

Adsorption and desorption of herbicide monosulfuron-ester in Chinese soils

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Abstract

Monosulfuron-ester is a new, low rate, sulfonylurea herbicide that is being promoted for annual broadleaf and gramineal weed control; however, there is a lack of published information on its behavior in soils. The adsorption and desorption of monosulfuron-ester by seven type soils were measured using a batch equilibrium technique. The results showed that the Freundlich equation fitted its adsorption and desorption well, and the Freundlich constant values (K_{f-ads}) ranged from 0.88 to 5.66. Adsorption isotherms were nonlinear with $1/n_{f-ads}$ values < 1 . Soil pH, organic matter (OM), and clay content were the main factors influencing its adsorption and desorption. Adsorption and desorption were negatively correlated with pH 4.0–8.0 while positively correlated with OM and clay content. The adsorption of monosulfuron-ester was mainly a physical process, because its free energy (ΔG) in seven soils was less than 40 kJ/mol. Monosulfuron-ester adsorption by three soils increased with increasing CaCl_2 concentration using CaCl_2 as a background electrolyte. Monosulfuron-ester desorption was hysteretic in all tested soils.

Key words: adsorption; desorption; monosulfuron-ester; Chinese soil; hysteresis

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Introduction

Monosulfuron-ester, N-[(4'-methyl) pyrimidin-2'-yl]-2-methoxycarbonyl phenyl-sulfonylurea (Fig. 1), developed by Pesticide National Engineering Research Center, Nankai University, China, is a novel sulfonylurea herbicide and exhibits potent, highly selective herbicidal activities at ultra-low application rates (15–22.5 g/ha) for annual broadleaf and gramineal weed control, such as pigweed, leaf mustard and *Descurainia sophia* in winter and spring wheat fields in Henan, Hebei, and Gansu provinces in China (Weng et al., 2008). The mode of action of monosulfuron-ester, like other sulfonylurea herbicides, is an inhibitor of acetolactate synthase (ALS). ALS is a key enzyme in the biosynthetic pathway of branched-chain amino acids, such as isoleucine and valine in plants, but is absent in animals and humans (Dinelli et al., 1997).

Adsorption and desorption of pesticides by soils is one of the most significant processes influencing the fate of pesticides in soil environments. Interaction at interfaces between soil components and pesticides affects not only the movement, volatilization, and degradation of the latter, but also their bioavailability, transformation

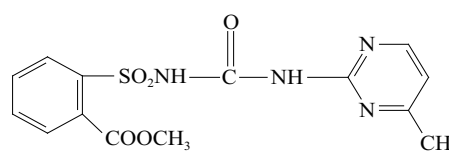


Fig. 1 Chemical structure of monosulfuron-ester.

by biotic agents, and the possibility of contamination of underground water or surface water (Patakioutas and Albanis, 2002). The extent of adsorption and desorption of a chemical compound is related to various soil properties, including organic matter (OM), type and amount of clay, ion exchange capacity, and pH. Moreover, various physicochemical parameters of the compound, such as water solubility, octanol-water partition coefficient, and pK_a value also play important roles in determining the extent of adsorption (Fernandes et al., 2003; Farahani et al., 2007; Shi et al., 2010).

The environmental behaviors of several sulfonylureas have been reported (Tang et al., 2009; Sondhia and Singhai, 2008; Weber et al., 2006). The results show that sulfonylureas are generally weakly adsorbed by soil. Soil pH, OM, or clay content are the main factors influencing their adsorption and desorption. The adsorption-desorption of sulfonylureas are pH dependant, and both are negatively

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correlated with pH. Sulfonylureas are weak acids and exist primarily in the anionic form in agronomic soils, their adsorption decreases with increasing pH, as a result of the increased amounts of anionic molecules in solution, mainly at $\text{pH} > \text{p}K_a$. Their sorptions are positively correlated with OM or clay content. The highest levels of sorption are measured in soils with low pH and high organic carbon and/or clay contents.

Sulfonylureas are assumed to be safe within the environment due to their low application rates and low toxicity to mammals (Battaglin et al., 2000; Cessna et al., 2006). However, there are several environmental concerns. First, off-site transport of sulfonylureas by drift or leaching may have severe ecological impacts due to their high phytotoxicity. Sulfonylureas can persist in the soil and may affect plant reproduction and crop or rotational crop yields beyond the application season (Bedmar et al., 2006; Hollaway et al., 2006; Lee et al., 2002; Kjær et al., 2006). Second, sulfonylureas are considered relatively mobile compounds in soils because of their anionic character, and may leach to the groundwater. Sulfonylureas, in general, have been reported to be found in both surface water and underground water (Cessna et al., 2006; Battaglin et al., 2000). Third, these chemicals pose potential risks to soil microorganisms, non-target organisms, and mammalian laboratory animals (Sabater et al., 2002; Healy et al., 2004; Arnold et al., 2001). Monosulfuron-ester is a relatively new sulfonylurea herbicide that has been shown to affect the photosynthetic processes of algae under low concentrations and could result in the decrease of the protozoan community with the increase of concentration (Pei et al., 2006). To date, no information is available about its adsorption and desorption in soils under either laboratory or field conditions.

The objectives of this study were to investigate the adsorption and desorption characteristics of monosulfuron-ester on seven selected Chinese soils using batch experiments, and to ascertain the influence of soil properties on its adsorption and desorption for predicting the persistence and mobility of monosulfuron-ester in the environment.

1 Materials and methods

1.1 Chemicals

HPLC-grade monosulfuron-ester for quantitative analysis, with a purity of 99.0%, was supplied by the Institute for the Control of Agrochemicals, Ministry of Agriculture, China. Technical grade monosulfuron-ester (95.0%) for

soil solution make-up was obtained from the Institute for the Control of Agrochemicals, Tianjin, China, and used without further purification. Its purity was measured by a high performance liquid chromatography (HPLC, Waters 2695–2996; Waters, USA). HPLC-grade acetonitrile (Fisher Scientific Company, USA) was used without further purification. Analytical grade CaCl_2 , NaOH , NaN_3 , and acetic acid were used.

Standard stock solution of monosulfuron-ester (1000 mg/L) was prepared in acetonitrile. All aqueous solutions were made in 0.01 mol/L CaCl_2 and 0.01 mol/L NaN_3 solutions. Aqueous stock solution of 20 mg/L was prepared by taking 5 mL aliquot from the 1000 mg/L monosulfuron-ester solution into a 250-mL volumetric flask. The flask was left open for evaporation of organic reagents at room temperature and finally was compensated with the marked volume with CaCl_2 - NaN_3 solution. Solutions with different concentrations were then obtained through diluting step by step for the following experiments.

1.2 Soil samples

The soils used were selected to obtain a range in physicochemical properties. Seven soils were collected from six provinces after wheat harvest. The seven collection sites are not applied monosulfuron-ester at least three years. Fresh soils from a 0–15 cm depth were collected, air-dried, gently ground, passed through a 2-mm mesh sieve, and stored in a dark place at room temperature prior to use. The physicochemical properties of the soils and the sampling locations are given in Table 1. Soil samples were classified according to “Texture AutoLookup (TAL) for Windows 4.2 (International)”, a computer program for the automatic classification of soil texture (Zhang et al., 2006).

1.3 Adsorption experiments

The batch equilibrium technique (US EPA, 1975) was used to determine the soil adsorption constants of monosulfuron-ester for seven soils. Triplicate samples of 2 g of air-dried soil and 10 mL of aqueous solution of monosulfuron-ester at concentrations of 0.625, 1.25, 2.5, 5.0, 10.0 and 20.0 mg/L were added to 50 mL polyallomer centrifuge tubes. The background electrolyte is 0.01 mol/L CaCl_2 , which was used to keep the ionic strength of the soil solution constant and to facilitate flocculation. NaN_3 of 0.01 mol/L was used to restrain microbial degradation. Blanks with the initial concentration without soil were also prepared. The tubes were shaken for 24 hr at $(25 \pm 2)^\circ\text{C}$ using a mechanical shaker. After equilibration,

Table 1 Physicochemical properties of the tested Chinese soils

Soil No.	Collection site	Soil texture	pH	OC (%)	OM (%)	Clay (%)	Sand (%)	Silt (%)	CEC (cmol (+)/kg)
S1	Harbin, Heilongjiang	Clay	5.89	2.17	3.73	38.8	49.2	12.0	19.1
S2	Taian, Shandong	Clay loam	7.46	1.19	2.04	30.3	50.9	18.8	19.0
S3	Pengzhou, Sichuan	Sandy loam	8.23	0.86	1.48	13.9	75.8	10.3	5.9
S4	Xinyu, Jiangxi	Silty clay	6.58	2.19	3.76	40.9	33.7	25.4	9.8
S5	Beibei, Chongqing	Clay loam	7.65	1.08	1.86	29.8	45.1	25.1	21.8
S6	Pixian, Sichuan	Silty clay loam	7.74	1.40	2.41	26.7	43.6	29.7	17.5
S7	Hefei, Anhui	Silty clay loam	6.31	1.76	3.02	37.3	27.9	34.8	21.9

OC: organic carbon content; OM: organic matter content; CEC: cation exchange capacity.

the suspension was centrifuged at 4000 r/min for 10 min, and then the supernatant solutions were decanted, filtered through a 0.45- μ m filter, and analyzed immediately by HPLC. The amount of herbicide adsorbed by each soil was calculated from the difference between the initial and final concentrations of monosulfuron-ester in solution. Control samples analyzed did not show any variation of initial concentration, therefore adsorption on polyallomer centrifuge tubes and microbial degradation can be excluded.

Time period intervals were selected through preliminary kinetic studies carried out by adding 10 mL of a 5 mg/L monosulfuron-ester solution to 2 g soil. At different time intervals (1, 3, 5, 7, 9, 12, 16, and 24 hr), the samples were removed and centrifuged at 4000 r/min for 10 min, and the supernatant was analyzed by HPLC.

In addition, the effects of soil solution pH and background electrolytes on monosulfuron-ester adsorption were also examined. Prior to the test, the pH values of methiopyr-sulfuron solutions were adjusted to 4.0, 5.0, 6.0, 7.0, and 8.0 with HCl or NaOH, and the amount adsorbed was quantified with the same procedure described for natural soils. The background electrolyte (CaCl₂) concentrations were 0.002, 0.01, and 0.05 mg/L. In these studies, 3 types of soils (S1 (clay), S4 (silty clay), and S5 (clay loam)), representing the different soil OM, pH value, and soil texture, were applied to determine the effect of pH and background electrolytes on monosulfuron-ester adsorption.

1.4 Desorption experiments

After the adsorption process described above, 5 mL of the supernatant solution was withdrawn and the amount of adsorbed herbicide was calculated. The remaining slurry was again brought to 10 mL by the addition of 5 mL of aqueous solution with 0.01 mol/L CaCl₂ and 0.01 mol/L NaN₃, equilibrated for 24 hr, and centrifuged. These steps (supernatant withdrawing and replacing followed by re-equilibrating) were repeated five times consecutively. The concentration of herbicide in solutions was determined, and the amount of herbicide adsorbed by the soil after each desorption step was calculated. Each level of dilution thus provided one point to the desorption isotherms.

1.5 HPLC analysis

The concentration of monosulfuron-ester was determined by HPLC (Fan et al., 2004). The system was assembled as follows: a Waters 2695 separation element equipped with a Waters 2996 variable wavelength diode array detector operating at 231 nm, Waters Empower Chem Station I, and a reverse phase Waters Symmetry[®] C₁₈ analytical column (5 μ m, 4.6 mm \times 250 mm) eluting with acetonitrile plus water (40/60 by volume, pH 4.0) at a flow rate of 0.8 mL/min. The retention time for monosulfuron-ester under the chromatographic conditions was 7.05 min. Quantitative determination of monosulfuron-ester was performed by using an external standard, and the standard concentration changed with the sample average peak area appropriately. Calculations were based on the average peak areas of the external standard. Standard solutions were

prepared using HPLC-grade monosulfuron-ester in a 0.01 mol/L CaCl₂ and 0.01 mol/L NaN₃ matrix. The standard solutions were periodically replaced to ensure no degradation. The detection limit for monosulfuron-ester was 0.05 mg/L, as calculated from the concentration of herbicide needed to obtain a detector response approximately twice the background signal.

1.6 Data analysis

The amount of monosulfuron-ester adsorbed after equilibrium was calculated according to the difference between the initial and final equilibrium solution concentrations by the following Eq. (1):

$$C_s = (C_0 - C_e) \times V/m \quad (1)$$

where, C_s (mg/kg) is the amount of monosulfuron-ester adsorbed by a soil; C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium aqueous concentrations, respectively. V (mL) is the solution volume; m (g) is the mass of the soil.

Adsorption and desorption were described by the linearized form of the Freundlich Eq. (2):

$$\log C_s = \log K_f + 1/n_f \log C_e \quad (2)$$

where, K_f is the adsorption coefficient characterizing the adsorption-desorption capacity, and n_f is the Freundlich equation exponent related to adsorption intensity that is used as an indicator of the adsorption isotherm nonlinearity. K_{f-ads} is the adsorption coefficient and K_{f-des} is the desorption coefficient of the Freundlich equation.

The hysteresis coefficient, H , for the adsorption and desorption isotherms was calculated according to Eq. (3):

$$H = (1/n_{f-des}) / (1/n_{f-ads}) \quad (3)$$

where, $1/n_{f-ads}$ and $1/n_{f-des}$ are the Freundlich constants obtained for the adsorption and desorption isotherms, respectively.

The OM normalized adsorption constant (K_{OM}) was calculated by normalizing K_{f-ads} to the fraction of OM according to Eq. (4):

$$K_{OM} = K_{f-ads} / OM \times 100\% \quad (4)$$

The free energy of adsorption of the herbicide in soil is calculated using the thermodynamic Eq. (5).

$$\Delta G = -RT \ln K_{OM} \quad (5)$$

where, ΔG (kJ/mol) is the free energy of adsorption, R (8.314×10^{-3} kJ/(K·mol)) is the mol gas constant, and T (K) is the absolute temperature.

All data analysis and model development were run by SPSS 13.0 for Windows.

2 Results and discussion

2.1 Adsorption kinetics

Figure 2 shows the adsorption kinetics after shaking seven soils with 5 mg/L monosulfuron-ester aqueous solution. The rapid adsorption phase took place within 3

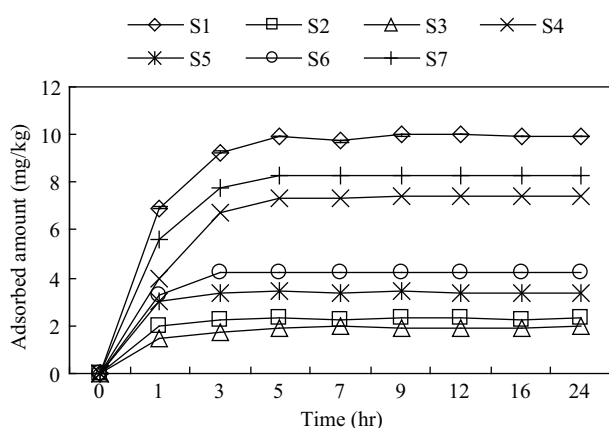


Fig. 2 Adsorption kinetics of monosulfuron-ester with aqueous solution of 5 mg/L at (25 ± 2)°C. S1–S7 refer to Table 1.

hr after shaking. During this phase, the soil adsorbed monosulfuron-ester molecules fast, so the herbicide concentration in soils increased sharply. After 3 hr, the herbicide concentration in solution varied with small changes, adsorption phase slowed, and the herbicide concentration in soils continued to increase slowly between 3–5 hr, but the chemical and physical reaction related to the adsorption continued to occur (Tang et al., 2009). According to Gilchrist et al. (1993), when a pesticide is mixed with soil it reacts with active sites that are available on the surfaces of the soil particles. Some are very reactive, so that they can hold pesticide molecules strongly, while others are not reactive enough. The loosely bound pesticide molecules desorb, so the adsorption and desorption happened at the same time, but the adsorption efficiency was greater than the desorption efficiency (Gilchrist et al., 1993). This study found that adsorption equilibrium was reached after 5 hr in all soils tested. Moreover, the amount adsorbed by soil remained steady. Further decreases in the monosulfuron-ester concentration in the supernatant after 24 hr were not significant. For laboratory convenience, 24 hr was taken as the equilibration time.

2.2 Adsorption characteristics

The Freundlich adsorption isotherms are shown in Fig. 3, and their parameters K_{f-ads} , $1/n_{f-ads}$ and R^2 are shown in Table 2. Correlation coefficients for the seven soils ($R^2 \geq 0.9762$) indicated that the adsorption equilibrium of monosulfuron-ester after shaking for 24 hr fit the empirical Freundlich equation. The adsorption isotherm of monosulfuron-ester was dependant on soil types, as the K_{f-ads} values ranged from 0.88 to 5.66, and the order of K_{f-ads} was S1 > S7 > S4 > S6 > S5 > S2 > S3. The highest

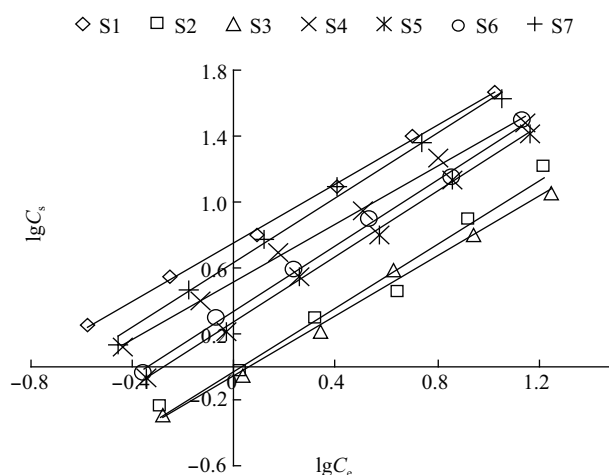


Fig. 3 Freundlich adsorption isotherms of monosulfuron-ester on soils.

K_{f-ads} value was obtained for S1, which had higher organic C, higher clay content, and the lowest pH, while the lowest K_{f-ads} value was obtained for S3, which had the lowest OM, the lowest clay content, and the highest pH value.

Table 2 shows that the values of $1/n_{f-ads}$ ranged from 0.86 to 0.97. In all cases the isotherms were nonlinear, with slopes ($1/n_{f-ads}$) of < 1, resembling the L-type curve described by Giles et al. (1960). Nonlinear sorption isotherms (convex curvature) contend with a modification of the affinity between pesticide molecules and soils when increasing concentration (Giles et al., 1960). An L-type curve suggests a relatively high affinity of the herbicide for the adsorbing sites. It has been recently described in the case of cultivated soils (Nemeth-Konda et al., 2002). Accessibility to free sorption sites decreased when solution concentration increased and led to a decreasing of the absorbed amounts by soils.

To determine the degree of influence of each soil characteristic on adsorption by statistical approximation, linear regression analyses between K_{f-ads} and selected soil properties were performed. The results are shown in Table 3. The highest correlation coefficient ($R = -0.9369$) was obtained when pH was used as the soil property ($P = 0.0018$). The correlation coefficients between K_{f-ads} and OC, OM, or clay were also significant ($0.05 > P > 0.01$), and there was no significant correlation between K_{f-ads} and other soil properties. The correlation between K_{f-ads} and pH was found to be negative, indicating that the extent of adsorption increases as soil pH decreases. The correlation between K_{f-ads} and OC, OM, or clay was positive, indicating that the extent of adsorption increases as the OC, OM, or clay increases.

Other researchers have reported similar pH, OM, and

Table 2 Freundlich parameters and free energy (ΔG) for the monosulfuron-ester adsorption isotherms on soils

Soil No.	pH	K_{f-ads}	$1/n_{f-ads}$	R^2	K_{OM}	ΔG (kJ/mol)
S1	5.89	5.66 ± 0.02	0.87 ± 0.02	0.9895	151.68	-12.45
S2	7.46	0.94 ± 0.02	0.95 ± 0.03	0.9762	46.21	-9.50
S3	8.23	0.88 ± 0.02	0.91 ± 0.02	0.9856	59.26	-10.12
S4	6.58	3.30 ± 0.04	0.86 ± 0.03	0.9912	87.74	-11.09
S5	7.65	1.85 ± 0.02	0.97 ± 0.04	0.9844	99.63	-11.41
S6	7.74	2.16 ± 0.03	0.98 ± 0.03	0.9781	89.71	-11.15
S7	6.31	4.25 ± 0.05	0.97 ± 0.03	0.9938	140.70	-12.26

Table 3 Linear regression analyses for Freundlich adsorption constant (K_{f-ads}) and selected properties of soils

Line regression parameter	pH	OC (%)	OM (%)	Clay (%)	Sand (%)	Silt (%)	CEC (cmol(+)/ kg)
Slope	-1.9269	2.9334	1.7055	0.1457	-0.0619	0.0253	0.0965
Intercept	16.4453	-1.7385	-1.7385	-1.8125	5.6066	2.1553	1.1369
Significant level (P)	0.0018	0.0105	0.0105	0.0487	0.2174	0.7828	0.4634
Correlation coefficient (R)	-0.9369	0.8722	0.8722	0.7578	0.5332	0.1300	0.3345

clay effects for other sulfonylureas. Álvarez-Benedí et al. (1998) discovered that sorption of tribenuron-methyl, chlorsulfuron, and imazamethabenz-methyl was correlated with OM and clay content. Boivin et al. (2005) found that adsorption of weakly acidic chemicals appeared to be governed by both OM content and pH. Tang et al. (2009) found that the content and chemical characteristic of the soil organic matter was considered to be one of the important factors leading to differences in sorption capacity. The extent of monosulfuron adsorption on soil was at rather high levels under low pH value conditions, and it decreased with increasing pH value.

The ΔG value of 40 kJ/mol was considered as a threshold for identifying the physical and chemical mechanisms of adsorption, and physical adsorption mainly was involved below the threshold (Carter et al., 1995). The ΔG values of seven soils at 25°C ranged from -12.45 to -9.50 kJ/mol (Table 2), the ΔG of monosulfuron-ester in seven soils was less than 40 kJ/mol, indicating that the adsorption of monosulfuron-ester by seven soils was mainly a physical process. The adsorption of monosulfuron-ester by soils also was a spontaneous process for the negative value of ΔG .

2.3 Effect of pH on monosulfuron-ester adsorption

Soil pH is one of the key factors influencing the adsorption and desorption of sulfonylurea herbicides. The dependence of monosulfuron-ester adsorption on soil solution pH was also tested (Fig. 4). It was found that adsorption decreases as soil pH increases, in agreement with the general trend observed for other sulfonylurea herbicides (Pusino et al., 2004; Tahir and Sing, 2007; Tang et al., 2009). If the same pH value is considered, it is necessary to note that S2 showed the greatest adsorption capacity when pH was > 6.0. This soil had the highest clay content and the highest OM content. This result possibly explains the significant correlation between K_{f-ads} and soil OM content (Zanini et al., 2009). This behavior is usually explained in terms of charge development at the surface of soil particles and speciation of the herbicide in aqueous solutions, as a function of pH (Berglöf et al., 2003). Since the surface charge of soil particles becomes more negative as the pH increases, the adsorption of the negatively charged monosulfuron-ester species becomes less favored by increasing pH as a consequence of electrostatic repulsion. In addition, although the adsorption of the neutral monosulfuron-ester species should not be affected by electrostatics, its concentration decreases by increasing pH, also leading to a less favorable adsorption as the pH increases.

You et al. (1999) indicated that increases in pH lead to increased solubility of OM due to either particle disper-

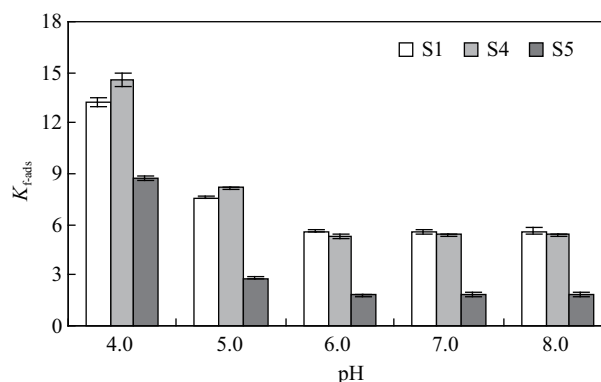


Fig. 4 Effect of pH on monosulfuron-ester adsorption by soil. Conditions: temperature $25 \pm 2^\circ\text{C}$; soil 2 g; volume 10 mL; equilibrated time 24 hr; centrifuged rate and time 4000 r/min and 10 min, respectively.

sion increases or the repulsion of the increasing negative charges on both organic matter and soil inorganic solid surfaces. Increases of dissolved OM in solution decreases the soil adsorption ability as pH increases, so that the herbicide adsorption decreases as well. Werkheiser and Anderson (1996) thought that sorption of neutral primisulfuron decreases as pH increases, because the proportion of the neutral species decreases. In addition, sorption of the anionic form also decreases as pH increases and the surface charge on Fe and Al oxides becomes less positive. Measured K_{f-ads} values exhibit a nonlinear dependence on the fraction of neutral primisulfuron with the steepest slope at low pH. The nonlinear dependence of K_{f-ads} on neutral primisulfuron may be caused by strong sorption of the anion on positively charged oxides at low pH, or by a greater affinity of organic matter for primisulfuron at low pH, where organic matter has a smaller net negative charge.

Previous studies have shown that the adsorption of sulfonylurea herbicides is also pH dependent (Tahir et al., 2005; Tahir and Sing, 2007). Since monosulfuron-ester is a weak acid, its speciation is pH dependent; this herbicide will dissociate above its pK_a value and tend to be present in the ionic form in neutral and alkaline soil solutions. Acidic pesticides are absorbed by organic soil colloids and the sorption depends on pH, being greater under acid conditions where the pesticides are absorbed in molecular (neutral) form (Weber, 1972). The high extent of adsorption measured at low pH values may be due to the lack of charge and higher lipophilicity of the neutral molecular species of the herbicide. The increase of solution pH increases the fraction of negatively charged monosulfuron-ester species. Moreover, a low solubility of monosulfuron-ester in water at a low pH could contribute to the high adsorption levels because the retention of a pesticide onto organic surfaces is often inversely correlated to its water solubility.

Table 4 Effects of pH on monosulfuron-ester adsorption by soils

Soil No.	OM (%)	k_{f-ads}				
		pH = 4.0	pH = 5.0	pH = 6.0	pH = 7.0	pH = 8.0
S1	3.73	13.19 ± 0.25	7.60 ± 0.08	5.62 ± 0.03	5.57 ± 0.11	5.62 ± 0.14
S4	3.76	14.53 ± 0.37	8.15 ± 0.05	5.34 ± 0.14	5.38 ± 0.08	5.38 ± 0.08
S5	1.86	8.72 ± 0.10	2.84 ± 0.08	1.82 ± 0.07	1.84 ± 0.10	1.83 ± 0.11

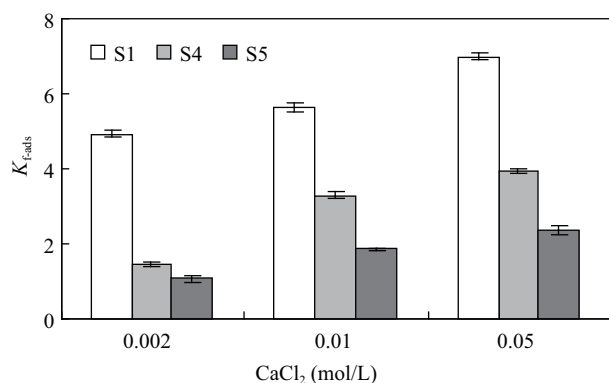


Fig. 5 Effect of CaCl_2 on monosulfuron-ester adsorption by soils. Conditions: temperature $25 \pm 2^\circ\text{C}$; soil 2 g; volume 10 mL; equilibrated time 24hr; centrifuged rate and time 4000 r/min and 10 min, respectively.

2.4 Effect of background electrolyte on monosulfuron-ester adsorption

The effect of CaCl_2 on monosulfuron-ester adsorption by three selected soils was investigated. The results are shown in Fig. 5. Monosulfuron-ester adsorption by three soils all increased with increasing CaCl_2 concentration.

The reaction of different kinds of pesticides was different when CaCl_2 was added as a background electrolyte (Gimsing and Borggaard, 2001; Spark and Swift, 2002). The addition of CaCl_2 to solution may cause several competing effects (Stumm, 1992) including (1) an increasing competition for adsorption sites by the electrolyte anions caused by increasing CaCl_2 concentrations, (2) an increasing aqueous complexation with the anionic pesticides as a consequence of increasing electrolyte cation concentrations, and (3) a decrease in the activity of the charged ions caused by increasing electrolyte concentrations. All three solution effects cause decreasing adsorption of anionic pesticides to mineral surfaces with a net positive charge. However, Dzombak and Morel (1990) found that surface complexation models indicate that the rate at which the potential decays with distance from the surface increases with increasing ionic strength, and an increase in ionic strength causes an increasing positive charge on the surface. Ali and Dzombak (1996) have demonstrated that Ca^{2+} is capable of forming complexes with simple organic acids, so adding CaCl_2 to the experiment leads to a possible complexation between the anionic pesticides and Ca^{2+} , which results in non-sorbing Ca^{2+} pesticide solution complexes. Haderlein and Schwarzenbach (1993) have demonstrated that Ca^{2+} can adsorb onto silanol surface sites, resulting in positive Ca^{2+} sites, to which negatively charged compounds will be attached, due to electrostatic interactions. Therefore, the increasing adsorption of anionic pesticides on kaolinite and quartz with increasing CaCl_2 concentration can be explained by Ca complexes bridging pesticides and minerals.

Chen and Huang (2009) found that *m*-dinitrobenzene and nitrobenzene sorption enhancements were significantly promoted with the increase of electrolyte concentration (KCl or NH_4Cl). The salting-out effect is insufficient to account for the sorption enhancement by original bentonite with increasing KCl or NH_4Cl concentration. X-ray diffraction patterns of bentonite suspensions indicated that the sorption enhancement of *m*-dinitrobenzene was attributed to the intercalation of K^+ or NH_4^+ into bentonite interlayers, followed by dehydration with *m*-dinitrobenzene to form inner-sphere complexes, which caused previously expanded bentonite interlayers to collapse in aqueous suspension, thus further enhancing the interactions of phenyl with siloxane surfaces. The sorption enhancement was attributed to the interaction between the exchanged cations (K^+ or NH_4^+) and the adsorbed *m*-dinitrobenzene or nitrobenzene.

2.5 Desorption characteristics

The monosulfuron-ester desorption data obtained by the dilution method were well-described by the Freundlich equation. Desorption data were fitted to the linearized form of the Freundlich equation; the respective constants for desorption are listed in Table 5. The desorption isotherms were nonlinear for monosulfuron-ester due to $1/n_{f-des} < 1$, and $1/n_{f-des} < 1/n_{f-ads}$, suggesting that a significant amount of the monosulfuron-ester adsorbed is not easily desorbed, monosulfuron-ester desorption was not reversible, and desorption cannot be predicted on the basis of adsorption isotherms.

The hysteresis coefficient, H , for the adsorption and desorption isotherms is a measure of the extent of hysteresis in the desorption. A value of 1 means that desorption proceeds as fast as adsorption and no hysteresis occurs. However, a value of $H < 1$ indicates that the rate of desorption is slower than the rate of adsorption, and that hysteresis takes place (Pusino et al., 2004). The H_a values in this study spanned a range of 0.35–0.76 (Table 5), indicating a hysteresis effect for all seven soils, similar to other sulfonylurea herbicides, such as azimsulfuron and monosulfuron (Pusino et al., 2004; Tang et al., 2009). In particular, these values indicate that the irreversibility of the desorption process increases with higher equilibrium starting point concentrations, since the H values of all other soils except for S2 and S5 decrease with increasing monosulfuron-ester concentration.

Desorption hysteresis has been reported for a large number of soil organic compound systems, and several explanations have been proposed for this phenomenon (Tang et al., 2009; Zhang et al., 2007), such as chemical or biological transformation, nonequilibrium conditions, and high-energy bonding. Huang and Weber (1997) measured

Table 5 Freundlich parameters and hysteresis coefficients (H) for the desorption of monosulfuron-ester by soils

Soil No.	$1/n_{f-des}$	Initial concentration (mg/L)	K_{f-des}	$1/n_{f-des}$	R^2	H	H_a
S1	0.87	5	8.43	0.37	0.9780	0.42	0.35
		10	14.44	0.32	0.9826	0.36	
		20	25.60	0.24	0.9616	0.28	
S2	0.95	5	1.16	0.59	0.9883	0.62	0.64
		10	1.94	0.68	0.9743	0.71	
		20	3.05	0.56	0.9816	0.59	
S3	0.91	5	1.23	0.83	0.9636	0.91	0.76
		10	1.44	0.70	0.9520	0.77	
		20	2.49	0.55	0.9721	0.61	
S4	0.86	5	4.41	0.60	0.9886	0.70	0.57
		10	7.21	0.49	0.9876	0.57	
		20	10.51	0.38	0.9890	0.45	
S5	0.97	5	2.20	0.85	0.9910	0.88	0.63
		10	5.33	0.48	0.9679	0.49	
		20	6.97	0.51	0.9885	0.52	
S6	0.98	5	3.14	0.75	0.9717	0.77	0.59
		10	5.30	0.49	0.9867	0.51	
		20	8.66	0.49	0.9897	0.50	
S7	0.97	5	6.28	0.72	0.9776	0.75	0.58
		10	8.51	0.56	0.9901	0.58	
		20	15.77	0.40	0.9636	0.41	

H_a : average values of H .

Table 6 Linear regression analyses for methiopyrsulfuron desorption hysteresis coefficients (H) and selected properties of soils

Line regression parameters	pH	OC (%)	OM (%)	Clay (%)	Sand (%)	Silt (%)	CEC (cmol(+)/ kg)
Slope	0.1212	-0.1900	-0.1105	-0.0101	0.0036	0.0002	-0.0090
Intercept	-0.2727	0.8791	0.8791	0.9307	0.4222	0.5862	0.7386
Significant level (P)	0.0157	0.0258	0.0258	0.0498	0.3137	0.9771	0.3093
Correlation coefficient (R)	0.8489	-0.8142	-0.8142	-0.7549	0.4478	-0.0135	0.4514

phenanthrene adsorption and desorption equilibria for 10 natural sorbents. They discovered that the adsorption affinities of these materials for phenanthrene, as well as their respective isotherm nonlinearities and hysteretic behaviors, were inversely correlated with the O/C atomic ratio. Samples containing more physically condensed and chemically reduced SOM matrices exhibited greater solute affinity, more nonlinear sorption equilibria, and more pronounced hysteresis. Neville et al. (2000) found that the lack of similarity between adsorption and desorption due to hysteresis is likely a result of binding to organic matter and mineral particles, particularly clay minerals.

Table 6 shows the linear regression analyses for monosulfuron-ester desorption hysteresis coefficients (H) and other selected properties of the different soils. The correlation between desorption hysteresis (averaged H values) and OC or OM was significant ($R = -0.8142$, $P = 0.0258$). In addition, there was a significant correlation between desorption the hysteresis coefficient and pH ($R = 0.8489$, $P = 0.0157$). The correlation coefficient between H and clay was also significant ($P = 0.0498$), but there was no significant correlation between H and other soil properties. Thus desorption hysteresis of monosulfuron-ester might be mostly attributed to the effect of soil pH, organic carbon or OM, and clay content.

3 Conclusions

By using the batch equilibrium experiments, the adsorption-desorption of monosulfuron-ester was deter-

mined in seven soil types found in six provinces of China. The Freundlich constant values (K_{f-ads}) ranged from 0.88 to 5.66, and soil pH, OM, and clay content were the main factors affecting monosulfuron-ester adsorption. Adsorption was negatively correlated with pH and positively correlated with OM and clay content. The $1/n_{f-ads}$ values < 1 indicated that the isotherms for monosulfuron-ester adsorption were nonlinear ($1/n_{f-ads}$ ranged from 0.86 to 0.98). The curves of the isotherm adsorption belong to the L type curve. The ΔG values of seven soils at 25°C ranged from -12.45 to -9.50 kJ/mol, which indicates that the adsorption of monosulfuron-ester of the seven soils was mainly a physical process. The monosulfuron-ester adsorption by three soils increased with increasing $CaCl_2$ concentration. Desorption of monosulfuron-ester in all tested soils was hysteretic and was positively correlated with the OM and clay content, but negatively correlated with soil pH.

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