## The impact of nitrogen fertilizers on degradation and leaching of chlorotoluron in soil

Minling Gao[a]; Shugui Dai[a]; Yongmin[b]
[a] College of Environmental Science and Technology, Nankai University, Tianjin, China [b] Center of Disease Control and Prevention, Tianjin, China

## PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

# The impact of nitrogen fertilizers on degradation and leaching of chlorotoluron in soil

MINLING GAO†, SHUGUI DAI*† and YONGMIN MA‡

†College of Environmental Science and Technology, Nankai University,
Tianjin, China, 300071
‡Center of Disease Control and Prevention, Tianjin, China, 300011

The effect of ammonium sulphate and urea on the degradation and leaching of chlorotoluron in soil was studied under laboratory conditions. The degradation rate of chlorotoluron increased with increasing soil depth. Adsorbed chlorotoluron desorbed readily from subsurface soil because the content of clay and soil organic matter was lower in subsurface soil than in topsoil. After ammonium sulphate and urea were applied to the soil, the degradation of chlorotoluron became slower than that in the untreated soils with fertilizers. Moreover, the degradation of chlorotoluron was faster for all the depths examined with soils amended with urea than for all the depths examined with soils amended with ammonium sulphate. Chlorotoluron was mobile in soils when using non-aged and aged soil columns in different treatments, with mobility increasing in the order ammonium sulphate treatments < urea treatments < control. The results indicated that ammonium sulphate and urea reduced chlorotoluron leaching losses. On the other hand, more chlorotoluron remained in the aged soil columns than in non-aged soil columns, indicating that the mobility of chlorotoluron decreased in aged treated soils.

*Keywords:* Chlorotoluron; Nitrogen fertilizer; Degradation; Persistence; Leaching

## 1. Introduction

Degradation and leaching of herbicides are important processes determining the fate of pesticides in the environment, and these have been of great concern in recent years. Assessing the mobility and degradability of pesticides has rapidly become an indispensable part of studies concerning the environmental safety of pesticides present in soil [1].

Nitrogen fertilizers are used in agricultural practice and applied at approximately the same time as herbicides. The fate of herbicides in soil may be affected by the fertilizer

*Corresponding author. Fax: +86-22-23504821. Email: sgdai@nankai.edu.cn

application, since they could influence such processes as adsorption, degradation, mobility, and transformation. For example, Liu *et al.* [2, 3] reported that application of ammonia fertilizer increased soil pH and dissolved organic carbon (DOC) content, resulting in a decrease in atrazine adsorption in soil. This result indicated that atrazine movement through ammonia-treated soil columns was enhanced. Singh [4] reported that co-application of metolachlor and organic manure-urea reduced metolachlor mobility and leaching losses in soil. Ammonia-based fertilizers such as anhydrous ammonia and urea initially increase soil pH and cause the release of organic matter (OM) from the soil matrix, increasing DOC in solution [5]. Moreover, nitrogen salts contained in fertilizers are also species that could react directly with the pesticide, forming degradation products being potentially transported outside the area of application [6].

Chlorotoluron (3-(3-chloro-*p*-tolyl)-1,1-dimethylurea) is a phenylurea herbicide for pre- or post-emergence control of annual grass and annual broad-leafed weeds in winter cereals (barley, wheat). Its solubility in water and log $K_{ow}$ is $74 \, mg \, L^{-1}$ and 2.4, respectively [7]. Degradation and leaching of chlorotoluron in bare soil have been reported in the past [8–13]. However, no information is available in the literature on its environmental fate in the presence of nitrogen fertilizers.

The objectives of this study were (1) to determine the degradation rate of chlorotoluron at different soil depths in bare and amended soil systems and (2) to discuss the effect of ammonium sulphate, urea, and ageing time on chlorotoluron leaching in soils.

## 2. Experimental

### 2.1 *Soil samples*

Soil samples were collected from a suburban farmland of Tianjin, China. This site had no history of pesticide application prior to the collection of soil samples. Materials were taken from the upper layer (0–30 cm), middle layer (30–60 cm), and subsurface soil (60–100 cm) of the soil profile by digging with different sterilized shovels. Then, the samples were put into sterilized stainless containers. These soils were air-dried and passed through a 2-mm sieve. Selected properties of these soils are listed in table 1.

Table 1. Selected properties of the soils studied.

| Soil depth (cm) | Field water-holding capacity (FC)% | pH | OM (%) | Mechanical analysis (%) | | |
|---|---|---|---|---|---|---|
| | | | | Sand | Silt | Clay |
| 0–30 | 28.42 | 8.09 | 1.75 | 10.78 | 50.29 | 38.69 |
| 30–60 | 34.98 | 8.00 | 1.31 | 5.50 | 69.10 | 25.26 |
| 60–100 | 25.61 | 7.89 | 0.86 | 58.22 | 25.87 | 15.59 |

## 2.2 *Chemicals*

Chlorotoluron (CT) 97% purity was supplied by Kuaida Stock Company of Jiangsu (Jiangsu, China). The fertilizers were ammonium sulphate (AS) and urea (UR), with a nitrogen content of 21% and 46%, respectively. They were purchased from Daomao Chemical Company of Tianjin (Tianjin, China) and Kewei Company of Tianjin University (Tianjin, China), respectively.

## 2.3 *Liquid chromatography*

An HPLC analysis was performed in an Agilent 1100 liquid chromatograph equipped with an ultraviolet detector (G1314VWD). The analysis was performed on a $C_{18}$ reversed-phase column ($3.9 \times 150$ 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$^{-1}$, and the injected volume was $20\,\mu$L. The wavelength of maximum absorption of chlorotoluron was 245 nm, and the typical retention time was 4.95 min. Chlorotoluron was quantified using the external standard method.

## 2.4 *Soil degradation*

Five portions of 300 g soil from each depth were weighed and put into each of five sterilized beakers, then amended with 60 mL methanol solution containing chlorotoluron to achieve an initial concentration of $20$ mg kg$^{-1}$ in each beaker (numbered 1–5). The samples were mixed thoroughly with different sterilized plastic shovels. Further, the beakers were placed in a hood for 24 h, and stirred once every 1 h with different plastic sterilized shovels to allow the methanol to volatilize and ensure thorough mixing of pesticides with the soil. In order to adjust the soil moisture level to approximately 60% of filed capacity (FC) into each beaker, distilled water and the corresponding solution of nitrogen fertilizers (AS or UR) were added into the beakers. To maintain the moisture level, water was added when necessary. The concentration of nitrogen was 1300 and 2600 mg of N per kilogram of soil (indicated hereafter by subindex 1 and 2, respectively). The beakers were sealed with plastic film and kept in the dark at $23 \pm 1°$C to allow aging for 1, 3, 6, 10, 17, 24, 38, 52, and 66 days. All experiments were done in duplicate.

## 2.5 *Analysis of soil samples*

Ten grams of soil from each depth were weighed and put into each of five beakers, then amended with chlorotoluron water solution to yield concentrations of 1, 5, 10, 15, and $20$ mg kg$^{-1}$ in each beaker, respectively. These samples were shaken for 45 min with 20 mL of methanol for liquid chromatography. After shaking, all samples were centrifuged (3600 rpm, 15 min), and the herbicide in the clear supernatants was measured directly by HPLC. The recoveries were 93.43, 90.39, and 93.78% for 0–30 cm, 30–60 cm, and 60–100 cm of soil, respectively.

For every aging time, duplicate samples (10 g of dry soil) were removed from each treatment. These samples were shaken, centrifuged, and measured directly by HPLC as described above.

## 2.6 *Soil columns leaching*

**2.6.1 Non-aged soils.** The air-dried and sieved soils (about 2 kg at each depth) were packed into PVC plastic hollow columns (110 cm × 7.5 cm i.d.). The bottom of the soil columns were placed inside a PVC plastic funnel containing a nylon membrane (40 µm effective pore size) and 100 g of sand for columns support. Before use, the sand was acid-washed with 6 M $H_2SO_4$ to remove DOC and rinsed with deionized water to obtain near-neutral pH. The soil columns were saturated with deionized water from bottom to top to remove the entrapped air. The difference between the weight of the saturated soil column and its dry column was used to calculate the value for the pore volume.

Three hundred grams of topsoil was treated with 60 mL of a 100 µg mL$^{-1}$ chlorotoluron methanolic solution, thoroughly mixed, and air-dried. After addition of ammonium sulphate and urea to a portion of each contaminated soil (50 g), the samples were mixed thoroughly in a beaker and added to the top of the soil columns. Distilled water (25 mL) was also added. Nitrogen fertilizer concentrations were 0, 1300, and 2600 mg of N per kilogram of soil. Then, acid-washed the sand and filter paper were placed on the surface to reduce drying by subsequent diffusion of nitrogen fertilizers from the surface. The soil columns were eluted at room temperature with 100 mL of distilled water every day for 30 days and leachates collected. Each test was done in duplicate. After leaching experiments, the columns were sliced into 10 segments of 10 cm each and the soils air-dried. Soil samples (5 g) were extracted with 10 + 10 mL methanol as described above.

**2.6.2 Aged soils.** Three hundred grams of topsoil were treated with chlorotoluron at the same rate as that used for non-aged soils, and then the soil moisture level adjusted to approximately 60% of FC with distilled water. The treated soils were placed in a glass beaker and then incubated for 66 days in the dark. After the incubation period, the soils were air-dried, and then the treated soils (50 g) were placed on the top layer of the soil columns. The soil columns were treated with fertilizers and eluted as described in the non-aged soil study. Each column was done in duplicate.

## 2.7 *Analysis of water samples*

About 1200 mL of leachates for each column was collected. One hundred millilitres was extracted with 20 + 20 + 10 mL of $CH_2Cl_2$ and concentrated to dryness. The residues were then redissolved with 2 mL of methanol for HPLC analysis. The samples were determined by HPLC as described above. The recoveries of chlorotoluron from water with concentrations of 0.2, 0.5, 1.0, and 2.0 mg L$^{-1}$ were in the range of 75–80%.

## 3. Results and discussion

### 3.1 *Degradation of chlorotoluron*

The pesticide degradation in soil can be described with the first-order kinetic equation as $dC/dt = -kC_0$. From this equation, we can obtain the following equations:

$$C = C_0 \exp(-kt) \tag{1}$$

Table 2. Chlorotoluron degradation rate coefficients.

| Soil depth (cm) | Degradation parameters | Treatments | | | | |
|---|---|---|---|---|---|---|
| | | CT[a] | CT + AS$_1$ | CT + AS$_2$ | CT + UR$_1$ | CT + UR$_2$ |
| 0–30 | $k$ (day$^{-1}$) | 0.0047 | 0.0037 | 0.0041 | 0.0042 | 0.0044 |
| | $R^2$ | 0.8530 | 0.8191 | 0.7023 | 0.7175 | 0.7679 |
| | $t_{1/2}$ (day) | 147 | 187 | 169 | 165 | 157 |
| 30–60 | $k$ (day$^{-1}$) | 0.0050 | 0.0040 | 0.0046 | 0.0045 | 0.0049 |
| | $R^2$ | 0.8358 | 0.7896 | 0.7353 | 0.8534 | 0.8585 |
| | $t_{1/2}$ (day) | 138 | 173 | 150 | 154 | 141 |
| 60–100 | $k$ (day$^{-1}$) | 0.0061 | 0.0046 | 0.0052 | 0.0047 | 0.0055 |
| | $R^2$ | 0.8164 | 0.7843 | 0.8712 | 0.9329 | 0.9245 |
| | $t_{1/2}$ (day) | 113 | 150 | 133 | 147 | 126 |

[a] CT: treatment with chlorotoluron without fertilizer application.

$$t_{1/2} = \frac{0.693}{k}, \qquad (2)$$

where $C$ is the concentration of chlorotoluron in the soil (mg kg$^{-1}$), $k$ is the degradation rate constant (per day), $C_0$ is the initial concentration of chlorotoluron in the soil (mg kg$^{-1}$), and $t_{1/2}$ is the half-life (days). The degradation parameters of chlorotoluron are listed in table 2.

The herbicide concentration decreased with increasing incubation time in all treatments. The degradation of chlorotoluron was faster in the untreated soil during the entire assay than in the soil treated with nitrogen fertilizers. These results showed that the application of ammonium sulphate and urea to soil slowed down the herbicide dissipation and increased the half-life of chlorotoluron in soils. Moreover, the half-life of chlorotoluron decreased when the concentration of nitrogen increased from 1300 to 2600 mg N per kilogram of soil at all the different depths studied. However, it was still longer than in the untreated soil.

Our former experiments showed that chlorotoluron adsorption increased after ammonium sulphate and urea were added to the soil, leading to higher chlorotoluron levels in soil, which was protected from degradation. Second, the addition of chemical fertilizers could affect the soil properties. Ammonium sulphate decreased the soil pH and dissolution of soil DOC [14], whereas urea had the opposite effect [4, 5, 14]. If pH or DOC alone controlled chlorotoluron behaviour in soil, then the effect of ammonium sulphate and urea on the degradation of chlorotoluron in soil should be different. However, the half-life of chlorotoluron increased in ammonium-sulphate- and urea-treated soil compared with the unfertilized soil. On the other hand, the amount of microbes, varieties, and activity may be affected by nitrogen fertilizers [15, 16], prolonging the half-life of chlorotoluron in fertilized soil.

A longer half-life for chlorotoluron was observed in ammonium-sulphate-treated soil than in urea-treated soil. Two mechanisms could be suggested to explain this behaviour: interactions between $NH_4^+$ and herbicide molecules were stronger in ammonium-sulphate-treated soil than in urea-treated soil, or the reaction mechanisms of ammonium sulphate–chlorotoluron and urea–chlorotoluron were different. The mechanisms need to be investigated further.

From table 2, we also observed that chlorotoluron was more persistent in topsoil than in subsoil for a single system, as well as chlorotoluron and nitrogen fertilizer

mixture systems. Chlorotoluron desorbed readily from sandy soil, probably owing to its macroporous nature, consequently leading to more extensive degradation. On the other hand, the sorption of chlorotoluron decreased because the content of OM in subsurface soil was lower than that in topsoil [17], resulting in an increase in chlorotoluron degradation in subsurface soil. Li et al. [18] found that the degradation rate of chlorotoluron was faster in sandy soil than in light- and mid-soils because degradation was greatly influenced by the content of clay and their cation-exchange capacity.

Half-lives were longer in the mixture systems than for chlorotoluron alone at different soil depths. In general, for a given soil, differences in half-life were more pronounced between single and multiple media systems than between topsoil and subsoil.

Reported laboratory half-life values for chlorotoluron degradation in the literature ranged from 28 to 56 days at 25°C [8], from 10 to 74 days at 25°C [10], and from 40 to 93 days at 20°C [19]. Values obtained in our experiment were remarkably longer than these results reported in the literature, probably due to the different soil properties.

### 3.2 Impact of nitrogen fertilizers on chlorotoluron leaching

The results of the column leaching experiment for chlorotoluron are shown in figures 1–4. Significant differences in distribution patterns of chlorotoluron in leachates and soil columns were observed among the different treatments.

At the 0–10 cm depth, soil pH showed no change in any of the treatments (table 3). At the 10–20, 20–30, and 30–40 cm depths, pH decreased with increasing soil depth and nitrogen concentration when ammonium sulphate was added to the non-aged and aged soil. However, at the 40–80 cm depth, the soil pH increased above that of the control. Ammonium sulphate treatments had no influence on soil pH below 80 cm. On the other hand, soil pH increased in urea-treated soil columns at 10–70 cm depth and subsequently decreased at 80–100 cm. These results indicated that urea had an influence on the entire soil column pH. The observed increase in pH of the soil columns was
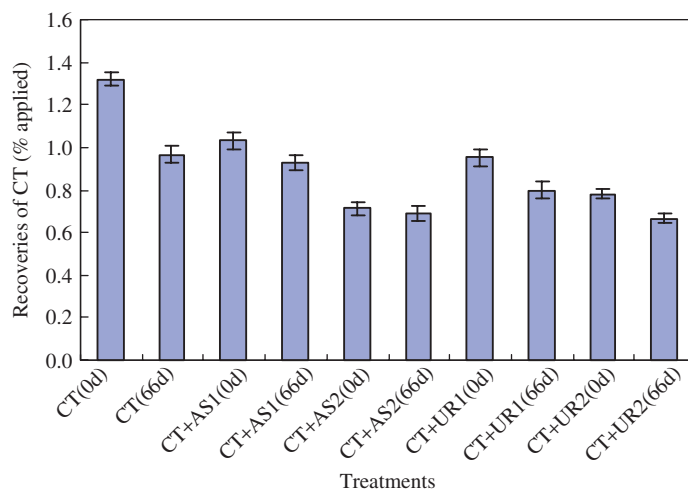


Figure 1. Distribution of chlorotoluron in leachate in all treatments.

probably due to the hydrolysis of urea to ammonia. The differences in pH were significant for different treatments ($p < 0.05$).

Higher recoveries of chlorotoluron in leachate (less chlorotoluron remained in the soil columns) were observed in CT treatment than in soil amended with ammonium sulphate and urea. For an application rate for ammonium sulphate and urea in non-aged soils of $1300 \, mg \, N \, kg^{-1}$, recoveries of chlorotoluron in leachates were 1.03 and 0.93%, respectively, whereas the recovery in bare soil was 1.32%. In the case of aged soils, recoveries were 0.95 and 0.80% in the amended soil, and 0.97% in the untreated soil. The increase to $2600 \, mg \, N \, kg^{-1}$ soil application decreased the leaching losses and
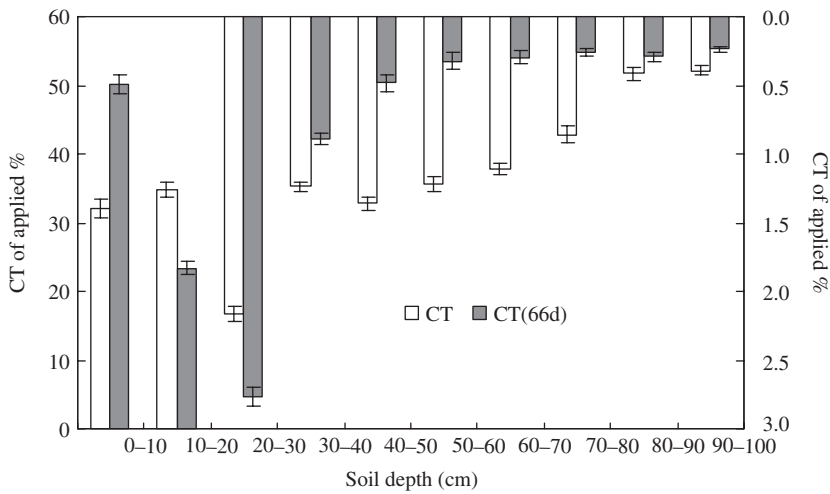


Figure 2.    Distribution of non-aged and aged chlorotoluron in soil columns.
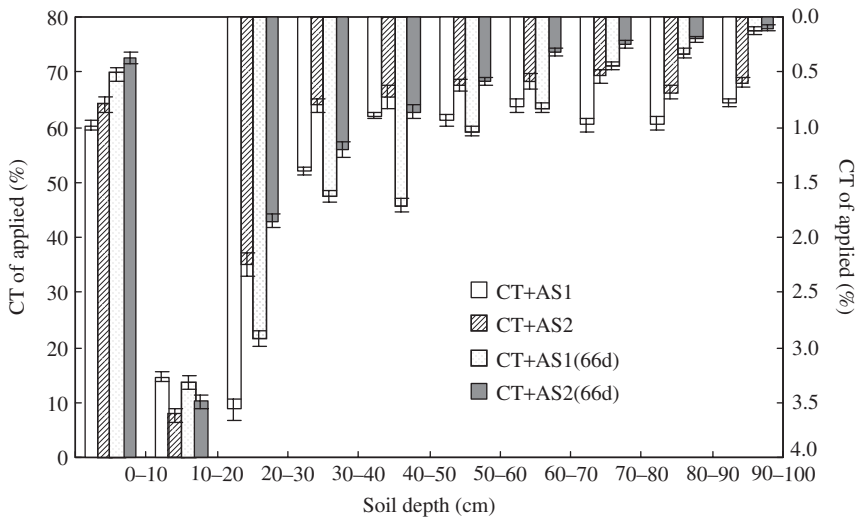


Figure 3.    Distribution of non-aged and aged chlorotoluron in AS-amended soil columns.
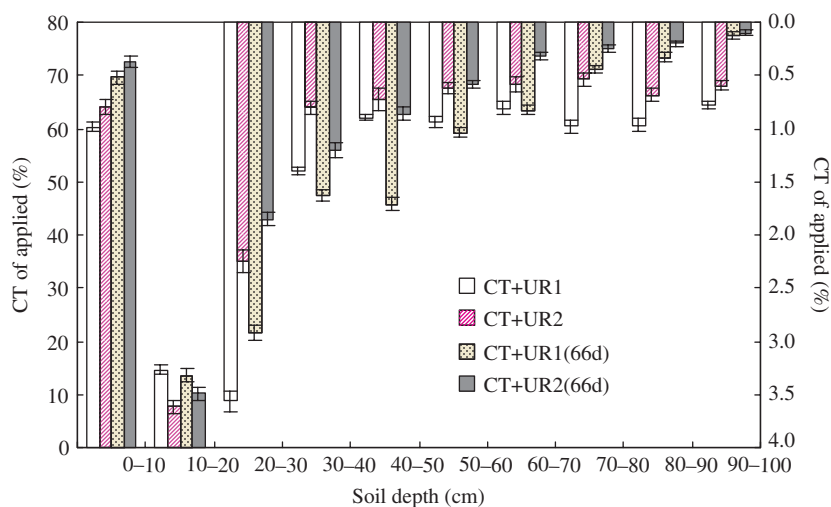
Figure 4.   Distribution of non-aged and aged chlorotoluron in UR-amended soil columns.

Table 3.   Soil pH after leaching ($p < 0.05$).

| Depth (cm) | Non-aged soil columns pH | | | | | Aged soil columns pH | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CT | $CT + AS_1$ | $CT + AS_2$ | $CT + UR_1$ | $CT + UR_2$ | CT | $CT + AS_1$ | $CT + AS_2$ | $CT + UR_1$ | $CT + UR_2$ |
| 0–10 | 7.95 | 8.03 | 8.07 | 8.09 | 8.15 | 7.97 | 8.00 | 8.02 | 8.06 | 8.18 |
| 10–20 | 8.08 | 7.80 | 7.65 | 8.10 | 8.27 | 8.02 | 7.78 | 7.60 | 8.12 | 8.26 |
| 20–30 | 7.98 | 7.71 | 7.58 | 8.26 | 8.30 | 8.00 | 7.69 | 7.58 | 8.20 | 8.30 |
| 30–40 | 8.00 | 7.57 | 7.46 | 8.22 | 8.33 | 8.01 | 7.60 | 7.42 | 8.28 | 8.35 |
| 40–50 | 8.03 | 7.65 | 7.50 | 8.32 | 8.42 | 7.98 | 7.70 | 7.49 | 8.32 | 8.41 |
| 50–60 | 7.99 | 7.75 | 7.67 | 8.38 | 8.50 | 7.99 | 7.78 | 7.65 | 8.35 | 8.48 |
| 60–70 | 7.99 | 7.82 | 7.82 | 8.55 | 8.56 | 7.97 | 7.83 | 7.79 | 8.43 | 8.53 |
| 70–80 | 8.00 | 7.86 | 7.75 | 8.39 | 8.30 | 8.01 | 7.88 | 7.83 | 8.35 | 8.32 |
| 80–90 | 8.10 | 8.09 | 7.99 | 8.35 | 8.27 | 8.02 | 8.00 | 7.98 | 8.29 | 8.25 |
| 90–100 | 8.11 | 8.10 | 8.13 | 8.32 | 8.10 | 7.96 | 8.05 | 8.06 | 8.22 | 8.13 |

content of chlorotoluron in leachates (figure 1). Statistical analysis showed that differences of chlorotoluron in the different treatments were significant ($p < 0.05$).

Chlorotoluron was mobile in all the treatments, increasing in the order $CT + AS_2 < CT + AS_1 < CT + UR_2 < CT + UR_1 < CT$ (figures 2–4). The results indicated that ammonium sulphate and urea reduced chlorotoluron leaching losses. More chlorotoluron remained in the soil columns amended with ammonium sulphate than in the soil amended with urea. After the application of $1300\,mg\,N\,kg^{-1}$ of ammonium sulphate and urea in non-aged soil, 39.72% and 65.91% of chlorotoluron was leached, respectively, whereas in the aged soil, leaching was 30.33% and 35.26%, respectively. In turn, the loss of chlorotoluron in unfertilized non-aged and aged soils was 67.92% and 49.93%, respectively.

These results could be explained by the greater degree of chlorotoluron sorption in ammonium sulphate and urea-treated soils than in untreated natural soils. The mobility of chlorotoluron in soils was related to adsorption and degradation. Our research

reported that the sorption of chlorotoluron increased in soils amended with ammonium sulphate and urea, since sorption of chlorotoluron increased with increasing nitrogen concentration. On the other hand, the degradation rate of chlorotoluron was faster in urea-treated soil than in ammonium-sulphate-treated soil, indicating that more chlorotoluron was made in solution in the urea-treated soil.

Although the changes in soil pH were different in ammonium-sulphate- and urea-treated soils, the impact of nitrogen fertilizers on the leaching of chlorotoluron from soil columns was uniform. The results indicated that the difference in affinity for chlorotoluron for different treatments might be due to a combined effect of soil properties, for example, microbial amounts, activity, variety [15, 16], clay content and amount of DOC, etc. Chlorotoluron behaviour was not controlled by soil pH only.

### 3.3 *Impact of ageing on leaching of chlorotoluron*

More chlorotoluron remained in the aged soil columns (figures 2–4) and less chlorotoluron in leachates (figure 1) than in the non-aged soil columns. The results indicated that the mobility of chlorotoluron decreased in aged soil columns compared with non-aged soil treatments. The explanation for the lack of leaching could be the increase in the adsorption of chlorotoluron in soil due to ageing. This effect had been described before for some pesticides [1, 20], whereby the active ingredient was first adsorbed to the outer positions of the soil aggregates followed by inner sorption sites, which were diffusion limited. Other possible processes were that the pesticide molecule in soil interacts with specific soil constituents in a dynamic manner over time, resulting in sequestration of a portion of the chemical, for example, by the consolidation of initially weak bonds, a change of mechanism of sorption/binding, or by the pesticide molecules being trapped in a nanopore [20]. Therefore, it was thought that chlorotoluron would hardly become desorbed from soils after ageing, and then the leaching potential would decrease. Similar results have been observed for leaching of other organic pollutants in soil [21–24].

Greater amounts of chlorotoluron remained in the 0–10 cm and 10–20 cm soil layer in all treatments, and lower amounts were leached at the lower depths (figures 2–4). This study indicated that ammonium sulphate and urea amendments could not enhance chlorotoluron leaching and indeed significantly reduced the leaching losses of the herbicide. The inverse relationship between the sorption and the percentage of chlorotoluron recovered from the untreated and ammonium-sulphate- or urea-treated columns suggested that sorption was the key process controlling the movement of chlorotoluron.

### 4. Conclusions

From the results of this laboratory study, it can be concluded that ammonium sulphate and urea affected degradation and leaching of chlorotoluron in soils. The half-life of degradation in topsoil, mid-soil, and subsurface soil was 147, 138, and 113 days in untreated soil, respectively. The dissipation of chlorotoluron was relatively rapid in subsurface soil for lower contents of clay and OM. Second, application of ammonium

sulphate and urea increased the persistence of chlorotoluron at all soil depths. Also, application of nitrogen fertilizers and ageing of chlorotoluron also effectively reduced leaching losses in soils.

Therefore, co-application of ammonium sulphate, urea, and chlorotoluron was a safe practice as far as leaching of chlorotoluron was concerned. However, the degradation of chlorotoluron also should be considered in agricultural practice.

## Acknowledgement

## References

[1] Y.B. Si, S.Q. Wang, J. Zhou, R.M. Hua, D.M. Zhou. *Chemosphere*, **60**, 601 (2005).
[2] Z.J. Liu, S.A. Clay, D.E. Clay. *J. Agric. Food Chem.*, **43**, 815 (1995).
[3] Z.J. Liu, S.A. Clay, D.E. Clay. *J. Environ. Qual.*, **24**, 7770 (1995).
[4] N. Singh. *J. Environ. Qual.*, **32**, 1743 (2003).
[5] A.I. García Valcarcel, J.L. Tadeo. *J. Agric. Food Chem.*, **51**, 999 (2003).
[6] G. Philip, F. Michael, J.S. Chib. *J. Agric. Food Chem.*, **50**, 7332 (2002).
[7] B.S. Xing, J.J. Pignatello, B. Gigliotti. *Environ. Sci. Technol.*, **30**, 2432 (1996).
[8] A.E. Smith, G.G. Briggs. *Weed Res.*, **18**, 1 (1978).
[9] D. Gross, T. Laanio, G. Dupuis, H.O. Esser. *Pestic. Biochem. Physiol.*, **10**, 49 (1979).
[10] Y. Lechón, C. Sánchez-Brunete, J.L. Tadeo. *J. Agric. Food Chem.*, **45**, 951 (1997).
[11] C. Zander, T. Streck, T. Kumke, S. Altfelder, J. Richter. *J. Environ. Qual.*, **28**, 1817 (1999).
[12] S. Beulke, C.D. Brown, C.J. Fryer, W. Beinum. *Chemosphere*, **57**, 481 (2004).
[13] A. Walker, M.S. Rodriguez-Cruz, M.J. Mitchell. *Environ. Pollut.*, **133**, 43 (2005).
[14] M.L. Gao, G.D. Shu, Y.M. Ma, P. Zhang. *Chin. J. Agro-Environ. Sci.*, **25**, 694 (2006).
[15] Y.L. Hou, S.G. Wang, W. Guo. *Chin. J. Soil Sci.*, **35**, 303 (2004).
[16] Z.J. Ren, Y.S. Chen, F.X. Tang, D.H. Wang, Y.Q. Zhang. *Chin. J. Plant Nutr. Fertil. Sci.*, **2**, 279 (1997).
[17] Y.A. Madhun, V.H. Freed, J.L. Young, S.C. Fang. *Soil Sci. Soc. Am. J.*, **50**, 1467 (1986).
[18] D.P. Li, R.W. Xu, W. Qi. *Chin. J. Soil*, **23**, 307 (1991).
[19] H. Rüdel, S. Schmidt, W. Kordel, W. Klein. *Sci. Total Environ.*, **132**, 181 (1993).
[20] A. Walker, S.J. Welch, I.J. Turner. In *BCPC Monograph 62, Pesticide Movement to Water*, p. 13, BCPC, Bracknell, UK (1995).
[21] M. Oi. *J. Agric. Food Chem.*, **47**, 327 (1999).
[22] J.S. O'Grodnick, P.G. Wislocki, J.L. Reynolds, M. Wisocky, R.A. Robinson. *J. Agric. Food Chem.*, **46**, 2044 (1998).
[23] K. Mikata, K. Ohta, S. Tashiro. *J. Pestic. Sci.*, **26**, 376 (2001).
[24] A. Enell, F. Reichengerg, P. Warfvinge, G. Ewald. *Chemosphere*, **54**, 707 (2004).