Bull Environ Contam Toxicol (2008) 80:391–394
DOI 10.1007/s00128-008-9359-z

Dissipation and Residue of *S*-metolachlor in Maize and Soil

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Received: 21 May 2007 / Accepted: 10 January 2008 / Published online: 13 May 2008

Abstract The purpose of this article was to establish a simple residue analysis method for *S*-metolachlor in maize and to study its dissipation and residue in maize field ecosystem. The results showed that *S*-metolachlor declined rapidly in maize seedling and soil after application. The half-lives of *S*-metolachlor in maize seedlings in Beijing and Changchun were 6.68 and 4.85 days, respectively, and in soil were 12.81 and 14.81 days, respectively. The terminal residues of *S*-metolachlor in soil samples were very low (around 0.005–0.045 mg/kg), and the residues in maize seeds were not detectable. The use of *S*-metolachlor according to the recommended dosages in maize could be considered safe.

Keywords Dissipation · Residue · *S*-metolachlor · Maize

S-metolachlor (*S*-2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide) is a new herbicide which was developed by *Syngenta* Ltd., Switzerland. It is widely used in controlling weeds in maize, cotton, soybean, and various crops. The commercial formulation of *S*-metolachlor is primarily comprised of 88% *S*-enantiomer and 12% *R*-enantiomer, but only *S*-enantiomer is the biological active ingredient (Dale et al. 2006). Compared to metolachlor (50% *S*-enantiomer and 50% *R*-enantiomer), *S*-metolachlor resulted in a substantial reduction of risks to applicators, consumers, and the environment (Peter et al. 1998; Mohammad and Waqar 2003; Soltani et al. 2004; Nader and Perer 2005; Pannacci et al. 2007). So this herbicide will play an important role in sustainable weed management.

Maize (*Zea mays*) is a major commercial crop in China, which suffers yield losses due to weed infestation. Several reports about the environmental behavior of *S*-metolachlor in soil (Vasilakoglou et al. 2001) and control of weed in cornfield (Jason and James 2005; Joshua et al. 2006) are available. Recently Ma et al. (2006) and Kabler and Chen (2006) reported their studies on the enantio-selective analysis of *S*-metolachlor in soil and water under the laboratory conditions. However, there were no related reports about analysis of *S*-metolachlor in maize by GC-ECD method in trial field. The purpose of present work was to establish a simple residue analysis method and to study the dissipation rate and final residue of *S*-metolachlor in maize field eco-system in order to evaluate its safety use in China.

Materials and Methods

The analytical standard of 99% *S*-metolachlor and 96% EC formulation were supplied by Switzerland *Syngenta*. Analytical grade n-hexane, petroleum ether, methanol, sodium chloride, anhydrous sodium sulfate, and basic alumina were purchased from Beijing Reagent Company (Beijing, China).

The residues of *S*-metolachlor were determined by an Agilent 6890N GC with ^{63}Ni ECD, attached with Agilent 7683 autoinjector and Agilent Enhanced ChemStation for data acquisition. A HP-5 column (30 m × 0.32 mm i.d. × 0.25 μm) was used. The injector and detector were operated at 250 and 300°C, respectively. The sample (1.0 μL) was injected in the splitless mode, and the oven temperature was programmed as follows: 120°C for 1 min, rising to 280°C

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(15°C min^{-1}) for 10 min. The carrier gas was nitrogen with the flow rate of 1 mL min^{-1}. The retention time of *S*-metolachlor was at 9.6 min.

The residues of *S*-metolachlor in harvested maize were confirmed by an Agilent 6890N GC with 5975B MS selective detector and 7683 autoinjector. A HP-5 column (30 m × 0.25 mm i.d. × 0.50 μm) was used. The injector was operated at 250°C and the oven temperature was programmed as follows: 60°C for 1 min, rising to 250°C (20°C min^{-1}) for 10 min. The carrier gas was Helium with the flow rate of 1.0 mL min^{-1}. MS ion source was EI, 70ev, and 230°C. The analysis used selected ion mode (SIM), and the selected ions of *S*-metolachlor were: m/z 162, 238, and 240. The sample (1.0 μL) was injected at the splitless mode and the retention time of *S*-metolachlor was at 10.7 min.

The field trials including the dissipation and terminal residue experiments were conducted in Beijing and Changchun, China during 2005–2006. All experiment treatment contained three replicate plots, and the area of each plot was 30 m^2 and was separated by irrigation channels.

In order to study the dissipation trends of *S*-metolachlor in maize and soil, 96% EC formulation was applied at 2250 mL a.i. ha^{-1} (1.5 times of the recommended dosage) 3 days after the maize seeds were sowed. Representative soil samples were collected at different intervals, i.e., 1 h, 1, 3, 7, 14, 21, 31, 46, 60, 75 and 90 days after the application of the herbicide. In order to study the dissipation of *S*-metolachlor in the maize plants, the maize seedlings were also collected at intervals (1, 2, 3, 5, 7, 14, 21, and 28 days) from the frondescence of the maize plants. The collected corn seedling samples were comminuted with a blender (Philips Company, China). Then the collected samples were stored at −20°C until further analysis.

The terminal residue field experiment was designed to spray *S*-metolachlor at two dosage levels, a lower level of 1,500 mL a.i. ha^{-1} (recommended dosage) and a higher level of 2,250 mL a.i. ha^{-1}, respectively. For each treatment, three replicate plots were set and another untreated plots were sprayed with water which was to be maintained as control. Representative maize seed and soil samples were collected randomly from each treatment plot 3 days before the harvest of the maize. Then the maize samples were comminuted into flour and stored at −20°C for further analysis.

Ten grams of maize samples or 20 g of soil were extracted by adding 60 mL methanol/water (80:20, v/v) and 0.2 g activated charcoal, and shaking on a reciprocating shaker for 2 h. The extracts were then transferred to a separator funnel containing 120 mL distilled water and 10 mL saturated sodium chloride solution. The aqueous was extracted by liquid–liquid partition with petroleum ether for three times at the volume of 30, 20 and 10 mL, respectively. The petroleum ether layer was combined into a flask and then evaporated under vacuum to dryness at 40°C. A glass chromatographic column (15 cm × 1 cm i.d.), which was packed with 3 g basic alumina between two layers of 2 cm of anhydrous sodium sulphate, was prepared for the cleaning-up procedure. The column was conditioned by 10 mL n-hexane/ether (2:1, v/v), followed by 10 mL n-hexane. The concentrated extract was transferred to the column by 20 mL n-hexane. The column was then washed slowly with 13 mL of n-hexane/ether (2:1, v/v), and the eluent was collected and evaporated at 40°C to

Table 1 Recovery and repeatability (RSD) for *S*-metolachlor in samples spiked at different levels

Type of samples	Spiked levels (mg kg^{-1})	Detected (mg kg^{-1})	Recovery (%)	RSD (%)
Soil	0.10	0.0801	80.1	2.8
	0.05	0.0498	99.6	3.8
	0.01	0.0105	104.6	1.8
Maize seedling	0.10	0.0942	94.2	5.2
	0.05	0.0443	88.7	2.7
	0.01	0.0104	103.9	1.8
Maize seed	0.10	0.0881	88.1	6.8
	0.05	0.0460	91.9	7.1
	0.01	0.0091	90.9	3.4

Number of replicates at each level (n = 3) (three extraction with three injections each), all made under the same conditions

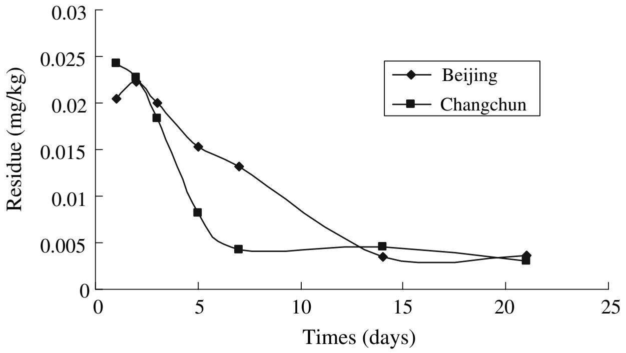

Fig. 1 The degradation curves of *S*-metolachlor in maize seedling

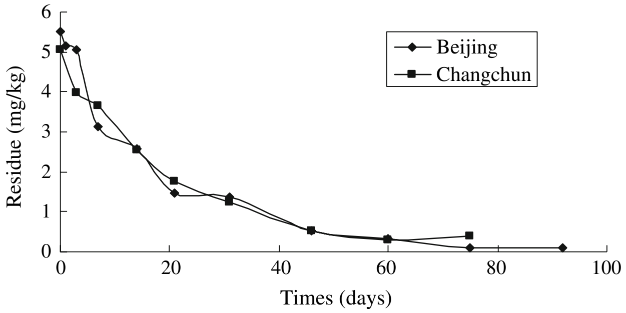

Fig. 2 The degradation curves of *S*-metolachlor in soil

Table 2 The terminal residues of *S*-metolachlor in samples from Beijing and Changchun in 2005 and 2006

Type of samples	Dosage (mL a.i. ha^{-2})	Residues (mg kg^{-1}), 2005		Residues (mg kg^{-1}), 2006	
		Beijing	Changchun	Beijing	Changchun
Soil	2250	0.0453	0.0360	0.0048	ND
	1275	0.0220	0.0123	ND	ND
Stalk	2250	ND	ND	0.0033	0.0045
	1275	ND	ND	0.0030	ND
Maize seed	2250	ND	ND	ND	ND
	1275	ND	ND	ND	ND

ND, not detectable (<LOD); replicates at each interval ($n = 3$)

dryness. The residue was dissolved in 5 mL n-hexane for analysis by GC-ECD or GC-MS.

Results and Discussion

The fortified recovery, the precision, and the limits of detection (LOD) of the residue analytical method were evaluated. The *S*-metolachlor standard solution was fortified to the untreated soil, maize seedling and maize seed at three concentration levels. The average recoveries obtained were shown in Table 1 and the recoveries ranged from 80.1% to 104.6% in different substrates, which were very satisfactory. The limit of detection established was 0.01 ng at the signal-to-noise ratio of 3. The limit of quantification was 0.003 mg kg^{-1}.

The results of dissipation data of *S*-metolachlor in maize seedling in Beijing and Changchun were shown in Fig. 1. As shown in the figure, *S*-metolachlor dissipated rapidly in maize seedling after application. The dissipation rates of *S*-metolachlor 3 days after treatment in Beijing and Changchun were 31.1% and 65.0%, respectively. The amount of *S*-metolachlor residue was below the LOD of the method 28 days after the treatment. The dissipation dynamics of *S*-metolachlor could be described as the following first-order rate equation: $C = 0.0248e^{-0.1037t}$, and $C = 0.0232\ e^{-0.1428t}$, with the square of coefficient $R^2 = 0.9051$ and 0.9262, respectively; the half-lives of *S*-metolachlor in maize seedlings in Beijing and Changchun were about 6.68 and 4.85 days, respectively.

The results of Fig. 2 showed the dissipation data of *S*-metolachlor in soil samples. The initial concentration level of *S*-metolachlor in soil was higher than in maize seedlings. This could be explained by the fact that most of the *S*-metolachlor was drift to the soil during application. The initial concentration of *S*-metolachlor in soil was 5.53 and 5.06 mg kg^{-1} after 2 h of the application. The amount of *S*-metolachlor was below the LOD after 92 days of treatment. A sharp decline of *S*-metolachlor within 21 days after the treatment could be observed. The dissipation dynamics of *S*-metolachlor in soil samples in Beijing and Changchun could also be described by the equation: $C = 5.112e^{-0.0480t}$, and $C = 4.2205e^{-0.0361t}$, with $R^2 = 0.9839$ and 0.9353, respectively. The half-lives of *S*-metolachlor in soils in Beijing and Changchun were about 12.81 and 14.81 days, respectively.

From the results, it is clear that the half-life of *S*-metolachlor in maize seedling in Beijing persisted a little longer than in Changchun. This could be explained by the different organic carbon contents of the soil. The organic carbon contents of the soil from Beijing and Changchun were 1.50% and 3.37%, respectively. The fertile soil could accelerate the growth of maize seedling in Changchun field. Consequently, the dissipation of *S*-metolachlor in maize seedling was speeded. On the other hand, the half-life of *S*-metolachlor in soil in Changchun was a little longer than in Beijing. This could be explained by the fact that Changchun lies to the north of Beijing and the annual average temperature was lower (4.8°C) than in Beijing (12°C).

The terminal residues of *S*-metolachlor in Beijing and Changchun were listed in Table 2. At harvest, the residues of *S*-metolachlor in soil, stalk, and maize seed samples were confirmed by GC/MS and were found to be lower than the USA EPA's maximum residue limit (MRL) of 0.1 mg kg^{-1} in maize. It could be considered as safe to human beings and environment.

Acknowledgment We are grateful to *Syngenta* Co., Ltd., China for their financial support.

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