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Dissipation and Residues of Nicosulfuron in Corn and Soil Under Field Conditions

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Abstract A simple, sensitive method for the analysis of nicosulfuron in corn and soil was developed. Samples were extracted with acetonitrile: water (2:3, V/V) mixture and partitioned with dichloromethane. After concentration, the soil sample extracts were detected using high performance liquid chromatography–ultraviolet detector (HPLC–UVD), and the corn sample extracts were detected using high performance liquid chromatography-mass spectrometry detector (HPLC–MSD). The fortified recoveries at 0.05–1.0 mg/kg were 79.7%–115.8%, with the relative standard deviation of 1.40%–13.8%. The limit of detection of the analytical method was 0.05 ng at a signal-to-noise ratio of 3, and the limit of quantification was 0.05 mg/kg for both corn and soil. The dissipation dynamics of nicosulfuron in the field trials in Beijing and Changchun were investigated. The half-lives of nicosulfuron in corn plants were 0.73 days in Beijing and 0.53 days in Changchun, both with a dissipation rate of 90% over 7 days after application. The half-lives in soil were 13.64 days both in Beijing and in Changchun with a dissipation rate of 90% over 21 days. Low residues and short half-life in corn suggested that nicosulfuron could be safely used in corn crops with the suitable dosage and application.

Keywords Nicosulfuron · Corn · Soil · Residues · Dissipation

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Nicosulfuron[2-[(4,6-Dimethoxypyrimidin-2-ylcarbamoyl) sulfamoyl]-*N*,*N*-dimethylnicotinamide] is a classic and broad-spectrum sulfonylurea herbicide. Since its introduction to the market in 1990s, nicosulfuron has been largely employed for the control of many grasses and broadleaf weed species in crop protection of vines, rice, citrus, corn, potatoes and tomatoes.

Corn is an important crop in China, which was cultivated throughout the country, and the production of corn in China ranks second in the world. Corn has good resistance to nicosulfuron which is wildly used to control many grasses and broadleaf weed species in corn field.

Although the residue analysis of sulfonylurea herbicides have been reported in many materials, the literatures were mostly about the multi-residue determination of the sulfonylurea herbicides in soil (Ye et al. 2006), surface waters (Polati et al. 2006) and some crops, such as soybeans (Qi et al. 2005) and rice (Sui et al. 2006). A HPLC method with UV and MS detection for the multi-residue determination of the sulfonylurea herbicides in soil was described (Ye et al. 2006). The soil sample was extracted by phosphate buffer (pH = 7.8): methanol (8:2, V/V) solvent with ultrasound wave three times, and then the SPE method was used as the cleaning-up procedure. It was relatively time-comsuming. Dissipation of nicosulfuron and rimsulfuron in surface soil was studied in a Sequatchie silt loam surface soil (Cheryl et al. 2002). The results showed that both herbicides alone and in mixture disappeared quickly, with $DT_{50} < 6$ days.

In this study, a simple and quick method of extraction and purification of nicosulfuron was developed, and the persistence, dissipation, and kinetics of nicosulfuron residues were investigate in corn crops and soil under the field conditions. Our objective was to provide a simple residue analytical method to evaluate the safe application rate of nicosulfuron for corn crops.

Materials and Methods

The nicosulfuron standards (98% purity) and formulations (75% WP) were obtained from Zibo New Agriculture Chemical Co. Ltd (Shandong, China). High-performance liquid chromatography (HPLC)-grade acetonitrile was supplied by Honeywell (Burdick &Jackson, US). Ultrapure water was purchased from Aquapro Ultrapure Water System (Chongqing, china). Analytical-grade dichloromethane, sodium chloride, acetic acid, and hydrochloric acid were purchased from the Beijing Reagent Company (Beijing, China).

All analysis was conducted with an Agilent 1100 HPLC equipped with ultraviolet (UV) detection and an Agilent 1100 HPLC–MS equipped with G1314AVWD,G1316A COL-COM,G1313AALS,G1311A Quatpump,G1379A Degasser and Ion Trap MSD (Agilent, USA). A reverse-phase C_{18} HPLC column (250 mm × 4.6 mm i.d., 5 μm particle size) was used as the UV separation column, while a reverse-phase C_{18} HPLC column (150 mm × 4.6 mm i.d., 5 μm particle size) was used as the MS separation column and was maintained at 25°C. The mobile phase consisted of acetonitrile/water/acetic acid (30/70/0.2% by volume), with a flow rate of 0.8 mL/min. The injection volume was 20 μL and the UV wavelength was 254 nm. The retention time for nicosulfuron in the ultraviolet (UV) detection condition was 12.4 min, while in the MS detection condition was 5.9 min.

In the field trials, including the dissipation experiments and the final residue experiments, were carried out both in Beijing and Changchun, China in 2009. Each experiment field consisted of three replicate plots with an area of 30 m^2 for each plots and was separated by irrigation channels.

After the emergence of 3–5 leaves of corn, nicosulfuron 75% WP was sprayed on the corn field. In order to reach the detection limits of the residue analysis method during the grow season, the applied dose was set as 202.5 a.i. mg/hm^2, which was three times the recommended dosage level. Representative corn plant and soil samples were randomly collected about 2 h, 1, 2, 3, 5, 7, 14, 21, 28, and 35 days after spraying. The collected corn plant samples were comminuted with a grinder (IKA, German). All collected samples were stored in a freezer at −20°C for further analysis.

The ultimate residue experiment was performed at a lower dosage level of 67.5 a.i. mg/hm^2 (the recommended dosage) as well as at a higher dosage level of 101.25 a.i. mg/hm^2 (one and half the recommended dosage), respectively. After the emergence of 3–5 leaves of corn, the high and low dosage treatment were sprayed one time. Corn and soil samples were collected on harvest days after the application of nicosulfuron (75% WP).

About 10 g soil and 5 g corn (corn plant or corn grain samples) were put in a 50-mL centrifuge tube and 30-mL acetonitrile: water (2:3, V/V) mixture was added. The samples were shaken in a reciprocating shaker for 30 min and centrifuged at 4,000 r/min for 5 min. Then the supernatant was collected in a 250-mL separatory funnel for the liquid–liquid extraction (LLE).

A 0.5-mL 6 N hydrochloric acid solution was added to the separatory funnel to adjust the pH ≤ 5,then 6 g sodium chloride was added to the funnel. The separatory funnel was shaken vigorously for about 30 s, and stayed to separate for 1 min. Then 15 mL dichloromethane was added, and the separatory funnel was shaken vigorously for about 30 s, and stayed to separate for 5 min. The organic phase was transferred to a 100 mL evaporating flask. The aqueous phase was extracted with another 15 mL dichloromethane again. When the second extraction was completed, the organic phase was combined and evaporated to dryness using a rotary vacuum evaporator at 45°C. The residue in the flask was dissolved in 1 mL of acetonitrile and the solution was transferred to a HPLC sample vial for instrumental analysis after filtered through the 0.45 μm organic filter. Soil sample extracts were determined using the HPLC–UVD, and the corn plant samples were detected using the HPLC–MS detector.

Results and Discussion

The method evaluation was carried out to determine the fortified recoveries, precision and limits of detection of the analytical method. The standard solution of Nicosulfuron was added to the untreated corn plant and soil samples at three concentration levels. The fortified samples were analyzed using the procedure described with three repetitions. The results were shown in Table 1. The average recoveries were 79.7%–115.8%, with the relative standard deviation of 1.40%–13.8%. The limit of detection of the analytical method was 0.05 ng at a signal-to-noise ratio of 3, and the limit of quantification was 0.05 mg/kg for both corn and soil. The recovery and precision results were acceptable according to the residues analysis quality control guide (General Administration of Quarantine of the People's Republic of China 2002).

The dissipation trends of nicosulfuron in corn plant were shown in Fig. 1. Nicosulfuron dissipated rapidly after application. The concentration of nicosulfuron 2 h after treatment was 36.3 mg/kg in Beijing and 30.1 mg/kg in Changchun, respectively. The amount of nicosulfuron residue was below the LOD of the method 7 days after the treatment. The dissipation dynamics of nicosulfuron in Beijing and Changchun could be described by the following first-order rate equation: $C = 38.301e^{-0.9473t}$ and $C = 5.0376e^{-1.3121t}$, respectively. The half-life time of nicosulfuron in corn plant was 0.73 days in Beijing and 0.53 days in Changchun .

Table 1 Fortified recoveries of nicosulfuron in corn and soil samples

Sample type	Added (mg/kg)	Recovery (%)			Average recovery (%)	RSD(%)
		1	2	3		
Soil	1.0	102.4	89.5	91.0	94.3	7.48
	0.1	111.4	106.4	85.2	101.0	13.77
	0.05	93.7	113.6	115.8	107.7	11.30
Corn plant	1.0	92.0	79.7	88.1	86.6	7.26
	0.1	113.9	111.3	109.7	116.3	1.90
	0.05	105.9	106.3	103.6	105.3	1.38
Corn grain	1.0	85.7	96.7	94.3	96.2	6.27
	0.1	114.3	101.5	113.7	96.0	6.58
	0.05	83.5	81.3	75.4	80.1	5.23

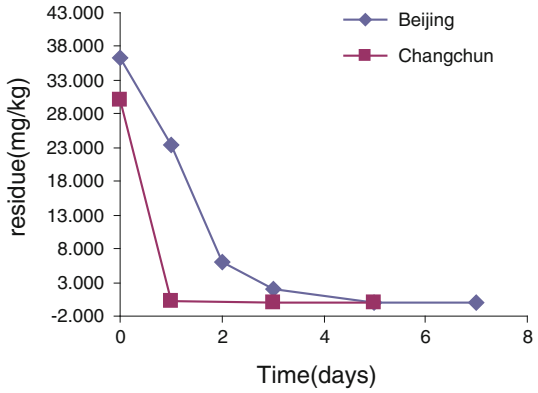

Fig. 1 Dissipation of nicosulfuron in corn plant in Beijing and Changchun, 2009

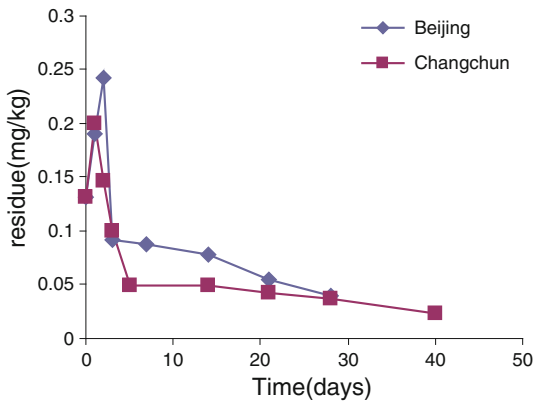

Fig. 2 Dissipation of nicosulfuron in soil in Beijing and Changchun, 2009

Figure 2 shows the dissipation data of nicosulfuron in the soil samples. The concentration of nicosulfuron in the soil 2 h after application was 0.132 mg/kg both in Beijing and Changchun. The amount of nicosulfuron was below the LOD after 21 days of the treatment, The dissipation dynamics of nicosulfuron in Beijing and Changchun could be described by the following first-order rate equation: $C = 0.1570e^{-0.0508t}$ and $C = 0.1252^{e-0.0508t}$, both with the half-life of 13.64 days.

Table 2 Ultimate residue of nicosulfuron in corn powder and soil

Sample type	Dosage (mg/kg)	Residue (mg/kg)			
		Beijing		Changchun	
		2008	2009	2008	2009
Corn grain	High dosage	ND	ND	ND	ND
	Low dosage	ND	ND	ND	ND
Soil	High dosage	ND	ND	ND	ND
	Low dosage	ND	ND	ND	ND

Note: ND: <LOD

After the application of nicosulfuron (75% WP) in high dosage and low dosage, the soil and corn samples were taken during the harvest time from the treated plots. The concentration level of nicosulfuron in corn grain and soil at harvest was determined. The ultimate residue data were shown in Table 2. The results showed that the concentration of nicosulfuron in corn grain and soil were both below 0.05 mg/kg.

Acetonitrile: water mixture was used as extraction solvent for the residue analysis of sulfonylurea herbicides in the literature reported. In this experiment 30 ml acetonitrile: water (2:3, V/V) mixture was used. The acetonitrile :water (2:3, V/V) mixture and the acetonitrile :water (3:2, V/V) mixture were compared as the extraction solvent. We found that a higher recovery could be obtained using the former. When the extraction step was carried out only once with 15 mL mixture solvent, the recovery was below 50%, and when it was carried out twice with 15 mL mixture solvent each, a suitable recovery could be obtained. Then, we found that a suitable recovery could also be obtained with 30 mL mixture solvent. With the purpose of saving time, 30 mL acetonitrile: water (2:3, V/V) mixture was used and the extraction step could be carried out only once.

In the literature published about nicosulfuron residue analysis in soil (Ye et al. 2006), SPE was used as the

cleaning-up procedure, but a very complicated extraction method was used, the sample should be extracted 3 times by buffer solution. Yang and Jiang (1998) reported the residue analysis of nicosulfuron in corn, but in that method, two different LLE steps and a SPE step were requird for the sample cleaning-up purpose, and each LLE method must be repeated twice at least.

Considering the high solubility of nicosulfuron in dichloromethane(CH_2Cl_2), in this method CH_2Cl_2 was used as the extraction solvent in the LLE procedure. Because nicosulfuron has a lower solubility in water when $pH < 5$, the hydrochloric acid solution was added to the separatory funnel to adjust the $pH \leq 5$ before the LLE procedure, so that the nicosulfuron would be almost transferred into the organic phase and the purpose of purification would be achieved. So dichloromethane was explored as the purification solution in LLE.

As shown in Figs. 1 and 2, a fast decline of nicosulfuron in corn plant can be observed. Nicosulfuron had very short half-lifes in corn plant (0.5–0.7 days) with the dissipation rate of 90% over 7 days, and the amount of the concentration of nicosulfuron was below the LOD 0.05 mg/kg 7 days after treatment. Nicosulfuron had longer half-lifes in soil (which were 15–17 days) than in corn plant. Besides that, the concentration of nicosulfuron in soil reached the highest level in 1 day after the treatment, but not in 2 h after treatment. This may be explained by the fact that most of the nicosulfuron reserved on the plant after spraying and then drifted or adsorbed to the soil in 1 day. After that a normal decline of nicosulfuron in soil could be observed.

FAO/WHO and Japan have established the maximum residue limits (MRL) of nicosulfuron in corn as 0.1 mg/kg. In South Korea the MRL value is 0.3 mg/kg.

Our results showed that it is acceptable to spray nicosulfuron 75% WP at the recommended dosage due to its lower toxicity to non-target species, very short half-life time in the corn plant, and the low final residues which was below the LOD. Although it has a relatively longer half-life in soil, but after a growing season, it is undetectable in the soil samples. Therefore, nicosulfuron could be considered as a good alternative to high-toxicity pesticides in China.

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