



Impact of atrazine and nitrogen fertilizers on the sorption of chlorotoluron in soil and model sorbents

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Abstract

Sorption of chlorotoluron in ammonium sulfate, urea and atrazine multi-solutes system was investigated by batch experiments. The results showed application of nitrogen fertilizers to the soil could affect the behavior of chlorotoluron. At the same concentration of N, sorption of chlorotoluron decreased as the concentration of atrazine increased on the day 0 and 6 in soil, respectively. The sorption of chlorotoluron increased from 0 to 6 d when soils were preincubated with deionized water, ammonium sulfate and urea solution for 6 d. That indicated incubation time was one of the most important factors for the sorption of chlorotoluron in nitrogen fertilizers treatments. The individual sorption isotherms of chlorotoluron in rubbery polymer and silica were strictly linear in single solute system, but there were competition sorption between pesticides or between pesticides and nitrogen fertilizers. That indicated the sorption taken place by concurrent solid-phase dissolution mechanism and sorption on the interface of water-organic matter or water-mineral matter.

Key words: sorption; chlorotoluron; atrazine; nitrogen fertilizer; competitive

Introduction

Most of the past information in the literature for the fate of pesticides in soil deals with a single pesticide (Nkedi-Kizza and Brown, 1998). However, in many agricultural situations, fertilizers and several pesticides are applied to soil within a growing season to provide nutrients for crop and to control weeds and pests. In multi-solutes system, an interaction between pesticide and pesticide is likely meaning sorption, degradation and transformation of multiple pesticides system differ from that in a system with only a single pesticide. Fortunately, the fate of pesticide in multi-solutes system has been concerned at present.

A few studies that deal with sorption of multi-solutes system have been considered in soil or model sorbents. Liu *et al.* (1995a, b) have shown that ammonia-induced changes in both pH and dissolved organic carbon (DOC) concentration appeared to influence atrazine adsorption and mobility characteristics. Singh (2003) studied the impact of organic manure and urea on the sorption and mobility of metolachlor. They found that both cow manure and urea applications increased metolachlor sorption in soil. Nkedi-Kizza and Brown (1998) have shown a decrease in the K_f value in a mixture with diuron and atrazine in subsoil (Red Bay), suggesting the competitive sorption between diuron and atrazine. The competitive sorption was tested between atrazine and cyanazine, prometon in soil and model sorbents. The competitive sorption was

attributed to dual-model sorption, in which partitioning could occur concurrently with specific interaction (Xing *et al.*, 1996).

Both chlorotoluron (CT) and atrazine (AT) are pre- or early post-emergence herbicide widely used to control annual grasses and broad-leaved weeds. Sorption and desorption of chlorotoluron in single solute have been studied in the past (Madhun *et al.*, 1986; Fouqué-Brouard and Fournier, 1996; Altfelder *et al.*, 1999; Konstantinou and Albanis, 2000), but sorption of chlorotoluron has not been reported in multi-solutes system. The objective of this study was to assess the impact of atrazine and nitrogen fertilizers on the sorption of CT in soil and model sorbents that include rubbery polymer, glassy polymer and macroporous silica.

1 Materials and methods

1.1 Soil samples

Soil samples (0–30 cm) were taken from suburban farmland of Tianjin. This site had no pesticide application prior to the collection of soil sample. These soils were air-dried and passed through a 2-mm sieve. Selected properties of soil in this study are listed in Table 1. Specific surface area and average pore size of soil were determined with Quantachrome NOVA automated gas sorption system report. Temperature of system was 77.4 K, nitrogen had been used as a sorbent, area of X-sec was 0.162 nm²/molecule, degassing temperature was 120°C and time of determine was 533.7 min.

Table 1 Selected properties of the soils studied

Soil depth	pH	Specific surface area (m ² /g)	Average pore size (nm)	Organic matter (g/kg)	Mechanical analysis (%)		
					Sand	Silt	Clay
0–30 cm	8.09	44.16	4.55	17.5	10.78	50.29	38.69

1.2 Pesticides

CT 97.0% purity was supplied by Kuaida Stock Company of Jiangsu, Limited (Jiangsu, China). AT 97.5% purity was supplied by Zhongshan Chemical Company, Limited (Zhejiang, China). The properties of CT and AT are given in Table 2.

1.3 Fertilizers

The fertilizers included ammonium sulfate (AS) and urea (UR) with a nitrogen content of 21% and 46%, respectively. They were purchased from Daomao Chemical Co. of Tianjin (Tianjin, China) and Kewei Company of Tianjin University (Tianjin, China), respectively.

1.4 Model sorbents

Crystallite cellulose was purchased from Shanghai Hengxin Chemical Co. Ltd. (Shanghai, China). X-5 resin was purchased from Nankai University Chemical Company (Tianjin, China). Macroporous silica was purchased from Qingdao Haiyang Company, Limited (Shandong, China). Specific surface area of crystallite cellulose, X-5 resin and macroporous silica was 2.06, 500–600, 300–550 m²/g, respectively; and average pore size of them was 5.83 nm, 29–30 nm and 8.0–10.0 nm, respectively. Average pore sizes of model sorbents were supplied by Chemical Company.

1.5 Sorption kinetic curves of CT in single and multi-solutes system in soil

The rate of CT sorption versus time was measured by batch experiments. Five grams of dry soil was equilibrated with 10 ml of CT, CT-AS, CT-UR and CT-AT solution, respectively. The concentration of CT, AT and nitrogen fertilizers was 1.6, 1.0, 500 µg/ml, respectively. The centrifuge tubes were airproofed by lids and polyethylene tape for avoiding volatilization. The samples included insterilized and sterilized treatments. They were shaken with a reciprocating shaker in darkness at 23±2°C. At different times (5, 20, 60 min etc.), the samples were centrifuged at 5000 g for 15 min. Finally, the equilibration concentration of CT was analyzed by HPLC. All experiments were done in triplicate.

1.6 Sorption of CT in tri-solute systems in soil and model sorbents

Five grams soil was placed in a centrifuge tube, and 5 ml of AS or UR treatment solution was added into

different centrifuge tubes at time 0, respectively. The nitrogen fertilizers were applied at 0, 2600 µg N/ml. Five milliliters of CT-AT solution were added immediately (this time/moment was considered as day 0) and 6 d after the fertilizers applied.

Two grams of model sorbents were treated as described soil amended with fertilizers at 0 d. Blanks without soil or model sorbent did not indicate sorption to the plastic tubes.

The CT and AT concentrations were 0.4, 0.8, 1.2, 1.6, 2.0 µg/ml and 0 (deionized water), 0.5, 1.0 µg/ml, respectively. Sodium azide 0.02% was added as a biocide. All experiments were done in triplicate. The centrifuge tubes were airproofed by lids and polyethylene tape for avoiding volatilization. The samples were shaken with a reciprocating shaker in darkness at 23±2°C. The samples were centrifuged and analyzed as described above after equilibrium. Sorbed concentrations were calculated from measured solution concentrations by difference, taking into account the loss of solute mass resulting from the removal of solution.

The suspension pH and dissolved organic carbon (DOC) were determined in parallel experiments without CT. The suspension pH was determined by ORP-431 (Shanghai Dapu Instrument Co. Ltd., China). DOC was determined by TOC (V_{CSH}, Shimadzu, Japan).

1.7 Liquid chromatograph system

HPLC analysis was performed with Agilent 1100 Liquid Chromatograph equipped with an ultraviolet detector (G1314VWD). The analysis was performed on a C₁₈ reversed-phase column (3.9 mm × 150 mm, Waters). The mobile phase was a mixture of methanol, Milli-Q water and acetic acid (60 : 40 : 0.1 v/v/v), the flow rate was 1 ml/min, and injected volume was 20 µl. The wavelength of maximum absorption of chlorotoluron was 245 nm and typical retention time was 4.95 min. The limit of detection was 0.1 µg/g chlorotoluron was quantified with external standard.

2 Results and discussion

2.1 Sorption kinetic curves of CT in single and multiple media system

All the sorption data are described by the Freundlich equation, and the data from blanks indicates no sorption of CT on centrifuge tubes. The equilibriums were attained practically with 20 h in single and multiple systems

Table 2 Physical and chemical properties of the herbicides

Common name	Molecular weight	lgK _{ow}	pK _a	Half-life (d)	Solubility in water (mg/L)
Atrazine	215.7	2.3–2.7	1.7	60	35
Chlorotoluron	212.7	2.41	Non-ionised	30	74

(Fig. 1a). Sorption of CT followed a rapid sorption phase in which the amount of adsorbed herbicide increased rapidly (rapid sorption), then it became slowly with the increasing of time (slow sorption). Sorption was known to occur within a few minutes following addition of the chemical to soil, whereas slow sorption may take much longer to become important. This time span was likely to be in the range of month or even years.

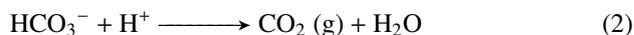
CT concentration was higher in sterilized treatments than that of CT in insterilized treatments (Fig.1). This indicated a portion CT was degraded by microorganism during the process of sorption. Moreover, the activity of microorganism became strongly with increasing of contact time between soil and CT. We also observed CT concentration decreased in insterilized soil solution during experiment process, especially in single system. However, CT concentration had scarcely any change in sterilized solution. So sodium azide was added as a biocide to reduce the effect of microorganism on the sorption. On the other hand, the concentration of CT without any change in 15 d and 24 h was chosen as equilibrium time to complete sorption.

2.2 Impact of nitrogen fertilizers on soil pH and DOC content

Application of nitrogen fertilizers to the soil might change its physicochemical properties, which in turn might influence herbicide behavior. From Table 3, solution pH decreased 0.11–0.24 units in AS-treated soil, however, pH increased about 0.5 units in UR-treated soil. AS is chemical and physiological acid fertilizer that could decrease pH after it was applied into soil. However, reaction products from urea hydrolysis caused change of soil pH whose reaction mechanism was different:



and CO₂ resulted from further reaction of HCO₃⁻ with H⁺ in soil,



Both Reactions (1) and (2) consumed H⁺ and, therefore, raised soil pH. At soil pH<8, most of the inorganic C released from urea by hydrolysis would diffuse from the soil as CO₂, consuming two H⁺ in the overall progress; when pH>8, some of C from urea hydrolysis might not form CO₂ but may remain as HCO₃⁻ or CO₃²⁻ species in the soil, thereby resulting in less H⁺ consumes per NH₄⁺ forms (Kissel *et al.*, 1988).

Application of AS to soil, the content of soil solution DOC decreased, however, it increased in UR-treated soil solution. The content of DOC decreased in AS treatment at day 0 and 6 d when compared to the control, however, it increased in urea treatment. After 6 d incubation, the concentration of DOC in AS-treated solution was more than the concentration of DOC at the day 0, while it was inversely in UR treatments. That may be because urea caused the release of organic matter from the soil matrix, increasing DOC in solution (García-Valcárcel and Tadeo, 2003) or urea hydrolysis. The primary cause should be investigated further.

2.3 Impact of AT and nitrogen fertilizers on the sorption of CT in soil

At the same concentration of nitrogen, K_f values of CT decreased as the concentration of AT increased at the day 0 and 6. Moreover, K_f values also decreased with increasing of N concentration when the concentration of AT was the same. On the other hand, the sorption of CT increased from 0 to 6 d when soils were preincubated with deionized water, AS and UR solution for the day 6, respectively (Fig.2).

Although the content of solution DOC was different, the sorption was no significant difference at the same concentration of AT and same incubation time. Application of nitrogen fertilizers to soil may influence soluble organic carbon decomposition in laboratory (Chantigny *et al.*, 1999). Schnitzer (Singh, 2003) proposed that various soil

Table 3 Impact of nitrogen fertilizers on soil pH and solution DOC content

Soil	Treatment	Soil pH		Solution DOC (mg/L)	
		day 0	day 6	day 0	day 6
0–30 cm	Control	7.95	8.03	87.0	90.9
	AS	7.84	7.79	46.2	63.4
	UR	8.36	8.47	811.1	251.0

AS: ammonium sulfate treated soil; UR: urea treated soil.

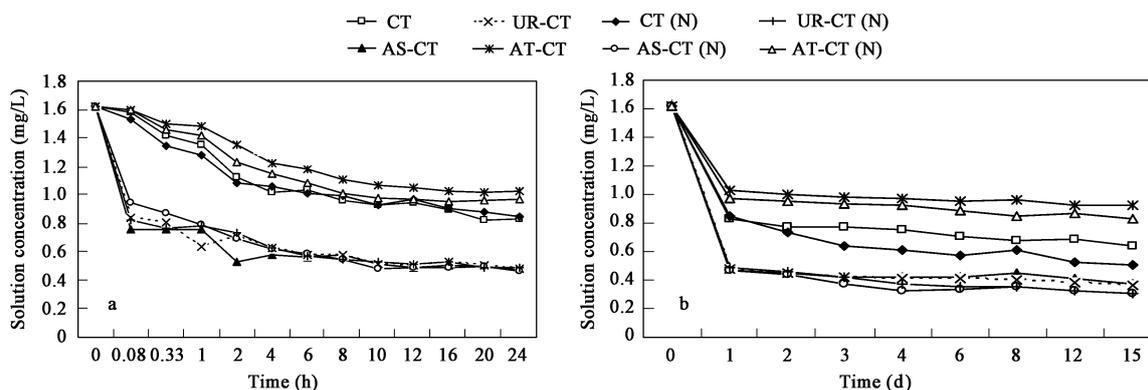


Fig. 1 Kinetic curves of chlorotoluron in single and multi-system in sterilized and insterilized treatments. (a) 24 h; (b) 15 d. CT: chlorotoluron; UR: urea treated soil; AS: ammonium sulfate treated soil; AT: atrazine; N: insterilized treatments.

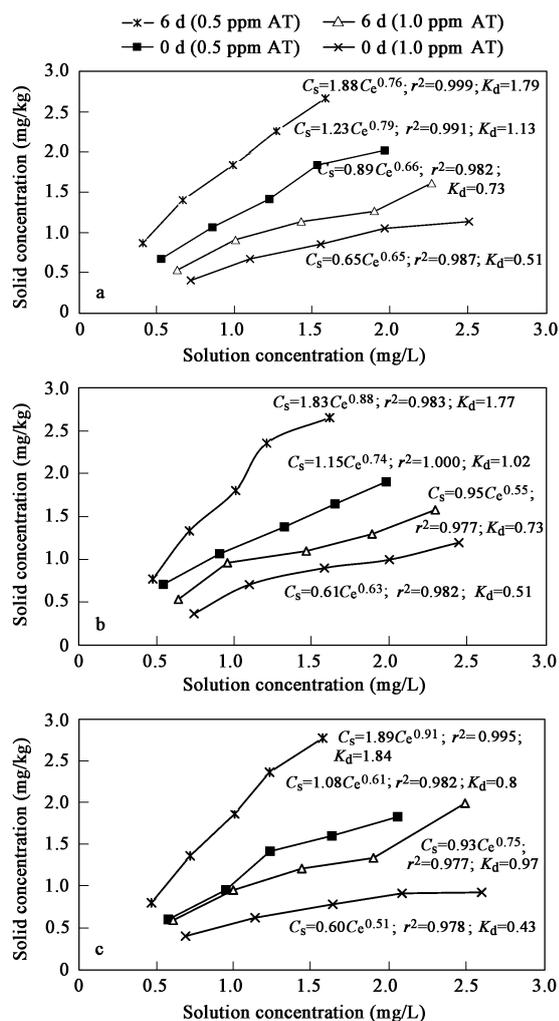


Fig. 2 Sorption isotherms of CT in soil. (a) CT sorption isotherms in CT-AT-water system; (b) CT sorption isotherms in AS-AT-CT system; (c) CT sorption isotherms in UR-AT-CT system.

organic matter components are capable of configurational changes between linear and sphero-colloidal shapes and these transformations are dependent on the ionic nature of the solution. We suggested that might be explained by the nature of DOC from AS-treated and UR-treated soil that may interact with CT. The different type of DOC may

influence the behavior of CT in the soils studied.

If pH or DOC alone control CT behavior in soil, then the impact of AS and UR on the sorption of CT in soil should be dissimilarity. However, sorption of CT increased in AS- and UR-treated soil than in unfertilized soil. So we thought that the sorption of CT was controlled by soil pH and the amount of solution DOC.

2.4 Sorption of CT in model sorbents

Organic matter and mineral of soil are important factors that influence the sorption of pesticides. X-5 resin, cellulose and silica were used to simulate the sorption of CT on "hard" carbon, "soft" carbon and mineral in multi-solutes system.

Glassy polymers have a more rigid, condensed structure, while rubbery polymers have a relatively expanded, flexible structure. The individual isotherm of CT in rubbery polymer was strictly linear in single system, but there were competition sorption between CT and AT or between CT and nitrogen fertilizers (Table 4). The results were inconsistent with solid-phase dissolution mechanism. However, they were consistent with some studies of sorption of both low- and high-polarity compounds in soils had shown nonlinear isotherms (Pignatello, 1991; McGlnley *et al.*, 1993; Frank and James, 1994) and competitive effects (McGlnley *et al.*, 1993).

Table 4 shows that the sorption of CT decreased in AS-treated cellulose with increasing concentration of AT compared to the control. However, the sorption of CT was higher in UR-treated cellulose than that of AS-treated cellulose, and the sorption of CT decreased with increasing of AT concentration. The subunits of cellulose are rich in polar groups $-RC(=O)NH_2$, ROR, and ROH- that might interact specifically with AT compounds by hydrogen bonding, and AT hold in the sorption sites of cellulose thus the sorption of CT decreased with increasing the concentration of AT. Moreover, solution pH and content of solution DOC affected the sorption of CT. Application of AS and UR to cellulose increased the content of solution DOC, however, the changes of pH were different (Table 5). We thought the sorption of CT in cellulose was not controlled singly by solution pH or content of DOC.

Table 4 Chlorotoluron (CT) sorption parameters with nitrogen fertilizers and atrazine (AT) treatments in model sorbents

Model sorbent	Treatment	AT conc. ($\mu\text{g/ml}$)	K_f	n	r^2	K_d
Cellulose	CT ¹	0	4.21	1.00	0.997	4.15
	CT ¹ + AT	0.5	3.83	0.95	1.000	3.76
		1.0	3.66	1.10	0.994	3.68
	CT ¹ + AS ² + AT	0.5	3.60	0.98	0.998	3.57
		1.0	3.19	1.13	1.000	3.42
	CT ¹ + UR ³ + AT	0.5	4.04	0.90	0.999	3.83
1.0		3.82	1.03	0.997	3.87	
Silica	CT ¹	0	10.63	1.00	0.992	10.57
	CT ¹ + AT	0.5	9.93	1.10	0.992	10.19
		1.0	7.91	0.94	0.982	8.23
	CT ¹ + AS ² + AT	0.5	10.22	0.82	0.996	10.75
		1.0	8.27	0.69	0.971	8.40
	CT ¹ + UR ³ + AT	0.5	9.87	0.72	0.994	10.59
1.0		7.64	0.71	0.975	8.48	

CT¹ referred to the concentration of CT was 0.4, 0.8, 1.2, 1.6, 2.0 $\mu\text{g/ml}$; AS² and UR³ referred to the concentration of nitrogen was 2600 $\mu\text{g/ml}$. AS: ammonium sulfate treated soil; UR: urea treated soil.

Table 5 Impact of nitrogen fertilizers on the pH and DOC in solution

Model sorbent	Treatment	N concentration (µgN/ml)	pH	DOC (mg/L)
X-5 resin	Water	0	7.54	139.6
	AS	2600	7.32	515.5
	UR	2600	7.70	1177.0
Cellulose	Water	0	5.30	177.0
	AS	2600	5.02	558.3
	UR	2600	5.49	1390.0
Silica	Water	0	5.55	248.0
	AS	2600	5.05	1834.5
	UR	2600	5.80	2754.5

AS: ammonium sulfate treated soil; UR: urea treated soil.

In contrast to the rubbery polymers, the sorption of CT in X-5 resin was the strongest. No CT was detected in solution when X-5 resin was a sorbent, indicating that it had strong sorption capacity for CT. A reasonable explanation was that X-5 resin had bigger specific surface area and pore structure than cellulose. Other possible reasons were solution pH and content of DOC. From Table 5, solution pH was greater in X-5 resin than that of in cellulose, however, content of DOC was less in X-5 resin than that of in cellulose. Impact of pH and content of solution DOC on sorption of CT was simultaneous.

The sorption isotherm of CT was linear in single solute system, and other isotherms were all nonlinear in silica (Table 4). CT sorption decreased with increasing of AT concentration. This showed AT competed with CT for sorption sites. CT was weakly polar molecule and incapable of H-bonding. AT adsorbed closer to the surface because the azo and amino nitrogens can act as H-bond acceptors with $\equiv\text{Si}-\text{OH}$ groups or strongly adsorbed water molecules. Tertiary amines form strong H-bonds to $\equiv\text{Si}-\text{OH}$ groups on dry silica (Xing *et al.*, 1996). On the other hand, sorption of CT decreased in UR treatment when compared to the control at the same concentration of AT. However, CT sorption increased in AS treatment when compared to the control at the same concentration of AT. The results also indicated application of nitrogen fertilizers influenced the sorption of CT in model sorbents.

Different regions of a soil or sediment matrix might contain different types, amounts, and distributions of surfaces and of soil organic matter, even at the particle scale. A variety of different classes of reactions between organic solutes and types of solid surfaces and quasi-solid organic matrices typical of those associated with environmental solids have been identified (Weber *et al.*, 1992). So the sorption took place by concurrent solid-phase dissolution mechanism and sorption on the interface of water-organic matter or water-mineral matter.

References

- Altfelder S, Streck T, Richter J, 1999. Effect of air-drying on sorption kinetics of the herbicide chlorotoluron in soil[J]. *J Environ Qual*, 28: 1154–1161.
- Chantigny M H, Angers D A, Prévost D, 1999. Dynamics of soluble organic C and C mineralization in cultivated soils with varying N fertilization[J]. *Soil Biology and Biochem*, 31: 543–550.
- Fouqué-Brouard C M, Fournier J M, 1996. Adsorption-desorption and leaching of phenylurea herbicides on soils[J]. *Talanta*, 43: 1793–1802.
- Frank C S, James W B, 1994. Thermodynamics of organic chemical partition in soils. 2. Nonlinear partition of substituted phenylureas from aqueous solution[J]. *Environ Sci Technol*, 28: 996–1002.
- García-Valcárcel A I, Tadeo J L, 2003. Influence of organic fertilizer application on pendimethalin volatilization and persistence in soil[J]. *J Agri Food Chem*, 51: 999–1004.
- Kissel D E, Cabrera M L, Ferguson R B, 1988. Division S-8-fertilizer technology and use? Reactions of ammonia and urea hydrolysis products with soil[J]. *Soil Sci Soc Am J*, 52: 1793–1796.
- Konstantinou I K, Albanis T A, 2000. Adsorption-desorption studies of selected herbicides in soil-fly ash mixtures[J]. *J Agri Food Chem*, 48(10): 4780–4790.
- Liu Z J, Clay S A, Clay D E *et al.*, 1995a. Ammonia fertilizer influences atrazine adsorption-desorption characteristics[J]. *J Agric Food Chem*, 43: 815–819.
- Liu Z J, Clay S A, Clay D E *et al.*, 1995b. Ammonia impacts on atrazine leaching through undisturbed soil column[J]. *J Environ Qual*, 24: 1170–1173.
- Madhun Y A, Freed V H, Young J L *et al.*, 1986. Sorption of bromacil, chlorotoluron, and diuron by soils[J]. *Soil Sci Soc Am J*, 50: 1467–1471.
- McGinley P M, Katz L E, Weber W J, 1993. A distributed reactivity model for sorption by soils and sediments. 2. Multicomponent systems and competitive effects[J]. *Environ Sci Technol*, 27: 1524–1531.
- Nkedi-Kizza P, Brown K D, 1998. Sorption, degradation, and mineralization of carbaryl in soils, for single-pesticide and multiple-systems[J]. *J Environ Qual*, 27: 1318–1324.
- Pignatello J J, 1991. In: *Organic substances and sediments in water*[M]. Chelsea, MI.: Lewis Publishers. Vol. 1, Chapter 16.
- Singh N, 2003. Organic manure and urea effect on metolachlor transport through packed soil column[J]. *J Environ Qual*, 32: 1743–1749.
- Weber W J, McGinley P M, Katz L E, 1992. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments[J]. *Environ Sci Technol*, 26: 1955–1962.
- Xing B S, Pignatello J J, Gigliotti B, 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents[J]. *Environ Sci Technol*, 30: 2432–2440.