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Residue analysis and dissipation of monosulfuron in soil and wheat

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Abstract: HPLC-UV residue analytical method for monosulfuron [N-[(4'-methyl) pyrimidin-2'-yl]-2-nitrophenylsulfonyl urea] in soil and wheat was developed. Monosulfuron residues were recovered by solvent extraction, followed by liquid-liquid partition, and C_{18} cartrige clean-up. Excellent method recoveries ranging from 95%—104% for both fortified soil and wheat grain were obtained with coefficients of variation 1.5%—11.8%. The minimum detectable quantities in soil and wheat were both 4 ng, the limit of detection was 0.02 mg/kg. When monosulfuron was applied according to double dosage of maximum recommended use direction(120 g ai/hm^2 of 10% monosulfuron wettable powder sprayed for once during development of wheat) in field studies conducted in Shandong Province and near Beijing, monosulfuron residues was not detected in soil and wheat samples collected 75 d after application. Laboratory soil degradation studies showed that monosulfuron degraded faster in acidic soil and strong alkaline soil than in neutral or weak alkaline soil. Half lives in Jiangxi soil, Shijiazhuang soil, Jiangsu soil and Heilongjiang soil were 41, 48, 87 and 84 d respectively. Monosulfuron residues dissipated rapidly in Shandong and Beijing field test sites with half-lives of less than 14 d.

Keywords: monosulfuron; wheat (*Triticum*, *aestivum* L.); soil degradation; residue analysis

Introduction

Sulfonylurea herbicides are characterized by its low use rates in broad-spectrum of weed control and its environment-benign properties (Fan, 2003a). More than 25 sulfonylurea herbicides had been commercialized worldwide (Tomlin, 2004). Monosulfuron [N-[(4'-methyl) pyrimidin-2'-yl]-2-nitrophenylsulfonyl urea] is a new sulfonylurea herbicide developed by Nankai University of China (Li, 1994). Bioassay and activity determination of acetolactate synthase (ALS) indicated that high concentration of monosulfuron inhibited growth of maize roots and activity of ALS from different maize cultivars *in vitro* strongly (Fan, 2003b). Recently monosulfuron has been registered in P. R. China for weed control in maize(*Zea mays* L.), wheat (*Triticum*, *aestivum* L.) and millet (*Panicum miliaceum* L.) fields with the use rates of 15—30 g ai/hm^2 (Fan, 2000).

Because of the low application rates and quick dissipation of sulfonylurea herbicide in crop environment, monitoring μg/kg level of sulfonylurea herbicides is very difficult. Since the early 1980s, many methods have been developed to determine the residue profile and environmental fate of sulfonylurea herbicides. Plant bioassays and extraction followed by high performance liquid chromatography(HPLC), gas chromato-graphy(GC), supercritical fluid chromatography (SFC), capillary electrophoresis (CE), enzyme linked immunosorbent assay(ELISA) and other technique such as HPLC/MS and molecular imprinted polymer had all been used with various degrees of success(Shalaby, 1992; Schlaeppi, 1994; Smith, 1995; Marek, 1996; Zhu, 2002). Among these methods, HPLC with UV detection is the most commonly used worldwide.

Documents were concentrated on residue analysis of two substituted heterocyclic sulfonylurea herbicides worldwide (Koeppe, 1995; Powley, 1998; Liu, 2003), the main objective of this paper was to develop the extraction, separation, cleanup and quantitation methods for residue analysis of monosulfuron—a monosubstituted heterocyclic sulfonylurea herbicide—in soil and wheat grain samples, and monitoring its dissipation in soil.

1 Materials and methods

1.1 Reagents

Reference standard of monosulfuron (> 97.9% purity) was synthesized by National Pesticide Engineering Research Center (Tianjin), Nankai University, China. Chemical structure of monosulfuron is shown in Fig. 1.

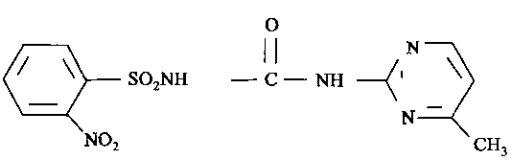

Fig. 1 Structure of monosulfuron
[N-[(4'-methyl)pyrimidin-2'-yl]-2-nitrophenylsulfonyl urea]

Monosulfuron (10% wettable powder) was provided by

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* Corresponding author

National Pesticide Engineering Research Center (Tianjin), Nankai University. Methanol and acetonitrile were of HPLC grade. Other reagents include anhydrous sodium sulfate, phosphoric acid, glacial acetic acid, chloroform, dichloromethane, acetone, petroleum ether and ammonium hydroxide were of analytical reagent grades. Double distilled water was used as part of mobile phase.

1.2 Soil

Field soil samples were collected from various locations near Beijing, Heilongjiang, Jiangsu, Jiangxi, Shandong and Shijiazhuang for residue method development and laboratory soil degradation studies. Soil characteristics are listed in Table 1.

Table 1 Basic physicochemical properties of test soil

Soil collection site	Organic matter, %	*CEC*, cmol/kg	pH	Soil type[a]
Beijing	2.2	14.8	6.7	Sandy loam
Heilongjiang	4.5	33.4	7.0	Clay loam
Jiangsu	1.3	14.0	6.8	Loam clay
Jiangxi	1.2	6.7	6.2	Clay
Shandong	1.2	12.9	6.6	Sandy clay loam
Shijiazhuang	2.0	14.3	7.6	Sandy loam

Note: [a] International soil taxonomy

All kinds of soil samples used were screened through 40-meshes, air-dried at room temperature in flat stainless steel trays and thoroughly mixed to ensure homogeneity, then stored at −20℃. Analysis must be done within one month, monosulfuron decomposed less than 0.8% under the condition of one month storage at −20℃.

1.3 Soil fortification and extraction

Monosulfuron standard solutions in acetonitrile were prepared as concentraion of 200, 20, 6.0, 3.0, and 1.0 μg/ml, respectively. Aliquot(1 ml) of standard solution was added to 20 g of soil. The solvent was allowed to evaporate at room temperature. The final concentration of monosulfuron were 10, 1.0, 0.3, 0.15, and 0.05 mg/kg, respectively. Triplicated soil samples for each fortification level were prepared.

Each of fortified soil sample (20 g) was extracted with 60 ml of methanol(0.2 mol/L) ammonium hydroxide (1∶1, v/v) for 2 h by shaking for 0.5 h. Extraction solvent was removed by vacuum filtration. This extraction step was repeated three times with 60 ml of the same extraction solvent. Solid soil mud samples were discarded after solvent extractions. Soil extracts were combined and clean up using solvent partitioning; 100 ml of 2% sodium sulfate was added to the combined soil extract, the mixture was adjusted to pH = 10.0 with 0.2 mol/L ammonium hydroxide and patitioned twice, each with 30 ml chloroform and petroleum ether, organic solvents were discarded. Aqueous extracts, acidified to pH = 3.0 using dilute phosphoric acid, was extracted three times by 40 ml of dichloromethane. After dried over by anhydrous sodium sulfate, the dichloromethane phase was evaporated to near dryness at < 40 ℃. Methanol(3 ml) was added to dissolve the concentrated soil extract(sonication if necessary), the final samples was cleaned up by C_{18} cartridge (500 mg). Finally, the sample was brought up to 2 ml of methanol(0.2 mol/L) ammonium hydroxide (1∶1, v/v) and stored dry in 5 ml volume of glass tube in a refrigerator within 8 h for HPLC analysis.

1.4 Wheat grain fortification and extraction

Wheat grain was air-dried in room temperature and ground to powder, stored at −20℃ for no more than one month before analysis. Powdered wheat grain sample(20 g) was extracted with 100 ml of acetone(0.2 mol/L) ammonium hydroxide(3∶2, v/v) for 2 h by shaking for 0.5 h. After filtration and washing three times with 50 ml of acetone(0.2 mol/L) ammonium hydroxide (3∶2, v/v) via vacuum filtration, the combined solution was evaporated to about 70 ml of volume at < 40℃ in order to remove most of acetone. Then 100 ml of saturated sodium chloride were added to the combined solutions. The mixture was adjusted to pH = 10.0 with 0.2 mol/L of ammonium hydroxide and washed by 30 ml chloroform and petroleum ether each twice respectively. The organic solution was discarded and the resulting aqueous solution was further processed following similar procedures as described for the extractions of soil residues.

1.5 Liquid chromatography

VISTA 5500 HPLC equipped with UV-200 detector, ODS Hypersil(5 μm) column with 250 × 4.6 mm(discovery C_{18}) and 500 mg of ODS C_{18} precolumn was used for analyses. For samples extracted from soil, the mobile phase was methanol/water/glacial acetic acid = 430/562/8(v/v/v), mobile phase flow rate: 0.8 ml/min, sensitivity: 0.02 Au/mV, sample injection volume: 20 μl, wavelength: 254 nm, column temperature: 40℃. For samples extracted from wheat, the mobile phase was methanol/water/glacial acetic acid = 430/562/8(v/v/v), mobile phase flow rate: 0.5 ml/min, sensitivity: 0.01 Au/mV, sample injection volume: 20 μl, wave length: 254 nm, column temperature: 40℃.

1.6 Laboratory degradation of monosulfuron

1 ml of 200 μg/ml monosulfuron standard solution was added to 20 g of Jiangsu, Jiangxi, Heilongjiang and Shijiazhuang soils, respectively, and the final concentration of monosulfuron was 10 mg/kg, after evaporation of solvent at room temperature, 8.5 ml of double distilled water was added, the bottle was sealed with laboratory film. 30 replicates of each soil sample were maintained in LRH-250-G lighting culture tank in the darkness at 30℃, 3 samples were get out each time at after maintainance of 1, 7, 15, 22, 30, 36, 45, 51, 60, 64, 90, 91, and 122 d according to the residue level of monosulfuron in different type of soil, monosulfuron residue in the sample was analyzed according to the methods discribed above.

1.7 Field experiments

Two field experiments were conducted in 1999 and 2000

at locations near Dongbeiwang, Beijing City and Taian, Shandong Province according to "The Guidline for Pesticide Residue Field Experiments" issued by Institute of the Control of Agrochemicals, Ministry of Agriculture, The People's Republic of China. A single application of monosulfuron in the field was carried out at the use rate of 60 and 120 g ai/hm^2. They were equivalent to maximum single and 2X of the label use rate. When wheat grew to elongation stage (F_3), 600 and 1200 g of 10% monosulfuron wettable powder by adding 750 kg of water was sprayed in 1 hm^2 of wheat field for one time. 0—15 cm depth of soils were collected at different intervals accordingly, wheat grain and soil samples were also collected at harvest for terminal residue analyses.

2 Results and discussion

2.1 Soil recovery of monosulfuron

Because there was much absorption of impurities in soil sample interfering the determination of monosulfuron at its maximum absorption of 225 nm, in order to obtain adequate sensitivity and also eliminate undesirable responses from coextracted materials, UV determination at 245 nm was chosen for the determination of monosulfuron. The typical HPLC-UV chromatogram of monosulfuron standard and soil blank and soil fortification is shown in Fig. 2. Under conditions expressed in materials and methods, peak area(y) had good relationship to the amount of monosulfuron(x) at 10—100 ng, regression equation was $y = 25.036x - 117.84$, $r^2 = 0.9975$. Different soils were fortified at three to four levels of monosulfuron from 0.05 to 10 mg/kg. Cleanup of soil extracts was necessary to prevent continuous off-scale response of the detector at required sensitivity. The average recoveries and coefficients of variation of the method were 94%—104% and 1.5%—11.8% respectively (Table 2). The minimum detectable quantity of monosulfuron was 4 ng, the minimum detectable concentration of monosulfuron in soil sample was 0.02 mg/kg. The results indicated that the method was accordance with the requirement of analysis for monosulfuron residue in soil according to the requirement of Ministry of Agriculture, The People's Republic of China.

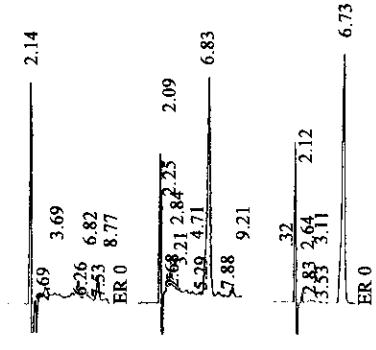

Fig.2 HPLC-UV chromatogram of monosulfuron standard, blank and fortification of Heilongjiang soil

Table 2 Accuracy of monosulfuron residue analysis in soil

Soil	Fortification concentration, mg/kg	Average recovery, %*	Standard deviation, %	Coefficient of variation, %
Shijiazhuang	9.7	94	2.7	2.8
	1	106	5.2	4.9
	0.1	107	8.7	8.1
Jiangsu	9.7	97	5.7	5.9
	1	109	7.9	7.3
	0.1	107	5.6	5.3
Beijing	1	99	11.7	11.8
	0.3	95	3.7	3.9
	0.15	104	2.1	2.0
	0.05	99	1.5	1.5

Note: *Data were the results of three replicates

2.2 Laboratory degradation of monosulfuron

After treatment of soil samples by solution extraction and C_{18} cartridge clearup, there were no UV absorption peak of impurities in the blank of Jiangxi, Shijiazhuang and Jiangsu soil samples affecting determination of monosulfuron. Because of the high concentration of organic matters in the soil sample collected from Heilongjiang, a very short UV absorption peak of impurities in the blank very slightly affected the anlysis of monosulfuron, this affect could be neglected (Fig. 2). Laboratory studies showed the half-lives (DT_{50}) of monosulfuron in Jiangxi soil, Shijiazhuang soil, Jiangsu soil and Heilongjiang soil were 41, 48, 87 and 84 d, respectively. Fig. 3—Fig. 6 described the laboratory degradation of monosulfuron in four soils tested.

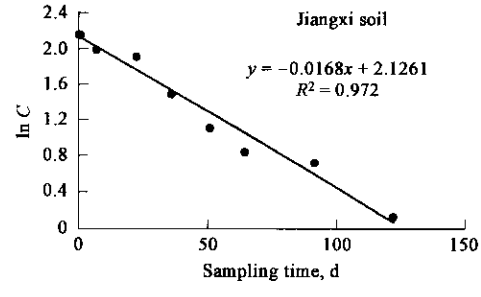

Fig.3 Semilog plot of monosulfuron degradation in Jiangxi soil

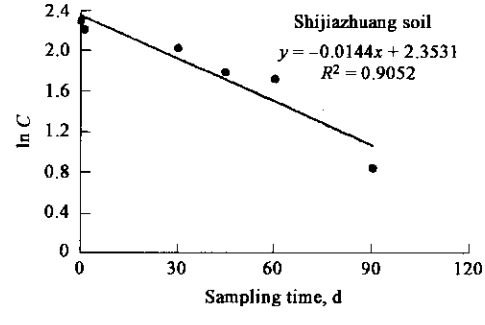

Fig.4 Semilog plot of monosulfuron degradation in Shijiazhuang soil

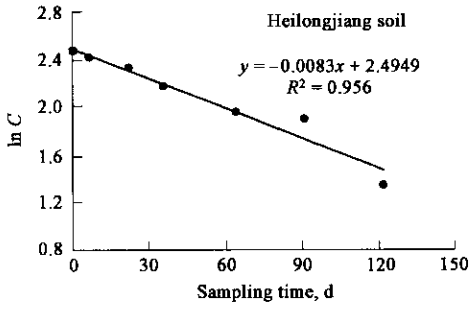

Fig. 5 Semilog plot of monosulfuron degradation in Heilongjiang soil

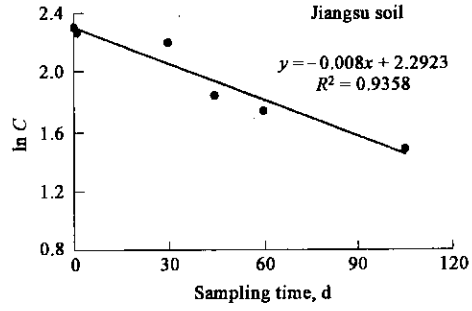

Fig. 6 Semilog plot of monosulfuron degradation in Jiangsu soil

2.3 Degradation of monosulfuron in field soil

Field experiment was carried out in Beijing and Shandong in 1999 and 2000. The results are shown in Table 3. Half-lives of monosulfuron dissipation in soils of Beijing and Shandong wheat fields were caculated from its semilog plot curve(Fig. 7) as 10 and 14 d, respectively.

Table 3 Degradation of monosulfuron in soils of Beijing and Shandong wheat fields(1999)

Time of sampling, d	Beijing					Shandong				
	Residue, mg/kg			Average	Dissipation, %	Residue, mg/kg			Average	Dissipation, %
0	0.26	0.23	0.42	0.31	-	0.20	0.17	0.17	0.18	-
3	0.22	0.26	0.33	0.27	48.6	0.13	0.13	0.12	0.12	28.9
5	0.06	0.05	0.06	0.06	89.4	0.08	0.09	0.10	0.10	48.9
7	0.05	0.05	0.04	0.05	91.0	0.06	0.06	0.06	0.06	59.8
15	0.05	0.04	0.04	0.04	91.9	0.05	0.03	0.03	0.04	80.0
30	0.03	0.04	0.03	0.03	94.0	0.05	0.03	0.03	0.04	80.0

Note: Data are the results of three replicates

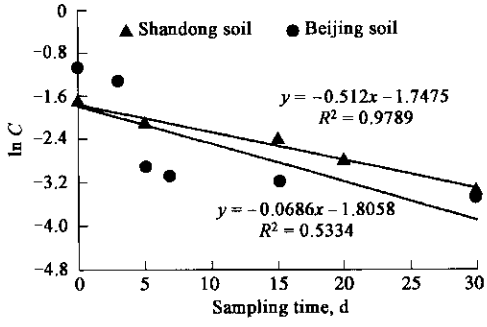

Fig.7 Semilog plot of monosulfuron dissipation in soils of Beijing and Shandong wheat fields

Monosulfuron degraded more rapid in soil located near Beijing than that near Shandong, there were little differences of organic matter, *CEC* and pH between two soils, because the soil type of Beijing was sandy loam and Shandong was sandy clay loam, soil type was an important factor affecting degradation of monosulfuron. Most important parameter was that 4 d after herbicide application, there were two heavy rains of 12.3 mm and 11.4 mm falling in Beijing. Three days after monosulfuron application, there were two rains of 11.0 mm and 1.3 mm falling in Shandong too. Laboratory studies indicated that monosulfuron is poorly absorbed and medium to high mobile in soil (data not shown). So the amount of rainfall is an important factor affecting monosulfuron dissipation in soil of wheat field too. Soil collected from Beijing had less clay than soil collected from Shandong, monosulfuron linched faster in sandy loam than in sandy clay loam because of the heavy rain in Beijing, therefore the concentration of monosulfuron residue detected in 0—15 cm of soil sample droped quickly from the 3rd day to the 5th day in Beijing, and this result was probably caused by joint affects of the soil properties and the rain fall. And the affects of microbe to dissipation of monosulfuron in soil deserved further reseach too.

2.4 Residue analysis of monosulfuron in wheat

There was good relationship between peak area(y) and amount of monosulfuron (x) at 10—100 ng under the conditions of HPLC analysis described in materials and methods, the regression equation was: $y = 92.313 - 157.3x$, $r^2 = 0.9999$.

Table 4 Recoveries of monosulfuron in wheat at different levels of fortification

Spiked concentration, mg/kg	Average recovery, %	Standard deviation, %	Coefficient of variation, %
0.05	93	5.1	5.4
0.1	97	4.6	4.7
1	91	6.2	6.8

Note: Data are the results of three replicates

The minimum detectable quantity of monosulfuron was 4 ng, minimum detectable concentration in wheat grain was 20 μg/kg. Wheat samples fortified at three levels, three replicates were made at each fortification level. The recoveries are listed in Table 4. Average recoveries of

monosulfuron in wheat fortification in the range of 0.05—1.0 mg/kg were 91%—97%, coefficients of variation ranged from 4.7% to 6.8%. The method satisfied the requirement of monosulfuron residue analyses.

Terminal residues of monosulfuron in soils and wheat grains were detected in Beijng and Shandong in 1999 and 2000, respectively, when wheat grew to elongation stage (F_3), 60 and 120 g of 10% monosulfuron wettable powder was dissolved in 750 kg of water, the solution was sprayed in 1 hm^2 of wheat field. After 75 d of wheat growth and development, the residue of monosulfuron in soil and wheat at this harvest time was not detected under the conditions of this experiment (Table 5).

Table 5 Terminal residue of monosulfuron in soil and wheat in Beijing and Shandong

Date	Dosage, g ai/hm^2	Application	Location	Sample[a]	Final residue, mg/kg[b]
1999	Lower(60)	One time	Beijing	3	Soil: ND; wheat: ND
	Higher(120)	One time	Shandong	3	Soil: ND; wheat: ND
2000	Lower(60)	One time	Beijing	3	Soil: ND; wheat: ND
	Higher(120)	One time	Shandong	3	Soil: ND; wheat: ND

Notes: [a]Samples were collected at the time of wheat harvest 75 d away from herbicide application; [b]data are the results of three replicates, ND≤0.02 mg/kg

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