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Adsorption and Desorption of Atrazine by Three Soils

G. Huang,[1] Q. Li,[2] X. Zhang[1]

[1] Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, Post Office Box 417, Shenyang 110016, People's Republic of China
[2] Institute of Soil Sciences, Chinese Academy of Sciences, Post Office Box 821, Nanjing 210008, People's Republic of China

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Atrazine is a widely used herbicide for control of annual grasses and broad-leaf weeds in maize, sugarcane and sorghum cultivation, tea plantation and orchard production. It was reported that the half-life of atrazine is long in soil, thus atrazine can be easily detected in surface and ground water (Soloman et al.1996; Sintein 1996; Barcelo 1996). Therefore, environmental pollution by the application of atrazine and other agricultural chemicals has become a worldwide problem. For instance, atrazine, simazine, methylparathion and parathion were detected in the treated drinking water in Spain (Barcelo et al.1996). Some pesticides were found in surface water in 17 states of the US and the concentration of the pesticides in many areas exceeded the EPA Standard (LHAL) (Dalsender et al.1997). Maguire (1993) found that atrazine concentrations in waters of the Yamaska river estuary and its 5 branches, Quebec, Canada were above the standard of water quality (<2ppb) set by the Canadian government for the protection of hydrophilous organisms.

Since 1980s, the herbicide has been intensively applied in China and the application amount has increased rapidly (about 20% per year). In the mean time, the application area has also been expanded to almost all the arable land. Long exposure to atrazine may have a risk of catching cancer, provided that the substance is listed on the suspicious environmental hormones (Kettles et al. 1997). Migration or leaching of atrazine from arable soil is the main way for the biocide to contaminate ground water or drinking water, but the fate of atrazine is influenced by the adsorption and desorption processes in soil (Moreau-Kervevan and Mouvet, 1997). In this context, Moreau-Kevevan and Mouvet (1998) have studied the adsorption-desorption behaviors of atrazine by some clays and humic acid. However, soils on the earth surface have divers properties, which are the key factors for controlling the behavior of adsorption and desorption of atrazine, thus there is still a need for further investigation of adsorption-desorption processes of atrazine on different soils in order to provide information for a proper use of the biocide in agricultural land.

Correspondence to: X. Zhang

MATERIALS AND METHODS

Composite surface soil samples (0-20cm) from three sites were used for the adsorption-desorption study. The three soils with different properties were classified as Brown soil, Cinnamon soil, and Meadow soil respectively (Table 1). The Brown soil was collected from the Experimental Station of the Institute of Land and Environment, Shenyang Agricultural University; Meadow soil was sampled from the Experimental Station of the Department of Horticulture, Shenyang Agricultural University, and the Cinnamon soil was taken from Chaoyang, Liaoning province. After sampling, the soils were kept at field moisture. Prior to adsorption-desorption experiments, they were then passed through a 1mm sieve. Atrazine (98.44%) was provided by the Standard Center of Pesticides, Shenyang Chemical Corporation.

The adsorption experiment was conducted as follows: A set of 5.0g of soil was added to plastic centrifuge tubes containing 25ml of $CaCl_2$ solution (0.010mol L^{-1}). Atrazine concentrations in the solution were set to 0, 0.5, 2.0, 6.0, and 10.0 mg L^{-1} respectively. The tubes were shaken for 48 hours at 20 °C and then centrifuged for 15 min at 3000g. Thereafter, the supernatant was transferred into 250ml extraction funnel and then was extracted by dichloromethane (CH_2Cl_2). The extract was dried by a rotary evaporator (EYELA, Tokyo). The atrazine residue was dissolved into hexane completely and then the hexane solution was desiccated by passing through 2g of Na_2SO_4 for measurement. Each treatment was repeated three times.

For desorption of the atrazine absorbed previously on the soils in the above experiment, each of the treated soils was extracted by a 25ml of $CaCl_2$ solution (0.010mol L^{-1}). After addition of the solution, the tubes were shaken for 24 hours at 20 °C and then centrifuged for 15min at 3000g. The desorption process was repeated three times. The atrazine in the supernatant was extracted in the same manner as above for measurement.

Finally, atrazine in the hexane solution was determined by a Gas chromatograph HP5890-II NPD (Agilent Technologies, Palo Alto, CA), equipped with a glass column of 1.2m*2mm (2.5% OV-17 and 3.3% QF-1 coated on W AW DMCS (80-100 mesh). The temperatures of oven, inlet and detector (NPD) were set to 170 °C, 200 °C and 250 °C respectively. N_2 was used as a carried gas and the flow rate was 50ml min^{-1}.

Statistics was carried out by using a software package of SPSS10. The differences were compared by one way analysis of variance (ANOVA) after post hoc separation.

Table 1. Soil properties.

Soil types	PH	Clay (%)	Silt (%)	Sand (%)	SOM (%)	CEC ($mel.100g^{-1}soil$)
Brown Soil	6.28	30	28	42	1.10	7.63
Cinnamon Soil	8.20	9	32	59	0.58	6.73
Meadow Soil	6.86	14	26	60	2.01	7.86

Sand(0.02-2mm), Silt (0.002-0.02mm), Clay (<0.002mm), SOM(soil organic matter) and CEC(cation exchange capacity)

RESULTS AND DISCUSSIONS

The adsorption isotherms of atrazine on the three soils are shown in Fig. 1. Apparently, the adsorption amounts of atrazine on the three soils increased with increasing equilibrium concentrations. We used a linear regression model firstly to simulate the adsorption process. The parameters from the linear regression analysis are listed in Table 2. It is clear that the linear correlation was not significant for the three soils. Therefore, we re-simulated the correlation by excluding the constants (still a linear model). Table3 shows the new parameters from the second linear model. Comparing R^2 in Table 2 with that in Table 3 it was found that the significance of the second linear regression was improved, the R squares being higher in Table3 than those in Table 2. Hence, the linear model obtained by excluding the constants well describes the adsorption isotherms of atrazine by the three soils.

According to the results of regression analysis in Table 3 the adsorption of atrazine on the three soils follows the equations below respectively.

$Y=6.190X$ for Brown soil
$Y=2.238X$ for Cinnamon soil
$Y=10.392X$ for Meadow soil

Where Y is the amount of atrazine absorbed on soils($\mu g\ g^{-1}$) and X, the equilibrium concentration of atrazine in solution ($\mu g.ml^{-1}$). In fact, the equations are one case of the Freundlich equation ($x/m=k_fCeq^n$) when the n value equals to 1. In the Freundlich equation x/m is the amount of atrazine absorbed on solid phase ($\mu g.g^{-1}$), Ceq is the equilibrium concentration of atrazine in solution ($\mu g.ml^{-1}$), and k_f is an empirical constant, which is related to adsorption character. One can estimate the adsorption capacity of atrazine on different soils by comparing k_f values (Hamaker, 1972). The results showed that the adsorption capacities of atrazine on the three soils were in the order: Meadow soil > Cinnamon soil > Brown soil. This finding suggested that the adsorption capacity

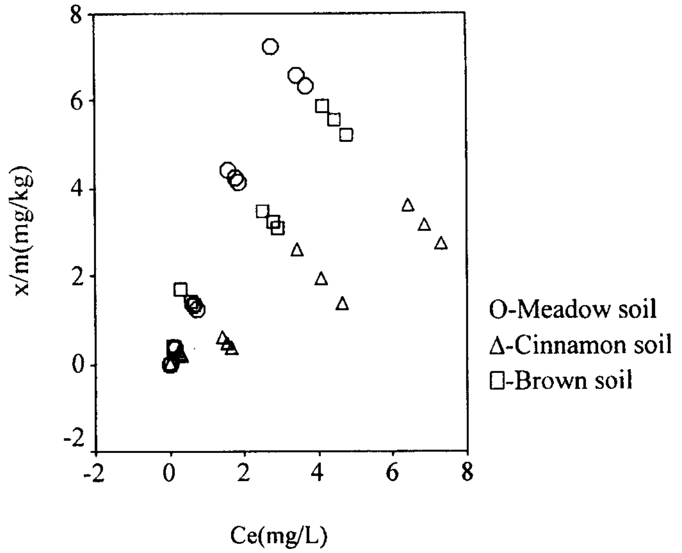

Figure 1. Adsorption isotherm of atrazine by three soils

Table 2. Parameters of linear regression analysis for adsorption by including the constants.

Soil	R^2	$Sig_R{}^2$	C	$Error_C$	Sig_C	K	$Error_K$	Sig_K	N
Brown soil	0.951	0.000	1.781	0.847	0.056	5.687	0.360	0.000	15
Cinnamon	0.884	0.000	-3.391	0.820	0.997	2.238	0.225	0.000	15
Meadow soil	0.942	0.000	0.660	1.187	0.588	10.12	0.695	0.000	15

R^2: Square of Regression Coefficients; $Sig_R{}^2$: Significant levels of Regression Coefficients; C: Constant; Sig_C: Significant levels of Constant; K: Unstandardized Coefficients; Sig: Significant levels of Unstandardized Coefficients; $Error_C$: Std. Error of C; $Error_K$: Std. Error of K; n: Number of samples

Table 3. Parameters of linear regression analysis for adsorption by excluding the constants.

Soil	R^2	$Sig_R{}^2$	K_f	$Error_K$	Sig_K	N
Brown soil	0.984	0.000	6.190	0.300	0.000	15
Cinnamon	0.968	0.000	2.238	0.154	0.000	15
Meadow soil	0.985	0.000	10.392	0.495	0.000	15

R^2: Square of Regression Coefficients; $Sig_R{}^2$: Significant levels of Regression Coefficients; K_f: Unstandardized Coefficients; Sig_K: Significant levels of Unstandardized K; $Error_K$: Std. Error of K; n: Number of samples

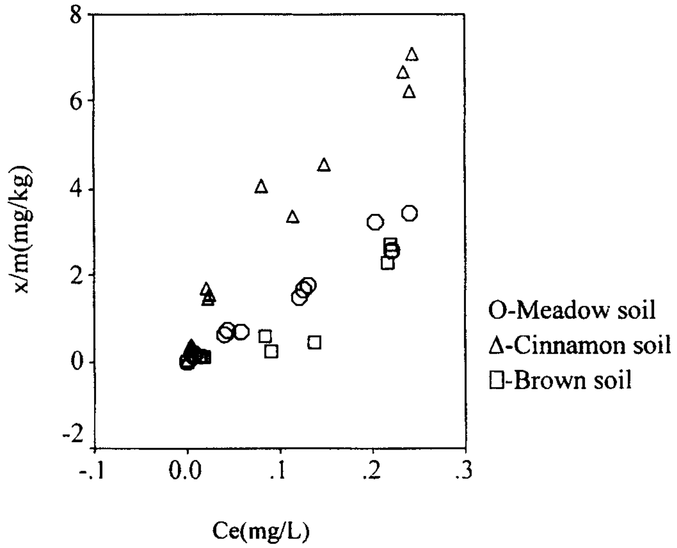

Figure 2. Desorption isotherm of atrazine by three soils

Table 4. Parameters of linear regression analysis for desorption by including the constants.

Soil	R^2	Sig_R^2	C	$Error_C$	Sig_C	K	$Error_K$	Sig_K	n
Brown soil	0.983	0.000	-0.014	0.036	0.696	0.068	0.004	0.000	12
Cinnamon	0.946	0.000	-0.028	0.057	0.693	0.070	0.007	0.000	15
Meadow soil	0.988	0.000	-0.004	0.025	0.862	0.032	0.001	0.000	15

R^2: Square of Regression Coefficients; Sig_R^2: Significant levels of Regression Coefficients; C: Constant; Sig_C: Significant levels of Constant; K: Unstandardized Coefficients; Sig: Significant levels of Unstandardized Coefficients; $Error_C$: Std. Error of C; $Error_K$: Std. Error of K; n: Number of samples

Table 5. Parameters of linear regression analysis for desorption by excluding the constants.

Soil	R^2	Sig_R^2	K_f	$Error_K$	Sig_K	n
Brown soil	0.991	0.000	0.067	0.003	0.000	12
Cinnamon	0.968	0.000	0.068	0.005	0.000	15
Meadow soil	0.994	0.000	0.032	0.001	0.000	15

R^2: Square of Regression Coefficients; Sig_R^2: Significant levels of Regression Coefficients; K_f: Unstandardized Coefficients; Sig_K: Significant levels of Unstandardized K; $Error_K$: Std. Error of K; n: Number of samples tended to be affected by soil properties, especially the content of soil organic matter. The adsorption capacity increased apparently with increasing soil organic matter contents (Stevenson, 1972). The adsorption phenomena could be also attributed to the differences in soil CEC and pH values (Stevenson, 1972). Atrazine is a weak base, thus it can be protonated under low pH conditions. This could be the explanation for the significant lower adsorption capacity of atrazine on the Brown and Meadow soils than that on the Cinnamon soil. It is also possible that the protonated atrazine is more preferential to move towards the colloids when soils have more negative charges.

The desorption isotherms of atrazine from three soils are shown in Fig. 2. Apparently, the desorption amounts of atrazine from the three soils increased with increasing equilibrium concentrations used in the adsorption experiment. We used a linear regression model firstly to mimic the desorption process. The parameters from the linear regression analysis are listed in Table 4. It is clear that the linear model was insignificant for the three soils. Therefore, the regression was conducted again by excluding the constants (still a linear model).

Table5 shows the new parameters from the second linear model. Comparing R^2 in Table 4 with those in Table 5 it was found that the significance for the second linear regression was improved, the new R squares being higher in Table5 than those in Table 4. Hence, the linear model after excluding the constants well describes the desorption isotherms of atrazine for the three soils. The equations are as follows:

$Y=0.067X$ ----Brown soil
$Y=0.068X$ ----Cinnamon soil
$Y=0.032X$ ----Meadow soil

Where Y is the amount of atrazine desorbed from soil ($\mu g\ g^{-1}$), while X is the equiliqum concentration of atrazine in solution ($\mu g.ml^{-1}$). Again as mentioned above, the equations are one case of the Freundlich equation ($x/m=k_fCeq^n$) when the n value equals to 1. In the Freundlich equation x/m is the amount of atrazine desorbed from the atrazine absorbed on soils in the adsorption experiment ($\mu g.g^{-1}$), Ceq is the equilibrium concentration of atrazine in solution ($\mu g.ml^{-1}$), and k_{fn} is an empirical constant, which is related to desorption character. One can estimate desorption extend of atrazine from different soils by comparing k_f values (Hamaker, 1972). The results showed that the desorption capacities of atrazine from the three soils were in the order: Meadow soil < Brown soil ⩽ Cinnamon soil. Obviously, the order is different from that of adsorption, indicating that the processes of adsorption and desorption are determined by different soil attributes.

The study indicates that soil organic matter is a key factor for both adsorption and desorption processes of atrazine by soils. The finding also suggests that, despite static mechanism plays an important role in atrazine adsorption on soils, other mechanisms, especially direct binding with soil organic compounds contribute significantly to the adsorption. The negative electronic charges and binding agents on soil organic matter determines mainly the capacity of adsorption. Once atrazine is adsorbed on the soils containing high soil organic matter levels, the strong binding between atrazine molecules and soil organic compounds can prevent the atrazine from release, thus reducing bio-availability. However, for those soils, which have low organic matter levels, the application of atrazine may have a risk of ground water contamination by leaching.

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