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Adsorption and correlation with their thermodynamic properties of triazine herbicides on soils

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Abstract: Adsorption of atrazine, prometryne and prometon was determined on six soils with different physical and chemical properties. The adsorption isotherms of three herbicides could well fit Freundlich equation. On all of six soils, adsorption of herbicides increased in the order: atrazine ≈ prometon < prometryne. This order is quite the same to the calculation result of by means of excess thermodynamic properties of triazine. The Freundlich adsorption constants, K_f, showed to have good correlation with organic matter(OM%) of soils for each of these herbicides, suggesting that OM is the main factor, which dominates in the adsorption process of these triazine herbicides.

Keywords: triazine herbicide; soil; adsorption; excess thermodynamic properties

Introduction

Adsorption of herbicides on soil from water is an important factor affecting their fate, biological activity, and persistence in soil-water system. It is often affected by several properties of soil. Better understanding of adsorption and its affecting factors will make it possible to adjust the herbicide dosage according to soil properties, thus reducing the environmental pollution of herbicides in the environment.

Among the post-emergent herbicides, triazine herbicides are most commonly used worldwide on control weeds on both agricultural and non-agricultural land (Newman, 1995). Unfortunately, they are also widely detected in water supplies and for this reason are considered to be an important indicator of pesticide contamination in the United States and elsewhere. The adsorption of several triazines has been studied and it was found that the adsorption of triazines highly related to soil organic matter content(Senesi, 1980; Garrison, 1996; Novak, 1999; Close, 1999). Multifunctional hydrogen bonds and charge-transfer bonds were found to be involved in the adsorption of atrazine and prometon on humic acids(Schnitzer, 1972). A direct comparison of adsorption experimental results from different laboratory is rather difficult because of the experimental conditions, such as the type of soil, temperature of bath, range of concentration, or sampling procedures, varying from study to study. Therefore, common rule and quantitative correlation on adsorption of the triazine group of herbicides are currently unavailable.

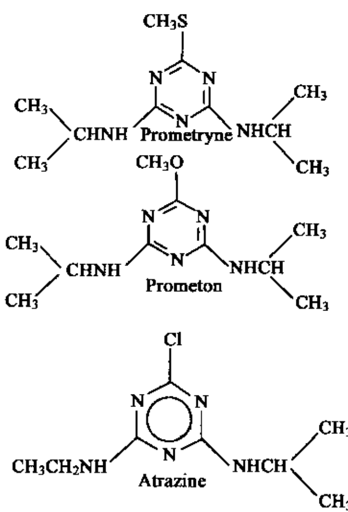

Fig.1 Structures of three triazine herbicides

The adsorption of three commonly used triazine herbicides, atrazine, prometryne and prometon, was studied. The structures of these triazine herbicides are shown in Fig.1. Our objectives were: (1) to determine and compare the adsorption isotherms of these herbicides on six soils with various physical and chemical properties; (2) to identify the main soil factors affecting adsorption; (3) to correlate the adsorption with the excess thermodynamic properties of the herbicides.

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1 Theory

In high performance liquid chromatographic (HPLC), the relationship of capacity factor k' and retention time T_R, T_M is:

$$k' = \frac{T_R - T_M}{T_M}. \quad (1)$$

When a component enters stationary phase(S) through the mobile phase(M), the mole excess Gibbs free energy change $\Delta\bar{G}^*$ is:

$$\Delta\bar{G}^* = -RT\ln k' + RT\ln\frac{n_s}{n_m}, \quad (2)$$

where n_s and n_m are the mole number of unit volume stationary phase and mobile phase, respectively. The relation between $\Delta\bar{G}^*$, and the mole excess enthalpy change $\Delta\bar{H}^*$, and the mole excess entropy change $\Delta\bar{S}^*$ is:

$$\Delta\bar{G}^* = \Delta H^* - T\Delta\bar{S}^*. \quad (3)$$

From Eqs.(2) and (3), we can get:

$$\ln k' = \frac{-\Delta\bar{H}^*}{RT} + \frac{\Delta\bar{S}^*}{R} + \ln\frac{n_s}{n_m}, \quad (4)$$

$$\log(k') = \frac{-\Delta\bar{H}^*}{2.303RT} + \frac{\Delta\bar{S}^*}{2.303R} + \lg\frac{n_s}{n_m}, \quad (5)$$

$$\log(k') = \frac{A}{T} + B, \quad (6)$$

where

$$A = \frac{-\Delta H^*}{2.303R};\ B = \frac{\Delta\bar{S}^*}{2.303R} + \lg\frac{n_s}{n_m}. \quad (7)$$

Therefore, $\Delta\bar{H}^*$ and ΔS^* can be obtained through the data of capability factor.

2 Materials and methods

2.1 Soil samples and chemicals

The samples of six soils were used in this study. They were collected in the area of Zhejiang Province of East China. Their physical and chemical properties are summarized in Table 1. The samples were air-dried and sieved to 1 mm. Soil pH was measured in a mixture of 1:1(w/w) soil: water with a glass pH electrode. Particle size distributions were evaluated using pipette method(Day, 1965) and the organic matter content(OM%) was measured by colorimetric method using chromic acid(NSICAS, 1978). The cation exchange capacity(CEC) was determined by following procedure reported(Hendershot, 1986).

Atrazine, prometryne and prometon (purity 99.1%, 99.0% and 99.1%, respectively) were purchased from Chem Service Inc., USA. The methanol was HPLC grade, and other chemicals were analytical grade.

Table 1 Selected physical and chemical properties of soil samples

No. of soils	pH	OM, %	Clay, %	Silt, %	Sand, %	Water, %	CEC, meq/100g
1	7.67	0.64	37.8	48.2	6.1	3.9	30.0
2	4.14	2.8	49.3	31.0	15.6	3.5	15.7
3	6.66	3.4	20.6	43.6	30.4	2.0	11.8
4	7.36	4.0	15.1	40.8	29.3	1.9	17.8
5	5.23	0.25	23.7	34.6	35.8	4.8	34.6
6	8.42	0.71	9.7	83.8	4.4	1.4	8.8

Humic acid (HA) was isolated according to conventional procedures (Senesi, 1989) from soil 4.

2.2 Herbicides analysis

The concentrations of these herbicides were quantified by HPLC analysis. To determine the dead time of herbicides, KNO_3 was added in herbicide solution. A spectra-physics liquid chromatograph, equipped with 200 mm × 4 mm(i.d.) reverse-phase YWG C_{18} 10 μm analytical column, a spectra 100 UV-VIS detector and a supper chromatography work station, was used. The flow rate of mobile phase was 1 ml/min. For detection of atrazine, prometryne and prometon, the HPLC detector was operating at 230 nm, and the mobile phase was composed of methanol and water with a ratio of 75:25 by volume(adjusted to pH = 3.0 using H_3PO_4). Under these conditions, the retention time of atrazine, prometryne and prometon was 6.70, 7.50 and 7.99 min, respectively.

2.3 Adsorption experiments of soils

Adsorption isotherms were obtained using the slurry-type method. Twenty milliliter volumes of herbicide solutions were added to 100 ml conical glass bottle with plugs, which contained 5.00 g soils for atrazine, prometryne or prometon, respectively. The initial concentration of the three herbicides ranged from 10 to 100 μmol/L. The maximum concentrations used all were lower than their water solubility. All experiments were duplicated. Equilibration was achieved by shaking for 24 h at 20 ± 2℃. Preliminary studies showed that all adsorption equilibration could be reached within 24 h. The supernatant was then removed by centrifugation at 12000 r/min for 10 min, filtered through a 0.2 μm syringe filter and stored in stopper glass vial for HPLC analysis.

3 Results and discussion

3.1 Adsorption isotherms of 3 triazine herbicides

Fig.2 shows the adsorption isotherms of these three triazine herbicides on 6 soils. Their L-shaped isotherms signified that soils had a high affinity for these herbicides, and they were probably adsorbed in a planar position on the surface with multifunctional bonding to soils.

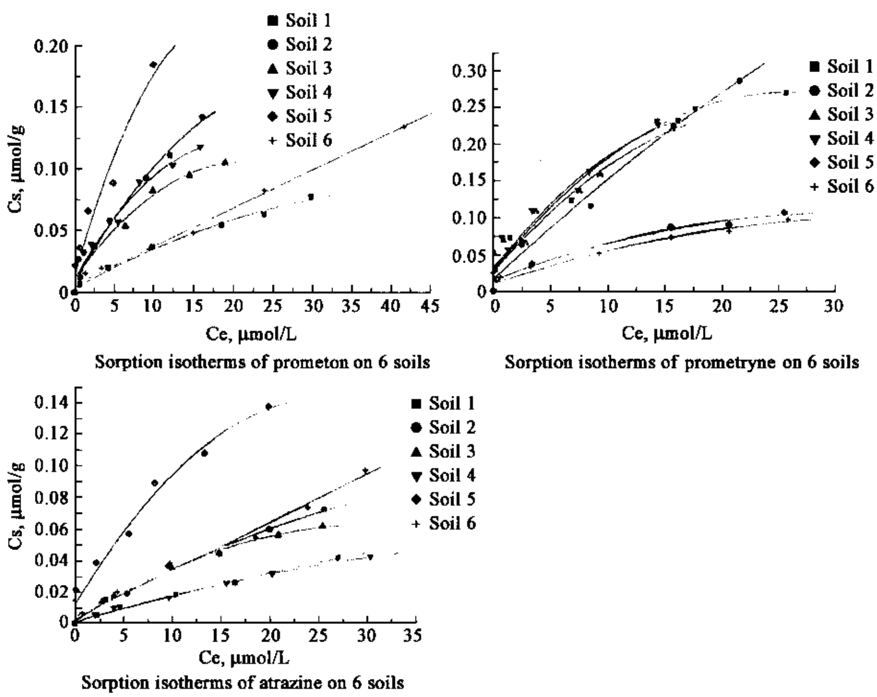

Fig.2 Adsorption isotherms of 3 herbicides on 6 soils

Freundlich Equation is often used in the description of adsorption of pesticides. The empirical equation can be expressed as follows:

$$Q = K_f Ce^{1/n}. \tag{8}$$

Where Q is the adsorbed amount of the soil(μmol/g), Ce is the concentration of herbicide in the solution at equilibration(μmol/L), K_f and $1/n$ are regression constants. It was found that the adsorption isotherms of these three triazine herbicides could fit Freundlich Equation well. The values of K_f, $1/n$ and correlation coefficients(r) are given in Table 2.

Table 2 Freundlich constants and correlation coefficients for adsorption of 3 kinds of triazine herbicides on 6 soils

No. of soil	Prometryne			Prometon			Atrazine		
	K_f	$1/n$	r	K_f	$1/n$	r	K_f	$1/n$	r
1	0.00556	0.782	0.990	0.00846	0.866	0.993	0.00628	0.786	0.987
2	0.03494	0.641	0.961	0.03268	0.783	0.992	0.02597	0.863	0.929
3	0.05208	0.792	0.962	0.03317	0.907	0.948	0.03701	0.887	0.952
4	0.07361	0.875	0.985	0.04285	0.934	0.909	0.04629	0.901	0.941
5	0.00569	0.672	0.994	0.00439	0.847	0.934	0.00482	0.874	0.915
6	0.00246	0.932	0.992	0.00916	0.755	0.946	0.00903	0.913	0.963

3.2 Correlation of adsorption with properties of soil

The correlation results of adsorption and desorption with soil properties can either be used to predicate the adsorption and desorption of pesticides on different soils, or help to find out the factors of soil which dominate in the adsorption and desorption process. The correlation of Freundlich constant K_f of adsorption for several pesticides with the selected soil parameters had been presented(Pusino, 1994; Mallawatantri, 1996). Actually, another Freundlich constant, $1/n$, is also a very important coefficient for the description of isotherms. The isotherms can differ a lot with the change of $1/n$. Linear regression analysis between K_f and soil parameters was performed. The correlation coefficients(r) are listed in Table 3.

Table 3 Correlation coefficients of K_f with soil parameters for 3 triazine herbicides

Name of herbicide	Sand	OM, %	Silt	Clay, %	Water	CEC
Prometryne	0.505	0.974	-0.415	-0.120	-0.456	-0.389
Atrazine	0.437	0.989	-0.328	-0.144	-0.545	-0.506
Prometon	0.341	0.994	-0.391	0.042	-0.476	-0.515

For all 3 herbicides, K_f showed better linear correlation with OM%. This meant that the main factor of soil which dominated the adsorption of these 3 triazine herbicides was OM%. The linear regression equations of K_f with OM% were:

$$K_f = 0.00577 + 0.01771(OM), \tag{9}$$

$$K_f = 0.00053 + 0.01073(OM), \tag{10}$$

$$K_f = 0.00213 + 0.01001(OM). \tag{11}$$

Eqs. (9), (10) and (11) correspond to prometryne, atrazine and prometon, respectively. The gradually increasing intercepts and slopes of these equations indicated that the adsorption extends on soils of these 3 triazine herbicides increased in the order: atrazine $\approx$ prometon < prometryne.

The main difference of these 3 triazine herbicides in structure is the diversity of one substitution group of aromatic cyclic triazine, which is $-OCH_3$, $-Cl$ and $-SCH_3$ for prometon, atrazine and prometryne, respectively. Each of these substitution groups can help the form of electron-transfer mechanism of bonding to quinone-like structures in HA, and the capability of conjugate order is $—SCH_3$ > $—OCH_3$ > —Cl. Possibly, this is an important factor to affect the adsorption.

3.3 Adsorption mechanism

The adsorption mechanism of triazine on soils have been researched very wildly (Senesi, 1980; Garrison, 1996; Ladlslau, 1994; Wang, 1998). In this paper, the adsorption mechanism is ignored.

3.4 Correlation of adsorption and excess thermodynamic properties of herbicides

Table 4 lists the lgk' in different compositions of mobile phase for 3 triazines. The result indicated the correlation of lgk' and C_w is linear. It meant the correlation of excess thermodynamic properties of herbicides and C_w is linear too.

Table 4 The lgk' in different compositions of mobile phase

Herbicide	Compositions of mobile phase C_w(H_2O/CH_3OH, V/V)					r	SD
	0.3	0.4	0.5	0.6	0.7		
Prometryne	0.552	0.729	0.913	1.009	1.286	0.991	0.044
Prometon	0.515	0.682	0.849	1.029	1.201	0.999	0.005
Atrazine	0.493	0.657	0.834	0.993	1.155	0.999	0.005

Table 5 lists the lgk' in different column temperature for 3 triazines. The excess thermodynamic properties of herbicides can be obtained by plotting the lgk' versus reciprocal of absolute temperature in degrees Kelvin. $\Delta\bar{H}^*$ can be obtained by the slope of curve and ΔS^* is direct ratio to the intercept of curve. The result is: prometryne $\Delta\bar{H}^* = -10.561$ kJ/mol; atrazine $\Delta\bar{H}^* = -5.674$ kJ/mol; prometon $\Delta\bar{H}^* = -5.770$ kJ/mol. Compared the numerical value of $\Delta\bar{H}^*$, the order of these 3 triazine herbicides is the same to the order of adsorption extends on soils. $\Delta\bar{H}^*$ is the energy factor, it maybe determine the affinity of soil and herbicide. $\Delta\bar{H}^*$ can be considered the size factor. It is determined by the size of molecule.

Table 5 The lgk' in different column temperature

Herbicide	Column temperature(K)						r	SD
	303.15	308.15	313.15	318.15	323.15	333.15		
Prometryne	0.729	0.712	0.652	0.621	0.605	0.576	0.971	0.016
Prometon	0.682	0.659	0.648	0.627	0.612	0.591	0.994	0.004
Atrazine	0.655	0.631	0.621	0.602	0.590	0.564	0.993	0.005

4 Conclusions

The L-shaped adsorption isotherms signified that the soil had a high affinity for these 3 triazine herbicides, suggesting that they were probably adsorbed in a planar position on the surface with multifunctional bonding to soils. The isotherms could fit Freundlich Equation well. The adsorption extends increased in the order: atrazine $\approx$ prometon < prometryne.

Analysis of linear correlation regression showed that K_f had good correlation with OM%. OM% is the main factor of soil, which dominates in the adsorption process.

The $\Delta\bar{H}^*$ order of these 3 triazine herbicides is the same to the order of adsorption extends on soils, so the excess thermodynamic properties could be an important parameter of herbicide.

References:

Close M E, Watt J P C, Vincent K W, 1999. Simulation of picloram, atrazine, and simazine transport through 2 New-Zealand soils using leachm[J]. Australian J of Soil Research, 37: 53—74.

Day P R, 1965. Particle fractionation and particle-size analysis[M]. Methods of soil analysis (Part I; Black C. A. ed). WI: Am Soc Agron Madison. 545—566.

Garrison S, Ladislau M N, Andrew Y, 1996. Atrazine complexation by soil humic acids[J]. J Environ Qual, 25: 1203—1209.

Hendershot W H, Duquette M A, 1986. Simple barium chloride method for determining cation exchange capacity and exchangeable cations [J]. Soil Sci Am J, 50: 605—608.

Ladlslau M N, Enl M V, Garrison S, 1994. Mechanism of atrazine sorption by humic acid: a spectroscopic study[J]. Environ Sci Technol, 28:1867—1873.

Mallawatantri A P, Macconkey B G, Mulla D J, 1996. Characterization of pesticide sorption and desorption in macropore linings and soil horizons of Thatuna silt loam[J]. J Environ Qual, 25: 227—235.

Nanjing Soil Institute of Chinese Academy of Sciences(NSICAS), 1978. Physical and chemical analysis of soils (In Chinese)[M]. Shanghai: Shanghai Science and Technology Press. 132—141.

Newman A, 1995. Atrazine found to cause chromosomal breaks[J]. Environ Sci Tech, 29: 450A.

Novak J M, 1999. Soil factors influencing atrazine sorption-implications on fate[J]. Environ Toxic and Chem, 18:1663—1667.

Pusino A, Liu W P, Gessa C, 1994. Adsorption and desorption of herbicide dimepiperate by soils[J]. Water Air and Soil Pollution, 73: 325—331.

Schnitzer M, Khan S U, 1972. Humic substances in the environment[M]. New York: Marcel Dekker Inc. 211—218.

Senesi N, Testini C, 1980. Adsorption of some nitrogenated herbicides by soil humic acids[J]. Soil Sci, 130: 314—320.

Senesi N, Sposito G, Holtzclaw K M *et al*., 1989. Chemical properties of metal-humic acid fractions of a sewage sludge-amended aridisol[J]. J Environ Qual, 18: 186—194.

Wang G S, Alben K T, 1998. Effect of preadsorbed background organic-matter on granular activated carbon adsorption of atrazine[J]. Sci of the Total Environ, 224: 221—226.

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