulfate (10), bisulfide, and polysulfides (11), thiourea may react with the other widely used chloroacetanilide pesticides such as alachlor, metolachlor, and acetochlor by a similar reaction process. The reaction between thiourea and propachlor may serve as an abiotic model of electrophilic contaminant transformation with thiourea or related sulfur nucleophiles. Thus, the significance of this reaction may be much greater than the single example presented in this work. Furthermore, the accelerated transformation reaction in thiourea-amended soil suggests that soil application of thiourea may be effective in numerous situations where nonpoint and point source contamination occurs due to improper disposal and accidental discharge to soil.

Acknowledgments

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Supporting Information Available

A figure showing EI mass spectra of transformation product and methylated substituted product obtained in reaction of propachlor with thiourea. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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