Journal of Environmental Sciences (China) Vol.4, No.4, pp.17–23, 1992 ISSN 1001–0742

Adsorption leaching of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea in soil*

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Abstract A study of adsorption of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) on four types of soil was performed by using the batch slurry method. Freundlich adsorption isotherm equations of CCU in each soil were obtained and the method and the procedure were described in detail. At the same time, Freundlich adsorption coefficient (K_d) and organic carbon adsorption coefficient (K_{oc}) were given for each soil.

The leaching of CCU on different soils was also investigated under laboratory conditions. The results showed that CCU possesses a weak tendency of leaching to the deep layer of soil or contaminating the underground water.

Keywords: adsorption; leaching; pesticide; insecticide; 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea.

INTRODUCTION

Adsorption and leaching are two important processes determining the ultimate fate of organic chemicals in soil. The extent of adsorption is related to various soil properties including the type of soil, the contents of clay and organic matter etc., and to physical and chemical parameters of the adsorbed compound, such as water solubility, and so on.

The Freundlich adsorption isotherm equation is always used to describe the adsorption behaviour of pesticide in soil:

$$Cs = K_d\ Ceq^{1/n},$$

where Cs is the amount of adsorbate taken up per unit mass of the adsorbent; Ceq is the concentration in solution at equilibrium, $1/n$ and K_d are constants representing the slope and the intercept of the isotherm, respectively. Karickhoff confirmed that $1/n$ equals to one only when the equilibrium concentration is very low.

In early years, it was believed that adsorption was mainly related to the content of clay (Baily, 1964), but through furthermore research, for neutral-organic pollutant, the factor which influences the adsorption is the organic matter content of the soil (Hamaker, 1972). Thus soil

* The study was supported by National Natural Science Foundation of China.

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organic carbon adsorption coefficient K_{oc} is more conveniently used to describe the adsorption behaviour of these compounds:

$$K_{oc}=K_d/OM\% \times 100,$$

where OM% is the organic matter content of the soil. In comparison with K_d value, K_{oc} is independent of soil. Therefore K_{oc} is a very useful parameter. The parameter K_{oc} is also useful in estimating pesticide leaching in soils (Hamaker, 1975), as well as for predicting bioconcentration factors (Kenaga, 1980).

Leaching is the movement of chemicals with percolate water through soil profiles. USEPA confirmed that leaching process could be an important contaminating pathway to the underground water.

1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) is one of the substituted phenyl urea compounds. It is only put into the commercial use here in China. No information for its adsorption and leaching behaviour were available. In order to predict whether CCU is hazardous to underground water, in this paper we report the determining of K_d and K_{oc} of CCU, describing the establishing of Freundlich adsorption isotherms. In the end, we give a conclusion that CCU will be little harmful to the underground water.

MATERIALS AND METHODS

1. Soils

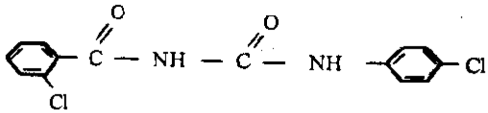
Four Chinese soil samples were collected from 0—20 cm of soil layers at different parts of China, Heilongjiang, Beijing, Jiangxi, Henan. Soils from Jiangxi and Henan were supplied by Nanjing Soil Institute, Chinese Academy of Sciences. Soil samples were all airdried and passed through an 1 mm sieve. Soil analysis data are summarized in Table 1.

Table 1 Analytical data of soil samples

Sampling sites (origin)	pH (1: 1)	Organic matter, %	Sand, %	Silt, %	Clay, %
Heilongjiang	5.44	6.50	10.0	68.0	22.0
Beijing	8.27	2.75	37.2	53.8	9.0
Jiangxi	4.84	0.77	56.2	23.0	20.8
Henan	8.14	0.40	58.2	29.0	12.8

2. Chemical

Technical grade CCU was supplied by Tonghua Pesticide Plant, Jilin Province. It was purified by repeated recrystallization in toluene for three times and 99% purity was obtained. The structure of CCU is as follows:



3. Adsorption

The method establishing the adsorption isotherm is close to the batch slurry method described by McCall (McCall, 1980) and Karickhoff *et al.* (Karickhoff, 1979). Soil-water ratio used in the study is shown in Table 2. A suitable amount of acetone solution of CCU was coated onto the wall of a 150 ml centrifuge tube. The acetone was evaporated at room temperature using a slow stream of nitrogen. According to the water-soil ratio, soil and distilled water containing 0.01 mol/L $Ca(NO_3)_2$ were put into the tube. The tube was shaken on a mechanical shaker for 24 hours at 25°C. The mixture was centrifuged at 4000 r/min for 10 min and 50 ml of water phase was drawn out and extracted with 3 × 50 ml dichloromethane. The extract was dried through anhydrous Na_2SO_4 column and evaporated in a Kuderna-Danish Concentrator just to dryness. The residue was dissolved in methanol and analyzed for CCU by HPLC. An aliquot of the soil paste was used to determine the content of water. Another aliquot of soil was weighed and mixed with 2–3 g of sodium sulfate and the mixture was extracted with 3 × 50 ml dichloromethane. The extract was dried by anhydrous Na_2SO_4 and evaporated in a Kuderna-Danish Concentrator just to dryness. The residue was dissolved in methanol and was analyzed for CCU by HPLC. The concentration of CCU in each phase were calculated, when calculating the concentration, of CCU in soil, the amount of CCU associated with the water in the paste was subtracted from the total amount of CCU in the paste.

Table 2 Solution to soil ratio used in the study

Sampling sites	Heilongjiang	Beijing	Jiangxi	Henan
Solution/soil, ml/g	50:1	10:1	5:1	5:1

4. Leaching

Two soil columns were used in the study. One was separable stainless steel column of 3.46 steel column of 3.46 cm in diameter and 21 cm in length, the other was plexiglass column.

The soil samples were put into the column and 10% water was added into the soil in advance, CCU methanol solution was added at the top of the column. A sheet of filter paper was coated at the surface of the soil column, a small amount of sand was put on the filter paper. After the leaching stopped, the column was sectioned, each section was 1.5 cm in length, the soil samples in each section was divided into two parts. One was weighed and analyzed for the water content, the other was extracted with 3 × 50 ml dichloromethane, the organic phase was dried by anhydrous Na_2SO_4 and then concentrated to dryness, the residue was dissolved in methanol and analyzed for CCU by HPLC.

Plexiglass column is 10.54 cm in diameter and 80 cm in length. 8697.9 g soil with 6.68% of water was added. The CCU methanol solution was added at the top of soil column, a sheet of filter paper and some amount of sand were added at the upper layer. After leaching stopped, soil samples at different depth were drawn out by cuprum tube. Soils at different depth were divided into two parts. One was used to determine the water content, the other was dried and extracted with dichloromethane for CCU content. The soil used in plexiglass column was obtained from Beijing.

RESULTS AND DISCUSSION

Adsorption study

An analysis of the data established the fact that they can be best represented in terms of the empirical Freundlich adsorption isotherm. In primary experiment, it showed that adsorption equilibrium was established within 24 hours. The Freundlich equation can be changed into linear form by taking logarithms of both sides: $\log C_s = \log K_d + 1/n \times \log C_{eq}$. In the present study, the data obtained gave reasonably good straight lines by plotting log C_s against log C_{eq}, as shown in Fig.1. The values of 1/n and K_d were obtained from linear regession programme using pocket-computer PC-1500 and listed in Table 3. In terms of correlation coefficient values, it gave an excellent linear relationship between log C_s and log C'_{eq}. All $1/n$ values is less than one, it indicated that as CCU concentration in water increaes, sorption sites on the soil particles begin to become saturated, so that increasing the concentration of CCU does not increase the amount of sorbed CCU proportionally. In addition, experiment results showed that K_d values increased with the increase of the organic carbon content, it means that soil organic matter content is the main factor which influences the adsorption behaviour of chemicals.

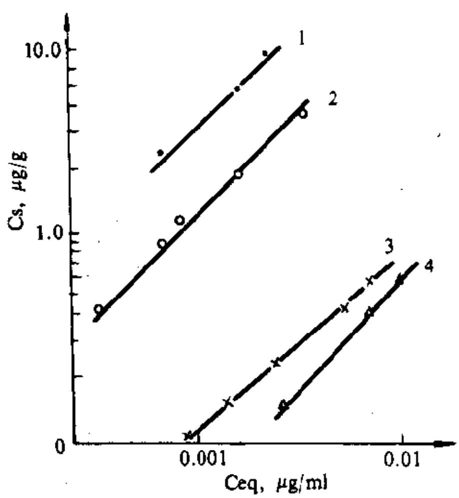


Fig.1 Adsorption isotherms of CCU by batch equilibrium method (25°C)
1. Heilongjiang 2. Beijing 3. Jiangxi 4. Henan

In terms of K_{oc} values listed in Table 3, the average organic carbon adsorption constant 1600 was obtained. In accordance with relationship between K_{oc} values and their mobility in soil (Table 4) presented by McCall *et al.* (McCall, 1980), CCU is closer to Lindane, it belongs to the low mobility chemicals in soil.

Table 3 Adsorption parameter of CCU in soil

Sampling sites	C%	Kd	1/n	R	K_{oc}	(K_{oc})average
Heilongjiang	6.50	202.6	0.907	1.00	3117	1600
Beijing	2.75	41.76	0.800	1.00	1518	
Jiangxi	0.77	4.20	0.860	1.00	545	
Henan	0.40	4.90	0.804	1.00	1225	

Table 4 Relationship between K_{oc} value of chemicals and their mobility in soil

Classification	K_{oc}	Mobility	Examples	
			Compound	K_{oc}
1	0－50	Very high	Dicamba	0
2	50－150	High	2,4-D	60
3	150－500	Medium	Carbaryl	390
4	500－2000	Low	Lindane	1300
5	2000－5000	Slight	Trifluralin	4300
6	>5000	Immobile	DDT	150000

Leaching behaviour study

Leaching experiment data in separable stainless steel column are shown in Table 5. The experiment conditions were almost the same, duration of leaching was 24 hours, total precipitation of leaching was 200 mm. As described in adsorption section, CCU is highly adsorbed by soil particles, so its leaching is slow in soils. Data listed in Table 5 show that the main quantitation of CCU with 95% of total residue was within upper 0－3 cm and that the maximum leaching distance was 4.5 cm. There was no obvious difference in leaching distance due to the difference of soil types. The reason may be the low solubility and high adsorption of CCU. In addition, leaching depth increased with the increase of leaching time. For instance, after leaching 40 hours, CCU in soil column packed with the soil from Beijing can leach to 9.0 cm deep in soil, but the maximum concentration was still within upper 0－3 cm range.

The leaching experiment data in two plexiglass columns are shown in Table 5. The total precipitation, leaching time and distribution of pesticide CCU in columns are also listed in Table 6. In order to representively study the transfer of pesticide in soil, leaching through large plexiglass columns packed with soil from Beijing areas were carried out. The diameters of two columns were nearly the same, the columns were 80 cm in length. The total precipitation, leaching duration, distribution of CCU in every soil section are listed in Table 6 and shown in Fig.2. The real line in Fig. 2 was depicted according to the model of transport and transfer of pesticide on

Table 5 Distribution of CCU in soil columns, ppm

Sampling sites	Heilongjiang	Beijing		Jiangxi	Henan
Precipitation/time, mm/h	200/24	120/24	240/40	200/24	200/24
Depths of soil, cm					
0 – 1.5	22.72	16.64	8.42	3.96	5.72
1.5 – 3.0	0.80	7.12	5.91	0.60	0.03
3.0 – 4.5	ND*	1.27	0.55	ND	ND
4.5 – 6.0	ND	ND	0.44	ND	ND
6.0 – 9.0	ND	ND	0.03	ND	ND
9.0 – 12.0	ND	ND	ND	ND	ND
12.0 – 15.0	ND	ND	ND	ND	ND
Leachate	ND	ND	ND	ND	ND

* ND: Not-detected

Table 6 The vertical distribution of CCU in soil columns, ppm

Columns	*A*	*B*
CCU applied, mg	12.5	15
Rainfall tensity, mm/h	5.863	5.375
Duration of leaching, h	29.5	34.7
Total precipitation, mm	173	186
Depth of soil, cm		
2.5	24.25	
3.0		22.41
5.0	14.60	
5.5		13.95
7.5	0.35	
8.0		7.64
10.0	0.08	
10.5		1.37
12.5	0.02	
13.0		ND
15.0	ND	ND
20.0	ND	ND

Notes: soil tested was from Beijing; within 20 – 80 cm soil layers, no CCU was detected.

unsaturated soil (Yang, 1990). The inner diameter of column *A* was 10.54 cm, soil dry density was 1.2 g/cm^3, the water content was 8%, rainfall intensity was 5.863 mm/h, the leaching time was 29.5 h, total precipitation was 173 mm, the maximum leaching distance was 12.5 cm, the residue maximum concentration of CCU was within surface layer of the soil column. The residue content of CCU decreased with the increase of the soil depth. Column *B*: Inner diameter was 10.34 cm, the initial water content was 10.54%, the leaching time was longer than that of in column *A*, the total precipitation was closer to that of column *A*. The leaching behaviour of CCU in column *B* was the same as that in column *A*, the maximum leaching distance was 10.5 cm.

The results as described above show that the pesticide CCU is strongly adsorbed by soil particles (K_{oc} value is 1600), moves slowly in soil. The texture, leaching time and the applied amount of CCU could only take a little influence on distribution of pesticide CCU in soil. At a precipitation of 200 mm, the maximum leaching distance on unsaturated soil was 12.5 cm. Therefore it will be confirmed that there is a little possibility to contaminate the underground water due to use of pesticide CCU.

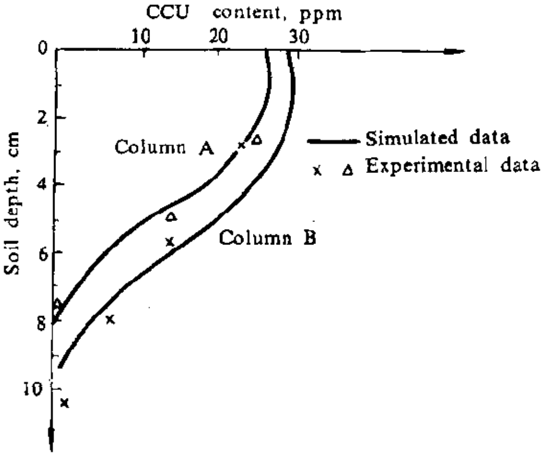


Fig. 2 The vertical distribution of CCU in soil profile

Acknowledgments We thank Zhang Lianzhong and An Fengchun of our laboratory; Yang Dawen of Department of Hydraulic Engineering, Tsinghua University, for their assistance during the studies.

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(Received November 19, 1991)