

Dynamics of Ethametsulfuron-Methyl Residue in Paddy Soils Revealed by HPLC-MS/MS

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Abstract

Ethametsulfuron-methyl (ESM) was extensively applied for weed control in rape seed, which taking turns with rice. Such farming model was predominant in southern of China and Southeast Asia. However, ESM damages subsequent rotation with rice, and potentially pollutes the environment. Residue of ESM dynamics in paddy soil is still ambiguous. In this study, a modified high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) method for the detection of traces of ESM residues in paddy soil was developed and validated. Dynamics of ESM residue was performed by laboratory mock and field trial. The limit of detection (LOD) and limit of quantitation (LOQ) of ESM in paddy soil were 1.10×10^{-6} ng and 1.27×10^{-3} $\mu\text{g}\cdot\text{kg}^{-1}$, respectively. At fortification levels of 0.2 and 2 $\text{mg}\cdot\text{kg}^{-1}$ in paddy soil samples, the recoveries ranged from 85.56% to 100.16% with relative standard deviations of 7.42-9.69% (n = 5). The dynamics of ESM in laboratory mock trial showed that the half-lives ($t_{1/2}$) of ESM in paddy soil were over 100, 16.35 and 10.35 days at 6 °C, 25 °C and 35 °C, respectively. The $t_{1/2}$ of ESM in the field trial was 34.66 days at recommended dose of 18 g active ingredient $\cdot\text{ha}^{-1}$. This work would contribute to safe utilization of ESM.

Keywords: ethametsulfuron-methyl, HPLC-MS/MS, half-life, rape seed, paddy soil

1. Introduction

Sulfonylurea herbicides are a very important group of herbicides, including over 30 compounds, used worldwide to control broad-leaved and grassy weeds in almost of all major agronomic crops, because of their relatively low application rates; less than 100 g active ingredient (a.i.) $\cdot\text{ha}^{-1}$ (Brown et al., 1990). Sulfonylurea herbicides kill weeds by inhibiting the activity of a key enzyme, acetohydroxy acid synthase (AHAS), which is involved in the biosynthesis pathway of branched-chain amino acids (valine, leucine, and isoleucine) in bacteria, fungi, and plants (Blair et al., 1988; Duggleby et al., 2000; Wang et al., 2009). Sulfonylurea herbicides are increasingly used in developing countries like China because of their high efficacies, multicrop selectivity, and low labor requirement. However, the drawbacks of the use of sulfonylurea herbicides are also strikingly concerns, such as damages to subsequent rotation of sensitive crops, and potential pollutants to environment (Rosenkrantz et al., 2013a; Tan et al., 2013; Wang et al., 2010b).

ESM, 2-((4-ethoxy-6-(methyl amino)-1,3,5-triazin-2-yl) amino carbonyl amino sulfonyl) benzoate, is a typical member of sulfonylurea herbicides and extensively applied for weeds control in rape seed, which rotates with rice. Such a farming model was predominant in southern of China and Southeast Asia. However, ESM damages subsequent rotation with rice by inhibiting its biosynthesis of AHAS like in weeds (Green, 2007). ESM persists from several months to more than 1 year in neutral to alkaline soils, the persisting duration of ESM was relatively longer in neutral or weakly basic soil than in acidic soil (Hollaway et al., 2006). Thus, great concern and interest have been raised regarding the environmental behavior of ESM residues in paddy soil.

Dynamics of sulfonylurea herbicides residues in soil (including paddy soil) is determined by synergistic action with many factors both physical and chemical such as soil pH, temperature, organic matters and relative water

content, and biological notably soil organism and biochemical activity (Ren et al., 2011; Song et al., 2013; Wang et al., 2010a). Given that narrow changes of biological and physical-chemical factors except temperature in a survey region during the farming of certain crops, especially the growth period of rapeseed from autumn to earlier spring when temperature moves from 35 °C to -5 °C in south China. So, temperature is the most strikingly factor affecting the fate of sulfonylurea herbicides in the soil. It is necessary to understand ESM residue dynamics at different temperatures in paddy soils.

In this work, a liquid-liquid extraction (LLE)-HPLC-MS/MS method was developed to detect traces of ESM residues in paddy soils. A laboratory mock trial was designed to investigate the dynamics of ESM residues at different temperatures, and additional field trial was conducted to determine the actual dynamics of the residues for safe utilization of MSE in rape seed.

2. Materials and Methods

2.1 Materials

ESM standard (99.0%) was purchased from Tianjing Orient Green Technology Co., Ltd (Tianjing, China), ESM formulation (20% ESM WP) was kindly provided by Hunan Haili Chemical Industry Co., Ltd (Changsha, China). Acetonitrile of HPLC grade was procured from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Deionized water (18 MΩ) was supplied from a Milli-Q Gradient A10 purification system (Millipore, Billerica, MA).

All reagents for trace detection by HPLC-MS/MS were filtered through 0.22 μm GH Polypro filters, and all samples solutions for ESM extraction in soils except of ESM formulation were filtered through 0.22 μm PVDF filters before use (Millipore, Bedford, MA, USA).

Paddy soils were collected from field in Lanli county, Changsha, Hunan province, China. Over past five years, the rice-rape seed planted in turn. The supervised field trial was laid out in the same field where soil samples were collected for laboratory mock trial in Lanli county, Changsha, Hunan province, China.

2.2 Methods

2.2.1 Soil Samples Treatment for Laboratory Mock Trial and for Field Trial

For the laboratorial mock trial, the paddy soils sampled from topsoil (0-10 cm) after pre-harvest of rape seed, 6 kg of paddy soils were sampled, dried in shade, sieved through a 40-mesh sieve before using.

To investigate the dynamics of ESM residue in paddy soil in the laboratory, partial of soil samples of each treatment were sprayed with the stock solution of ESM (ESM standard dissolved into acetone) according to initial concentration. Soils were added after acetone was volatilized. Soil samples were put into plastic basin and covered by black thin film, which had several little holes for ventilating. All treatments were triplicate. The plastic basins were incubated at 6 °C, 25 °C, and 37 °C, and sampled at interval times of 0 (1 h post treatment), 1, 5, 7, 14, 21, 30 and 90 days. All samples were stored at -20 °C until analyzed.

For the supervised field trial, the trial was conducted at the beginning of June 16th, 2012. The daily mean temperature was 30 °C in the whole trial. The recommended dosage level (18 g a.i.·ha⁻¹, dissolved in 50 L of water) using ESM (20% WP). The mixture was sprayed only once in the bare field. A non-treated plot of the same size was set as control. Each treatment was triplicate, and each repetition was of 200 m², and total field trial region was of 1200 m². Representative soil samples were randomly collected by the quartation method from topsoil (0-10 cm) by soil sampler in each repetition randomly at 0 (1 h post treatment), 3, 5, 9, 14, 21, 30 and 45 days after ESM application.

2.2.2 ESM Extraction and Cleanup

The processes of sample extraction and cleanup were operated according to modification of literature (Ye et al., 2006). Briefly as below, for laboratorial mock trials, the total soil samples (20 g) were selected, for supervised trials, 20 g samples were obtained from 1 kg samples of topsoil (0-10 cm) collected from trial field by the quartation method. All of soil samples were dried in shade, sieved through a 40-mesh sieve.

The sampling soils were put into triangular flask (250 mL), and then mixed with 40 mL of acetonitrile, vortexed for 15 min; afterthat, total extract was filtrated, and discarded the precipitation. The filtrate fraction was collected into polyethylene tube, which pre-loading with 5 g NaCl, vortexed for 1 min, and then stood for 15 min, splitting drawn 0.2 mL of supernatant into 20 mL of graduated centrifuged tube, diluted to 10 mL by acetonitrile, mixed and transferred of 1 mL of acetonitrile layer into eppendorf tube, which contained 10 mg of C18 and 15 mg Carb. The sample mixed vigorously by vortexing for 0.5 min and centrifuged for 5 min at 8200 r·min⁻¹. Acetonitrile

layer was filtered through a 0.22 µm filter membrane and transferred into autosample tube for HPLC-MS/MS analysis.

2.2.3 HPLC-MS/MS Analyses

The trace detection of ESM by HPLC-MS/MS performed on a little modification of previous reported protocols (Degenhardt et al., 2006; Yan et al., 2011; Ye et al., 2006). An Agilent 6410 Triple Quadrupole HPLC-MS/MS (Agilent Technologies, USA) was used for the analysis. Acquity uplc BEH C18 column (50 mm × 2.1 mm, 1.7 µm) column (Waters, USA), was operated at a flow rate of 0.4 mL·min⁻¹, and the column temperature was 35 °C. The mobile phase was composed of ultra-pure H₂O (solvent A) and acetonitrile (solvent B), the gradient elution conditions employed as shown in Table S1. The inject volume was 5 µL by autosampler using full loop injection.

Nitrogen was used for both nebulizer and collision gas. The ions were electrospray ion (ESI) and monitored in positive multiple reaction mode (MRM), the MRM conditions listed in Table S2. The instrument conditions were as follows: ESI temperature, 120 °C, desolvation temperature, 350 °C, capillary voltage, 0.5 kV, desolvation gas flow, 650 L·h⁻¹, cone gas flow, 50 L·h⁻¹, collision gas flow, 15 L·h⁻¹.

The ESM was qualitatively determined by comparative analysis of retention time and a pair of ions (major ion and two minor ions), and quantitatively by major ion and maximum response value of two minor ions (Table S2).

Table S1. The gradient elution program of liquid phase

Time (min)	Mobile phase	
	Solvent A (% v/v)	Solvent B (% v/v)
0.0	95	5
2.0	0	100
3.0	0	100
3.5	95	5
5.0	95	5

Table S2. MRM monitor conditions

Major ion	Minor ion	Cone voltage (eV)	Collision energy (eV)
411.04	167.99	38	30
411.04	196.03	38	16

2.3 Validation of Method

For quantitation of ESM residue in soil, the linearity regression quantitation equation of soil samples was operated in the gradient concentrations of five calibration points (0.001, 0.005, 0.01, 0.05 and 0.1 mg·L⁻¹), each level was spiked in soils and five replicates. The linearity regression quantitation equation was set up by least-squares regression of concentration versus peak area of calibration standards.

For evaluating extraction efficiency of the methods established, a recovery experiment was conducted. Different known concentrations of ESM in soils (0.2 and 2 mg·kg⁻¹) was spiked. Extraction and analysis were performed in triplicate with the procedures described above.

2.4 Statistical Analyses

The dissipation kinetics of ESM in soil samples in laboratorial mock trial and field trial were determined by plotting the concentration of the residue against the time of sampling. The best fit curves of equations were determined by the maximum squares of correlation coefficient. Exponential relationships were applied for all the soil samples, corresponding to the first order rate equation. The first order kinetic was graphically displayed from the following equation:

$$C_t = C_0 e^{-kt}$$

where

C_t represents the concentration of the ESM residue at the time of t ;

C_0 represents the initial deposits after ESM application;

k is the degradation rate constant per day.

The half-life ($t_{1/2}$) was calculated from the k value for each experiment as described by Zhang et al. (2012):

$$t_{1/2} = \ln 2/k$$

3. Results

3.1 Method Validation

The linearity of soil samples was operated in the gradient concentrations of five calibration points (0.001, 0.005, 0.01, 0.05 and 0.1 mg·L⁻¹), each level was five replicates, by matrix-matched standard calibrations method. Linear calibration equation was $y = 994.04x - 157.25$ ($R^2 = 0.9998$) by least-squares regression of concentration versus peak area of calibration standards, herein y means MS/MS peak area of ESM, x means ESM concentration of calibration.

The extraction efficiency and relative standard deviation were determined by fortification ESM in paddy soil at two levels (0.2 and 2 mg·kg⁻¹). The detected results showed in Table 1. The extraction efficiencies at two levels of ESM in paddy soil were 100.16% and 85.56%, and relative standard deviation were 7.42% and 9.69%, respectively.

The LOD of ESM in paddy soil was 1.10×10^{-6} ng based on a signal-to-noise (S/N) ratio of 3. The LOQ of ESM in paddy soil was 1.27×10^{-3} µg·kg⁻¹ according to S/N ratio of 10.

Table 1. Extraction efficiency of LLE method

Fortification concentrations (mg·kg ⁻¹)	Extraction efficiency (%)					Mean (%)	RSD (%)
	1	2	3	4	5		
0.2	102.30	100.87	109.03	100.16	88.46	100.16	7.42
2	91.38	83.19	82.54	95.97	74.71	85.56	9.69

3.2 Dissipation of ESM in Soil at Different Temperatures

The residue dynamic of ESM in paddy soil was monitored at 6 °C, 25 °C, and 37 °C. The initial deposit concentration of ESM in paddy soil was 2.00 mg·kg⁻¹, the regression equation and other calculated parameters (regression equation and coefficient, degradation constant and half-life of ESM) were shown in Table 2. Strikingly, as shown in Figure 1A, the dynamic of ESM residue in paddy soil at 6 °C was not supported by the regression equation, because of negligible degradation of ESM in paddy soil at such low temperature. The half-life of ESM in paddy soil at 25 °C and 37 °C was 16.35 days and 10.35 days, respectively (Figures 1B and 1C).

Table 2. Half-life and other parameters of ESM in soil

Temperature (°C)	Regression equation	Regression coefficient R^2	Degradation constant (day ⁻¹)	Half-life (day)
6	/	/	/	/
25	$y = 2.0687e^{-0.0424x}$	0.9735	0.04239	16.35
37	$y = 1.4714e^{-0.0670x}$	0.8539	0.06697	10.35

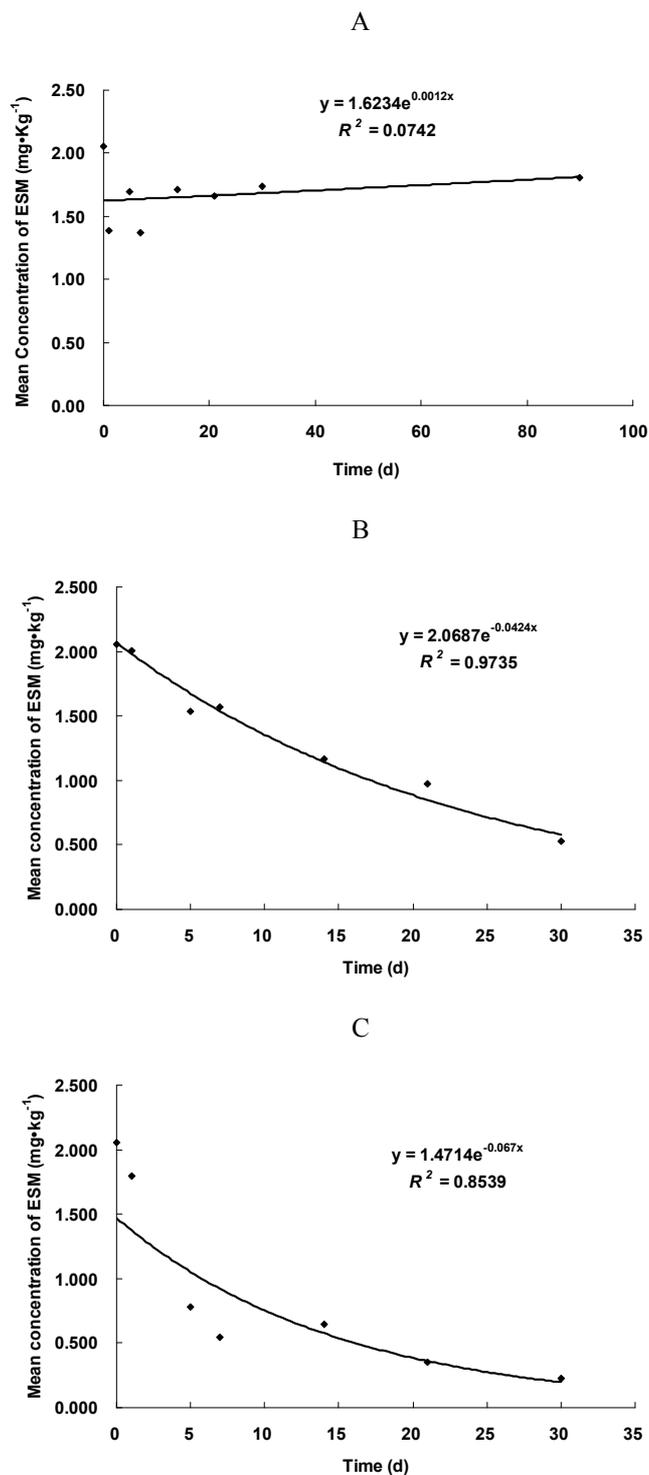


Figure 1. Regression analysis of ESM residue dynamics in paddy soil at different temperates. A, 6 °C; B, 25 °C; C, 37 °C

3.3 Field Trial

The dynamic of ESM residue in the field at the recommended application rate of 18 g a.i. ha⁻¹ was congruent with the regression equation ($y = 0.007e^{-0.02x}$) with a relative low coefficient ($R^2 = 0.745$) (Fig 2), 34.66 days of half-life of ESM.

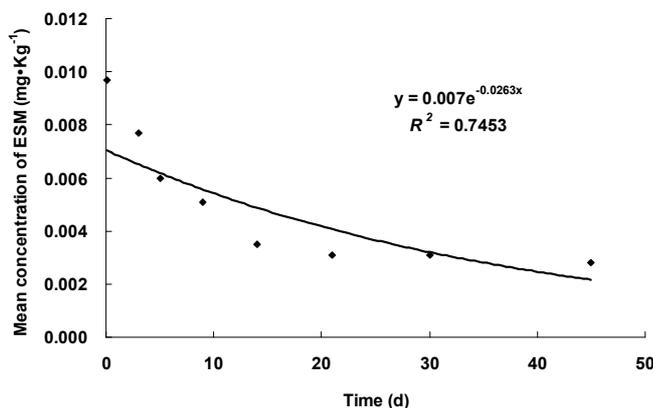


Figure 2. Regression analysis of ESM residue dynamics in the field

4. Discussion

For controlling weeds in rape seed field, ESM was almost the dedicated and sole herbicide in quite a while in China. The residue of sulfonylurea herbicides, which be phytotoxic to next crops (generally is rice and corn in China) and contaminating cropland ecological system was well documented (Patton et al., 2010; Tan et al., 2013). Li et al. (Li et al., 2007) found that metsulfuron-methyl could inhibit growth of two rice varieties (“Xiushui 63” and “Zhenong 952”) by changing the several key enzymes activity of rice, including catalase, superoxide dismutase and peroxidase besides of acetolactate synthetase at trace concentration (0.025 mg·kg⁻¹). It is reasonable to deduce that ESM also be toxic to subsequent crops and cropland ecological system at trace concentration (0.025 mg·kg⁻¹). Thus, it is indispensable to uncover the fate and dynamic of ESM in paddy soil.

The trace detection, including extraction and test approach, of ESM and other compounds of sulfonylurea herbicides were primary and crucial for monitoring its fate and dynamic. To this end, a number of trace detection methods were developed, for example, liquid phase extraction with micellar electrokinetic chromatograph (MEKC) (Yi et al., 2013; Zhang et al., 2011), solid phase extraction (SPE) with capillary liquid chromatography (Bouri et al., 2012), SPE with capillary zone electrophoresis (Quesada-Molina et al., 2010), SPE with HPLC (Fang et al., 2010; He et al., 2012), and SPE with LC-MS/MS (She et al., 2010), and so on. All of these methods could detect effectively at ng·kg⁻¹ level of six to twelve sulfonylurea herbicides in different samples. Comparing with these methods, the LLE with HPLC-MS/MS in this study could also highly extract and accurately detect of ESM, with the merits of easily operation, labor saving and be economical for samples extraction and cleanup.

After ESM was sprayed into the soil for preventing weeds, there were several key factors (including soil pH, organic matter content, soil microbial activity and temperature, and so on) involving in the dissipation of ESM (Si et al., 2005, 2006; Wang et al., 2010a; Rosenkrantz et al., 2013b; Ren et al., 2011; Qiu et al., 2005). The laboratory study showed the half-life of ESM was short when organic matter content decreasing (Si et al., 2005). Further study manifested that desorption level of ESM was increasing when organic matter content decreasing (Si et al., 2006). The dissipation of metsulfuron-methyl was enhanced by increasing soil moisture and soil temperature (Wang et al., 2010a). The increase of soil pH would enhance the retention of chlorimuron-ethyl and thus effectively retard chlorimuron-ethyl from entering the aqueous phase (Ren et al., 2011). It could deduced that it was higher of soil microbial activity, the dissipation of ESM was rapid for the evidence of biodegradation of others contaminants in soil by soil microorganism (Xu et al., 2013).

As to temperature, itself not only affected the dissipation of ESM (Headley et al., 2010), but also influenced key factors involving in the dissipation of ESM above. In general, the temperature was increasing, the dissipation of ESM was rapid (Headley et al., 2010). And along with increasing of temperature, it is reasonable to deduce the dissipation of ESM was rapid for raising the soil microbial activity, organic matter content and desorption of ESM (Yang et al., 2012; Xu et al., 2013; Si et al., 2005, 2006).

The dynamics of ESM in laboratorial mock trials showed that temperate was lower, longer half-life of MSE was (Table 4). It was agreement with dissipation trend of ESM of previous studies (Headley et al., 2010; Anderson et al., 2001), the probably reasons as above discussion. ESM was negligible degradation at 6 °C in paddy soil (Figure 1), it was coincided with previous publication, the ¹⁴C labeled ESM was mineralized only 2.2-6.0% after 84 d of incubation at 15 °C in soil (Wang et al., 2010a), and it is striking to subsequent crop because the low

temperature had been sustained after ESM was sprayed in the period of duration of rape seed, ESM would robust exist in paddy soil when rice or other subsequent crops planted. The half-life of ESM in field trial (daily average temperature was 30 °C) was longer than laboratorial mock trials even if at 25 °C. It is not surprised because of more complication of ESM synergic action of pH, organic matter, temperature, adsorption and sorption in field (Anderson et al., 2001; Ren et al., 2011; Rosenkrantz et al., 2013b; Wang et al., 2010a). This result also hinted ESM (at recommendation dose of 18 g a.i. ha⁻¹) would be utilized at least 35 days ahead of rice or others sensitive crops planting.

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