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Dissipation and Residues of the Herbicide Mesotrione in Maize and Soil in Open Field

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Abstract The purpose of this article was to establish a simple residue analysis method for mesotrione in maize using high performance liquid chromatography tandem mass spectrometry. The method was then used to study the dissipation and residues in maize seedling and soil. The half-lives of mesotrione in maize plants and soil were 1.37, 4.31 days in Beijing, and 0.97, 1.80 days in Shandong, respectively. The ultimate residues of mesotrione were undetected in soil, maize grain and stem at the harvest time, suggesting that mesotrione could be safely used in maize crops with an appropriate dosage and application.

Keywords Mesotrione · Dissipation · Residue · Maize · Soil · HPLC–MS/MS

Mesotrione [2-(4-methylsulfonyl-2-nitrobenzoyl)-1, 3-cyclohexanedione] was a recently registered triketone herbicide for pre-emergence and post-emergence broadleaved weed control in maize field (Mitchell et al. 2001; O'Sullivan et al. 2002). The chemical structure of mesotrione was represented in Fig. 1. Mesotrione acted by competitive inhibition of the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD), which affects carotenoid biosynthesis (Mitchell et al. 2001). It was a very effective residual herbicide for the control of a number of important broadleaved weeds and selected annual grasses in maize (Sutton et al. 1999; O'Sullivan et al. 2002).

There were a few articles about the residue analysis of mesotrione until now. Alferness and Wiebe (2002) established a method to determine the residue of mesotrione and its metabolites in crops (included corn grain, fodder, forage and sugar cane), soil, and water by liquid chromatography with fluorescence detection. Pang et al. (2007) established a method to detect the residue of mesotrione in soil using high performance liquid chromatography with the ultraviolet detector (HPLC-UVD). However, the residue analysis and dissipation in maize plants and soil were rarely reported to our knowledge.

In this work, a simple, relatively fast and efficient high performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS) method was developed for the determination of mesotrione in maize and soil. Mesotrione was applied in maize to investigate its degradation behavior in field trial and to afford evidence for registration in China. This would facilitate the establishment of the maximum residue limit (MRL) for mesotrione in maize, to evaluate this herbicide for its safe use in maize and to establish adequate method for monitoring its residue.

Materials and Methods

Mesotrione standard (99% purity) and 10% suspension concentrate (SC) formulation, were supplied by Dalian Songliao Chemical Co., Ltd., China. HPLC-grade methanol and acetonitrile was supplied by Fisher Scientific (US). Ultrapure water was purchased from Aquapro Ultrapure Water System (Chongqing, China). Analytically pure sodium chloride was purchased from Beijing Reagent Company (Beijing, China).Graphitized carbon

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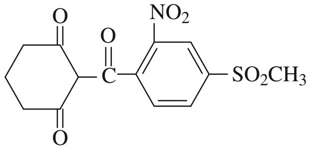

Fig. 1 The chemical structure of mesotrione

black (GCB) and primary secondary amine (PSA) were provided by Agela (Tianjin, China).

Field experiments were conducted in Beijing and Shandong, China, in 2009. Three treatments were set for the field trial, and each treatment was replicated three times. A buffer area was set to separate the different treatment plots in the same field. Ten plots were settled for the trials and every plot was 30 m^2. Maize seeds were planted in each plot.

To investigate the dissipation of mesotrione in maize seedling and soil, when the maize plant was at 3–8 leaf stage, mesotrione formulation was dissolved in water and sprayed onto the surface of maize seedling by a manual sprayer (PS16-7, 40.5 cm × 17 cm × 57 cm, 161 volume, max. pressure 1.0 mPa) at a dosage of 585 g a.i.ha^{-1}(three times of the recommended dose). Two hours after spraying, about 200 g of maize seedling and 500 g soil samples were collected from several randomly selected sampling points within each plot. This sampling regime was repeated 1, 2, 3, 5, 7, 14, 21, 28, 35 and 40 days after spraying, respectively. Maize seedling and soil were sprayed on 3 June 2009 in Beijing and on 7 June 2009 in Shandong.

The final residue field test was designed at two dosages. Mesotrione formulation was sprayed at two doses: 195 g a.i.ha^{-1} (recommended dose) and 292.5 g a.i.ha^{-1} (1.5 times of the recommended dose). At harvest time, from each ultimate residue field 3 kg maize cobs, 200 g maize stems and 500 g soil samples were collected for residue analysis.

The samples of maize seedling and maize stem were cut into small pieces with a vegetation disintegrator. The samples of the maize grain were obtained by threshing 1–2 kg of maize cob, and then 200 g of the grain was concentrated with the corn-and-quartering method and grounded to coarse powder with a vegetation disintegrator. The soil samples were sifted through a 40-mesh sieve, and then 100 g soil was concentrated with the corn-and-quartering method. All collected samples were stored in a freezer at −20°C before analysis.

A 5-g subsample of homogeneous soil samples and 20 mL methanol/water (1:1, v:v) was placed into a 50 mL centrifuge tube. Then the centrifuge tube was shaken mechanically for 30 min. After that, the mixture was extracted for 10 min with an ultrasonic bath and was centrifuged at 2,500×*g* for 5 min. The supernatant was transferred to a HPLC sample vial for HPLC–MS/MS analysis after filtration through a 0.22 μm nylon filter.

A 4-g subsample of a homogeneous maize seedling samples was placed into a 50 mL centrifuge tube, 10 mL acetonitrile and 10 mL ultrapure water were added. In the cases of maize grain and stem, 10 and 2 g was weighted, respectively. The centrifuge tube was shaken mechanically for 30 min. After that 8 g sodium chloride was added and then vortexed for 1 min. The mixture was centrifuged at 2,500×*g* for 5 min. After the extracts were centrifuged, the supernatant was being cleaned up with the next procedure.

The extraction supernatant was cleaned up with dispersive solid phase extraction. 25 mg GCB and 25 mg PSA (for maize seedling) or 20 mg PSA (for maize grain and maize stem) was put into a 2 mL centrifuge tube. 1 mL of the supernatant was transferred into the tube and was vortexed for 1 min at a high speed, then centrifuged for 3 min with a mini-centrifuge (TDL-40B, Anting Scientific Instrument Factory, Shanghai, China). The solution was filtered with a 0.22 μm nylon filter to an auto sampler vial for the HPLC–MS/MS analysis.

The residues of mesotrione in maize seedling, grain, stem and soil were conducted with an Agilent 1200 HPLC and an Agilent 6410B Triple Quad HPLC–MS/MS. The spectral acquisition was done in the negative electron spray ionization, and multiple reaction monitoring (MRM) was utilized. The parent-daughter ion pair was m/z 338.1/291.1. The gas temperature was 350°C and the gas flow rate was 8.0 L/min, the nebulizer was 35.0 psi, the fragmentor was 85 V and the collision energy for the parent-daughter ion pair was 5 eV. The column used for the HPLC–MS/MS was a Zorbax C_{18} (50 mm × 2.1 mm i.d., 1.8 μm particle size), maintained at 30°C. The mobile phase was acetonitrile: water = 70:30 (V:V) with a flow rate of 0.3 mL/min. The injective volume was 5 μL. The retention time (Rt) for mesotrione was 0.5 min.

Results and Discussion

For most chromatographic procedures a linear relation could be observed between detector response (y) and analyte concentration (x). The linear relation for mesotrione calibration could be expressed as a linear regression equation: $y = 170{,}155x - 121.8$, $R^2 = 0.9999$, where y = peak area, x = mesotrione injection amount (ng), and R = correlation coefficient within the rage 0.025–2.5 ng.

The recovery tests were carried out three replicate at each spike level. To do the fortified recovery test, the standard solutions at levels of 0.05, 0.1 and 1 mg/kg was added to the weighed soil, maize seedling and stem samples in the centrifuge tube, and at levels of 0.02, 0.05 and 0.1 mg/kg for maize grain. Then the samples were shaken for 1 min and placed stable for 30 min. After that, it was followed by the sample pretreatment. The fortified recoveries of mesotrione in soil,maize seedling, maize grain and maize stem samples were 74.17%–89.46%, 103.43%–108.41%, 68.87%–93.01%, 82.97%–95.60%, respectively; and the relative standard deviations (RSDs) of the recovery data were 1.66%–11.67%. The results suggested that the fortified recovery and the precision were both satisfactory.

To measure the limit of detection (LOD) and the limit of quantification (LOQ), a series of diluted mesotrione matrix standard samples was used. The LOD of mesotrione was 0.005 mg kg^{-1}, when the signal-to-noise ratio(S/N) was 3:1. The LOQ was established as 0.01 mg/kg for soil, 0.01 mg/kg for maize seedling, 0.005 mg/kg for maize grain and 0.025 mg/kg for maize stem at the S/N 10:1.

After the application of mesotrione in the maize seedling and soil, its dissipation behavior in maize seedling was shown in Fig. 2. The half-life of mesotrione in maize seedling in Beijing was 1.37 days and the dynamics could be described by the equation ($C = 1.1185e^{-0.5048t}$) with square of coefficient $R^2 = 0.9893$, and the half-life of mesotrione in maize seedling in Shandong was 0.97 days and the dynamics could be described by the equation ($C = 6.3257e^{-0.7147t}$) with $R^2 = 0.9212$.

The dissipation data of mesotrione in soil was shown in Fig. 3. The half-life of mesotrione in soil in Beijing was 4.31 days and the dynamics could be described by the equation ($C = 0.0936e^{-0.1609t}$) with square of coefficient $R^2 = 0.9622$, and the half-life of mesotrione in soil in Shandong was 1.80 days and the dynamics could be described by the equation ($C = 0.3356e^{-0.3846t}$) with $R^2 = 0.9261$.

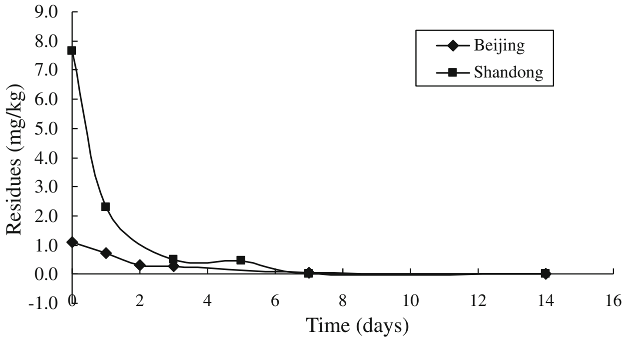

Fig. 2 The degradation curves of mesotrione in maize seedling, 2009

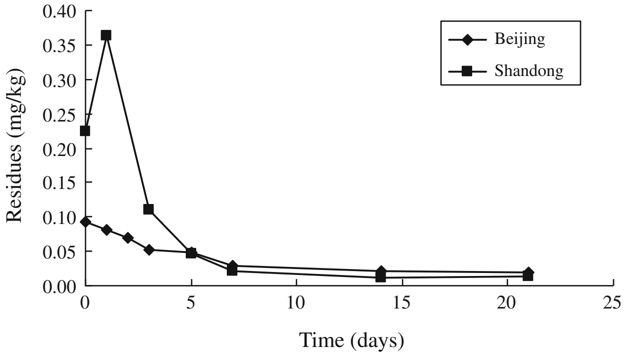

Fig. 3 The degradation curves of mesotrione in soil, 2009

In order to detect the final residues of mesotrione, the formulation was sprayed when the plants were at 3–8 leaf stage, and the samples were collected when the plants were harvested. The experiment results (data not shown) showed that the final residues of mesotrione in maize grain, maize stem and soil were all undetectable (lower than the LOD) in Beijing and Shandong, no matter the lower or the higher dosage was sprayed on the crops. From spraying the mesotrione formulation to the collection of samples, it has lasted nearly 90–130 days. It was reasonable that no residue had been determined at harvest time, and it suggested that mesotrione should be safe for human and animal and be safe to the environment.

In this research, a simple, relatively fast and efficient HPLC–MS/MS method for the residue analysis of mesotrione was developed. Alferness and Wiebe (2002) used liquid chromatography with Fluorescence Detection to detect the mesotrione and its metabolities in crops, soil, and water. The crop and soil extracts, and water, were cleaned up using reverse-phase HPLC with mesotrione and 4-methylsulfonyl-2-nitrobenzoic acid (MNBA) isolated using a fraction collector. The collected mesotrione and MNBA fractions were converted into 2-amino-4-methylsulfonyl-benzoic acid (AMBA) via oxidation followed by reduction in the case of mesotrione, or by reduction alone in the case of MNBA. After the conversion, all fractions needed the post-conversion cleanup. The conversion and post-conversion cleanup procedure was very complicated. Pang et al. (2007) used 30, 20 mL acetonitrile to extract mesotrione from soil samples twice. In this article, only 10 mL solvent was needed for one sample, and as the HPLC–MS/MS was used, it only needed 2 min and less solvent to determine mesotrione in one sample.

Acetonitrile/water mixture (1:1, v:v) was used to macerate the crop samples efficiently (Alferness and Wiebe 2002). However, when the extraction solution was used to extract mesotrione in soil, the fortified recovery was only 47.06%. Then 5 mL water and 20 mL acetonitrile were used to extract mesotrione in the soil, the fortified recovery was also unsatisfied which was 62.12%. Zhang (2004) used methanol/water mixture (4:1, v:v) to extract sulcotrione in soil with an ultrasonic bath. Mesotrione and sulcotrione were both triketone compounds, and they had the similar chemical structures, so the method was tried with methanol/water mixture to extract mesotrione in soil. The methanol/water (4:1, v:v) and methanol/water (1:1, v:v) were used to compare the extraction efficiency of mesotrione from soil sample. The results showed that methanol/water (1:1, v:v) got a higher fortified recovery which was 80.52%.

In order to reduce the matrix effect, 20 mg PSA was used to clean up the matrix in the maize grain and maize stem. However, there was too much pigment in the maize seedling and GCB was effective for the pigment, so 25 mg PSA and 25 mg GCB were used for cleaning up the maize seedling simultaneously.

The results of the degradation study of mesotrione in Beijing and Shandong showed that, although the initial residues were different, mesotrione degraded fast in maize seedling and soil. The residues of mesotrione in soil in Shandong were increased on the first day and then declined as expected. This could be explained by the fact that, the initial residue in the maize seedling is higher in Shandong than in Beijing, on the first day most of the mesotrione was drifted to the soil during application in Shandong.

In the final residues experiments, the residues of mesotrione in the maize grain, maize stem and soil of Beijing and Shandong were undetectable (lower than the LOD) when it was harvest. These results showed that 10% mesotrione formulation was safe for the maize plants when it was sprayed with the recommended dosage.

The MRL is the safety limit of pesticides in agricultural products and food. FAO/WHO has not published MRL for mesotrione. From the results of final residue experiments, no residues of mesotrione were observed in maize grain and maize stem. It provided a quantitative basis for revising the application of this herbicide to maize crops. We recommend that it is safe for maize crops sprayed with mesotrione (SC, 10%) at a dosage 195 g a.i.ha^{-1}.

Mesotrione is used to control broad-leaved and some grass weeds in maize. In this work a relatively fast and efficient HPLC–MS/MS method for the residue analysis of mesotrione was established, and the degradation trends of mesotrione residues in maize seedling and soil in open field were investigated. The results showed that mesotrione (SC, 10%) degraded fast in maize seedling and soil, and the half lives were about 1 d and 3 d. The final residues of mesotrione in maize grain and maize stem were undetected, so it could be considered as safe for human beings and environment. This work would help to establish adequate monitoring of the residue of this newly introduced herbicide and its judicious incorporation in weed management strategies in crop fields.

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