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# Residues of $^{14}$C-metsulfuron-methyl in Chinese paddy soils†

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## Abstract

**BACKGROUND: Metsulfuron-methyl is widely used for controlling many annual grasses and broadleaf weeds in cereal crops. Nonetheless, increasing evidence has demonstrated that even extremely low levels of metsulfuron-methyl residues in soil can be toxic to subsequent crops or non-target organisms. The behavior of herbicides in soils is mostly related to their residual forms. The intent of the present study was to investigate the dynamics of extractable residues (ERs) and non-extractable residues (NERs) of $^{14}$C-metsulfuron-methyl in twelve Chinese paddy soils and their relationships to soil properties.**

**RESULTS: ERs decreased gradually after application, whereas NERs increased rapidly during the initial 28 days, and gradually decreased thereafter. ERs and NERs were respectively 10.1–67.9% and 5.6–28.7% of applied radioactivity in soils at 224 days after application. ERs correlated positively with soil pH and silt fractions, and negatively with microbial biomass carbon (MBC) and clay fractions, but the opposite was observed for NERs.**

**CONCLUSION: Both ERs and NERs may be present in the soil at the time of planting following rice crops, and the risk of phytotoxic effects needs to be considered. Soil pH, MBC and clay/silt fractions were the main factors in affecting the amounts of both ERs and NERs of metsulfuron-methyl in the tested soils.**

**Keywords:** metsulfuron-methyl; extractable residues; non-extractable residues; soil pH

## 1 INTRODUCTION

The increasing use of herbicides has created serious concerns about the adverse effects of herbicide residues on the surrounding environment, agricultural production and human health. To evaluate the potential impact of soil herbicide residues on crop production and environmental quality, it is necessary to distinguish and investigate the behavior of extractable and non-extractable residues in soil. Soil extractable residues (ERs) are those that are extractable by organic solvents. ERs have higher bioavailability and are susceptible to degradation.[1] The dissipation of ERs generally follows a decreasing pattern with time in soil. Studies with $^{14}$C-radiolabeled pesticides have shown that a significant fraction of the added pesticide becomes non-extractable or tightly bound in soil.[1,2] Non-extractable residues (NERs) are operationally defined as the parent compound and its metabolites that remain in soil after extraction with organic solvents for 24 h using a Soxhlet extractor.[2] The build-up of NERs in soil is due to the interactions between chemicals and organic or mineral constituents of the soil. Although the formation of NERs may detoxify or hinder the mobility of chemicals in soils, the biologically mediated release of NERs in soil has been observed in several studies.[3–5] Therefore, the possible release of NERs, their bioreactivity in soil and their impact on the environment and food safety have attracted a great deal of attention over recent years.[6,7]

Metsulfuron-methyl is a sulfonylurea herbicide used worldwide for controlling broadleaf weeds in cereals; it has high herbicidal activity, low mammalian toxicity and can be applied at low application rates.[6] It has been shown that the dissipation of metsulfuron-methyl in soil involves both chemical and microbial processes.[8,9] Persistence of metsulfuron-methyl in soil mostly depends on soil properties, tillage management and environmental factors. Soils with higher organic matter can generally adsorb more metsulfuron-methyl than those with lower organic matter.[10,11] Higher persistence of metsulfuron-methyl has been found in soils at pH 7 than at pH 5.5,[12] and liming soils decreased the adsorption of metsulfuron-methyl.[11] NERs increased when either the soil water content or temperature decreased.[13] Residue recovery

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of $^{14}$C-metsulfuron-methyl at day 32 after application was 60.0% and 64.1% in planted and unplanted treatments respectively.[14]

Although the typical soil application rate of metsulfuron-methyl for field crop use ranges from 4 to 12 g active ingredient (AI) ha$^{-1}$, even the extremely low residues in soil may still cause high phytotoxicity to rotation or substitution crops such as sugar beet, maize, cotton, sunflower, soybean or rape.[8] Nearly 50% of metsulfuron-methyl residues were found to be still present in soil 131 days after application.[14] Carryover of soil metsulfuron-methyl residues into succeeding rice crops is of particular concern in Chinese continuous rotation systems of wheat–rice or wheat–rice–rice. In these systems, metsulfuron-methyl is commonly used for control in wheat, but has been found to inhibit the growth of rice seedlings in the following cropping season.[15] Beyer *et al.*[16] reported that, even if the concentration in soil were less than 1 μg kg$^{-1}$, sulfonylurea herbicides might still have a residual herbicidal activity. For chlorsulfuron, residues as low as 0.1 μg kg$^{-1}$ could reduce the growth of susceptible crops.[17]

There have been a number of studies on the degradation and persistence of metsulfuron-methyl in upland soils. However, little information concerning metsulfuron-methyl residues in paddy soils is available. The present research was initiated to provide information on the persistence of metsulfuron-methyl residues in paddy soils. The main objectives of this study were to determine the dynamics of extractable and non-extractable residues of metsulfuron-methyl in twelve Chinese paddy soils using radiolabeled material, and to understand their relationships to soil properties. The findings will provide needed information for the safe and effective use of the compound in paddy soils.

## 2 MATERIALS AND METHODS

### 2.1 Chemicals

Metsulfuron-methyl was purchased from Chem Service (West Chester, PA, USA), and the chemical purity was >98.0%. The $^{14}$C-labeled metsulfuron-methyl, labeled on the fourth carbon of the *s*-triazine ring, was synthesized at the Institute for Application of Atomic Energy, Chinese Academy of Agricultural Sciences, Beijing, China. Its specific radioactivity was $4.55 \times 10^4$ Bq mg$^{-1}$, and the radiochemical purity and chemical purity were greater than 97.3%.

### 2.2 Soils

Twelve paddy soils (0–15 cm) were taken from Zhejiang Province, which is representative of the rice-growing region in southeastern China. The fresh soil samples were taken to the laboratory immediately after sampling, hand picked to remove discrete plant residues, sieved through a 2 mm mesh, homogenized thoroughly and then stored in the dark at 4 °C until used for the incubation experiments. A subsample of the <2 mm soil particles was taken from each soil, air dried, ground and sieved to pass through a <0.149 mm plastic mesh and analyzed for physical and chemical properties. Selected properties of these soils are listed in Table 1. Soil pH was measured in a suspension of soil + water (1 + 2.5 by weight) after shaking for 1 h, and soil texture was determined using the pipette method.[18] The soil organic carbon (OC) was determined by the Walkley–Black procedure, and total nitrogen content by the Kjeldahl method.[18] The fresh soil samples with a moisture content of 50% water-holding capacity (WHC) were incubated at 25 ± 1 °C in the dark for 5 days, soil microbial biomass carbon (MBC) was extracted by the chloroform fumigation extraction method and total organic carbon in the extracts

**Table 1.** Selected properties of the paddy soils tested

| Paddy soil no. | Soil taxonomy | pH ($H_2O$) | OC[a] (g kg$^{-1}$) | MBC[b] (mg kg$^{-1}$) | TN (g kg$^{-1}$) | CEC (cmol(+) kg$^{-1}$) | Clay | Silt |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | (%) | |
| S1 | Loamy mixed superactive thermic aeric endoaquepts | 5.61 | 6.6 | 257.8 | 2.9 | 12.3 | 17.2 | 7.4 |
| S2 | Clayey illitic thermic typic endoaquepts | 5.82 | 11.8 | 728.9 | 2.5 | 15.9 | 22.1 | 50.3 |
| S3 | Clayey montmorillonitic thermic typic endoaquolls | 6.5 | 24.3 | 782.2 | 4.2 | 27.6 | 44.3 | 46.4 |
| S4 | Loamy mixed superactive thermic typic endoaquepts | 5.78 | 17.9 | 524.4 | 3.5 | 22.0 | 40.4 | 48.0 |
| S5 | Loamy mixed active thermic typic endoaqualfs | 8.40 | 28.7 | 886.7 | 4.2 | 81.1 | 15.8 | 74.2 |
| S6 | Loamy mixed active thermic aeric endoaquepts | 7.06 | 19.5 | 302.2 | 2.9 | 16.3 | 8.0 | 71.3 |
| S7 | Calcareous loamy mixed active thermic mollic endoaquepts | 9.04 | 5.5 | 160.0 | 1.8 | 7.1 | 24.3 | 71.1 |
| S8 | Clayey illitic thermic typic epiaqualfs | 6.20 | 23.6 | 928.9 | 3.9 | 25.1 | 35.3 | 60.6 |
| S9 | Clayey illitic thermic typic umbraqualfs | 6.22 | 18.3 | 995.6 | 3.7 | 28.5 | 38.0 | 57.0 |
| S10 | Loamy mixed active thermic aeric endoaqualfs | 6.00 | 13.4 | 1146.7 | 2.2 | 9.0 | 29.0 | 32.3 |
| S11 | Clayey kaolinitic thermic plinthaqualfs | 5.36 | 9.1 | 417.8 | 2.1 | 13.7 | 39.0 | 41.1 |
| S12 | Clayey kaolinitic thermic aeric endoaqualfs | 6.32 | 22.9 | 973.3 | 3.7 | 30.6 | 45.6 | 43.9 |

[a] OC = organic carbon; MBC = microbial biomass carbon; TN = total nitrogen; CEC = cation exchange capacity.

[b] Microbial biomass was measured 5 days after incubating fresh soils at moisture levels of 50% water-holding capacity (WHC) and 25 ± 1 °C in the dark.

was measured using a total organic carbon analyzer[19] (TOC-500; Shimadzu Corp., Kyoto, Japan).

### 2.3 Incubation experiment

The soil samples were retrieved from the storage at 4 °C and kept for 5 days at 25 ± 1 °C in the dark prior to treatment. A spiking solution was prepared by dissolving $^{14}$C-metsulfuron-methyl in methanol + water (1 + 1 by volume) to give a concentration of 1000 μg mL$^{-1}$. A sample of soil (60 g, oven-dry basis) was placed in a 250 mL Erlenmeyer flask and treated with 0.6 mL of the spiking solution, giving an initial metsulfuron-methyl concentration of 10 μg g$^{-1}$ soil. The treated soil was thoroughly mixed with a glass rod under a fume hood. After the methanol was completely evaporated, soil moisture was adjusted to 50% WHC by adding autoclaved distilled water. The pesticide application rate (10 μg g$^{-1}$) used in the present study was higher than the normal agronomic doses (about 1.5 μg g$^{-1}$),[13] and the higher rate was used to facilitate chemical analysis.

A vial containing aqueous sodium hydroxide solution (0.5 M; 10 mL) was hung under the rubber stopper of each flask to trap the evolved $^{14}$C-carbon dioxide, and was replaced weekly throughout the incubation period. All flasks were incubated at 25 ± 1 °C in the dark and aerated weekly. During the course of incubation, soil water content was kept constant by adding autoclaved distilled water when necessary. Aliquots of 6.0 g (oven-dry basis) soil subsamples were taken from each flask at 0, 7, 14, 28, 56, 112 and 224 days after $^{14}$C-metsulfuron-methyl application (DAA) and subjected to extraction and analysis as described in Section 2.4. There were three replications for each treatment.

### 2.4 Extraction and measurement

Soil subsamples (6.0 g, oven-dry basis) were shaken for 2 h with 40 mL methanol and then centrifuged for 10 min at 955 × *g*. The extraction procedure was repeated 5 times for each subsample, and the supernatants were then mixed together and made up to 200 mL with methanol. Previous experiments by the present authors had shown that the radioactivity of extractable $^{14}$C-metsulfuron-methyl residues by methanol at the sixth time was as low as that of background, and that the efficiency of this extraction method was 95.1–103.6% with a mean ± SE value of 97.8 ± 3.2%. By comparison, the recovery of extractable $^{14}$C-residues by 24 h Soxhlet extraction ranged from 86.7 to 105.5% with a mean ± SE value of 90.9 ± 5.4%. A quantity of 1 mL of the extract was mixed vigorously with 10 mL of scintillation cocktail I [2,5-diphenyl-1,3-oxazole (PPO) + 1,4-bis(5-phenyl-1,3-oxazo-2-yl)benzene (POPOP) + dimethylbenzene + glycol ether: 5 g + 0.4 g + 600 mL + 400 mL] and stored for 24 h in the dark prior to radioactivity analysis by a liquid scintillation counter (LSC) (Wallac Winspectral-1414; Wallac, Turku, Finland).

After extraction, the residual soil was left in a fume hood to be air dried for analysis of NERs. Aliquots of residual soil (1 g, oven-dry basis) were combusted for 5 min in a biological oxidizer (OX-600; Harvey Instrument Corp., Hillsdale, NJ, USA), and the evolved $^{14}$C-carbon dioxide from combustion was trapped in 15 mL of scintillation cocktail II (PPO + POPOP + ethanolamine + glycol ether + dimethylbenzene: 5 g + 0.4 g + 175 mL + 350 mL + 475 mL) for radioactivity measurement by LSC. The combustion efficiency for each soil was measured in triplicate by fortifying soil samples with $^{14}$C-metsulfuron-methyl solutions of known activity immediately before combustion. The $^{14}$C recovery ranged from 92.3 to 104.1% with a mean ± SE value of 96.8 ± 4.2%, and the detection limits of non-extractable$^{14}$C-metsulfuron-methyl residues for the method was 0.008 mg kg$^{-1}$.

## 3 RESULTS AND DISCUSSION

### 3.1 Extractable $^{14}$C-metsulfuron-methyl residues in soil

There was a gradual reduction in ER of $^{14}$C-metsulfuron-methyl in all paddy soils tested as time after application of metsulfuron-methyl increased (Fig. 1). The extractable radioactivity ranged from 70.0 to 91.5% of the applied amount in soils at 7 DAA, and quickly fell to 28.4–85.5% at 28 DAA. From 28

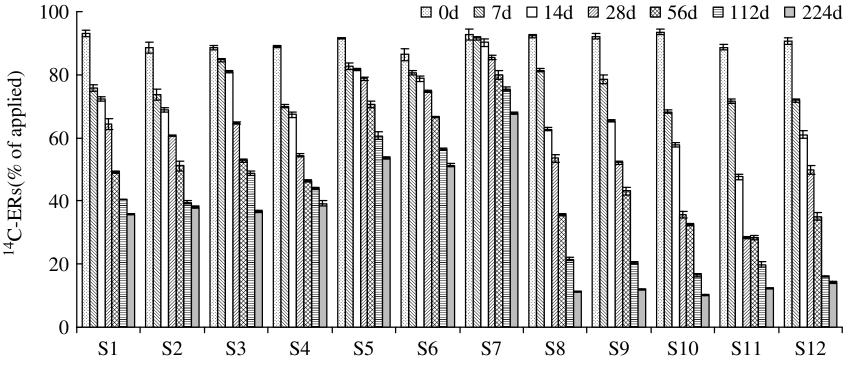

**Figure 1.** Extractable $^{14}$C-metsulfuron-methyl residues ($^{14}$C-ERs) in paddy soils. Bars are ± the standard error of mean. The soil numbers in this figure are the same as given in Table 1.

DAA to 224 DAA, the extractable radioactivity in soil tended to decrease. At 224 DAA, the extractable residues ranged from 10.1 to 67.9% of the applied amount in soils.

These losses of extractable radioactivity with time can be attributed to $^{14}$C-carbon dioxide being produced by degradation of $^{14}$C-metsulfuron-methyl and its $^{14}$C-metabolites and non-extractable $^{14}$C originating from metsulfuron-methyl and its metabolites. The rate of $^{14}$C-carbon dioxide evolution in the soils treated with $^{14}$C-metsulfuron-methyl ranged from 15 to 40% of the applied radioactivity in 120 days.[20,21] The amount of $^{14}$C-carbon dioxide evolved during the initial 84 day incubation period was found to account for 6.7–33.5% of initial radioactivity (data not listed), which resulted from the complete microbial degradation of the $^{14}$C-labeled triazine part of the $^{14}$C-metsulfuron-methyl molecule. Furthermore, in a study to identify the extractable metsulfuron-methyl residues in soil, Bossi *et al.*[22] showed that the extractable residues mainly consisted of 2-amino-4-methoxy-6-methyl-1,3,5-triazine, methyl 2-(aminosulfonyl)benzoate and the parent compound, but the complete degradation of triazine amine was slower than that of metsulfuron-methyl in soil. Seven metabolites of extractable $^{14}$C-metsulfuron-methyl residues in soil were identified by Li *et al.*[21] Additional non-identified metabolites have also been found in extractable residues of $^{14}$C-metsulfuron-methyl in soil.[13]

### 3.2 Non-extractable $^{14}$C-metsulfuron-methyl residues in soil

NERs increased rapidly during the initial 28 days, and then gradually decreased afterwards (Fig. 2). All 12 soils tested had the highest non-extractable residues at 28 DAA, which ranged from 11.4 to 55.7% of the applied radioactivity in soils. The steep increase in NERs in soils coincided with the rapid decrease in ERs during the initial 28 days, which indicated a faster incorporation of ERs into NERs in soils. From 28 to 224 DAA, a gradual decrease in NERs was observed in soils, which indicated that NERs of $^{14}$C-metsulfuron-methyl in soil could be released or mineralized (Fig. 2). The activity of microorganisms is thought to be the primary factor responsible for the release of non-extractable pesticide residues.[6] About 28.3–68.9% of non-extractable radioactivity observed 28 DAA disappeared through degradation at 224 DAA. NERs at 224 DAA ranged from 5.6 to 28.7% of the applied radioactivity.

The non-extractable $^{14}$C-metsulfuron-methyl was associated mainly with humic substances.[21] The likely binding mechanisms between soil organic matter and metsulfuron-methyl or its metabolities mainly consist of ionic bonding, charge transfer complexes, hydrogen bonding and hydrophobic sorption.[6] A significantly positive correlation has been observed between soil organic matter content and adsorption of metsulfuron-methyl.[10]

### 3.3 $^{14}$C-metsulfuron-methyl residues in relation to soil properties

Many soil factors have been reported to influence the fate and behavior of metsulfuron-methyl applied in soil, such as soil pH, organic matter content, moisture, temperature and microbial biomass.[10,13] The results in Figs 1 and 2 show that both ERs and NERs of metsulfuron-methyl were closely dependent on the paddy soil type.

The amounts of $^{14}$C-metsulfuron-methyl residues in soils were strongly influenced by soil pH throughout the incubation period (Table 2). Increasing soil pH significantly decreased NERs and increased ERs of $^{14}$C-metsulfuron-methyl in paddy soils. This is in good agreement with earlier reports on the dependency of metsulfuron-methyl dissipation on soil pH.[9,23] With decrease in pH, the protonated metsulfuron-methyl readily undergoes chemical hydrolysis. It is well known that the chemical process of metsulfuron-methyl degradation plays a major role in acidic soils.[9] At higher pH, metsulfuron-methyl exists mainly in anionic form and would be repelled by the negatively charged clay particles. This would result in less adsorption of metsulfuron-methyl by neutral and alkaline soils. Therefore, more ERs and fewer NERs of $^{14}$C-metsulfuron-methyl exist in soils with higher pH, and fewer ERs and more NERs in soils with lower pH.

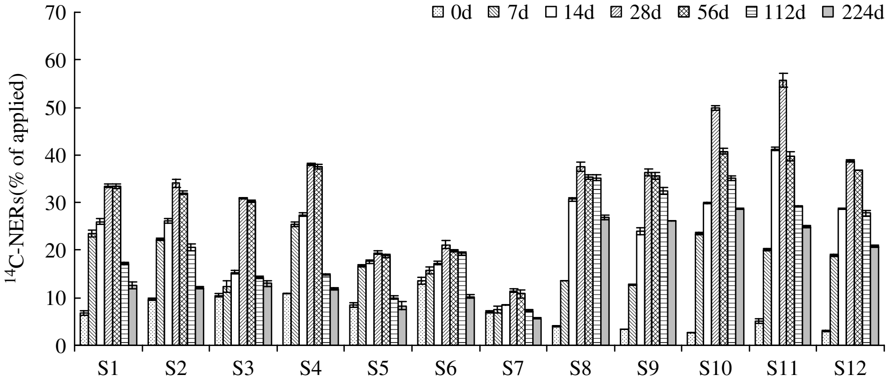

**Figure 2.** Non-extractable $^{14}$C-metsulfuron-methyl residues ($^{14}$C-NERs) in paddy soils tested. Bars are ± the standard error of mean. The soil numbers in this figure are the same as given in Table 1.

**Table 2.** Correlation coefficients between soil $^{14}$C-metsulfuron-methyl residues and properties of paddy soils

| Residues | DAA[a] | pH | OC | MBC | TN | CEC | Clay | Silt |
|---|---|---|---|---|---|---|---|---|
| Extractable residues | 7 | 0.790**[b] | 0.115 | −0.319 | 0.141 | 0.201 | −0.264 | 0.592* |
| | 14 | 0.786** | 0.100 | −0.385 | 0.140 | 0.236 | −0.474 | 0.458 |
| | 28 | 0.789** | 0.118 | −0.423 | 0.155 | 0.301 | −0.577* | 0.511 |
| | 56 | 0.851** | −0.002 | −0.493 | −0.036 | 0.257 | −0.621* | 0.576* |
| | 112 | 0.764** | −0.069 | −0.613* | −0.079 | 0.181 | −0.581* | 0.478 |
| | 224 | 0.735** | −0.107 | −0.630* | −0.125 | 0.163 | −0.595* | 0.445 |
| Non-extractable residues | 7 | −0.674* | −0.181 | 0.085 | −0.146 | −0.118 | 0.027 | −0.640* |
| | 14 | −0.812** | −0.128 | 0.265 | −0.123 | −0.193 | 0.387 | −0.505 |
| | 28 | −0.852** | −0.129 | 0.391 | −0.128 | −0.294 | 0.542 | −0.598* |
| | 56 | −0.917** | −0.006 | 0.485 | 0.087 | −0.245 | 0.602* | −0.656* |
| | 112 | −0.614* | 0.059 | 0.592* | −0.012 | −0.253 | 0.375 | −0.262 |
| | 224 | −0.586* | 0.069 | 0.627* | 0.023 | −0.194 | 0.510 | −0.301 |

[a] DAA=days after metsulfuron-methyl application; OC = organic carbon; MBC = microbial biomass carbon; TN = total nitrogen; CEC = cation exchange capacity.

[b] * Significant at the 0.05 probability level; ** significant at the 0.01 probability level.

In a previous study it was also found that the extent of NERs formation was greater in an acidic soil than in an alkaline soil.[13]

Metabolism of metsulfuron-methyl in soil is also highly dependent on soil microbial populations.[14,22,24] A positive correlation has been found between soil microbial biomass and metsulfuron-methyl degradation, indicating that a larger soil microbial biomass would result in lower residues of metsulfuron-methyl in soil.[10] It is reasonable that soil microbial biomass carbon negatively correlated with ERs of $^{14}$C-metsulfuron-methyl at 112 and 224 DAA (Table 2). The fact that no relationship existed for earlier sampling dates might be related to the toxicity of metsulfuron-methyl to soil microorganisms. El-Ghamry *et al.*[25] showed that soil microbial biomass was significantly reduced in a loamy sand soil during the initial 10 days after metsulfuron-methyl application at rates of 0.1 and 1.0 $\mu g\,g^{-1}$, and was then restored to an untreated soil level. This suggests that the higher application rate, i.e. 10 $\mu g\,g^{-1}$, used in this research would cause an even larger decrease in soil microbial biomass, and a more prolonged period of impact.

Surprisingly, no relationship was observed between either ERs or NERs and soil organic carbon at any sampling date (Table 2). This indicates that, although organic carbon levels varied considerably among the 12 paddy soils tested, this apparently had no controlling effect on metsulfuron-methyl residues. In a study of six Brazilian soils with organic carbon levels ranging from 3.5 to 74.5 g $kg^{-1}$, Oliveira *et al.*[26] found that the sorption coefficient of metsulfuron-methyl by soils correlated with soil organic carbon, but the influence of organic carbon on the sorption coefficient variation was very small. However, soil clay contents correlated negatively with ERs at 28, 56, 112 and 224 DAA, and positively with NERs only at 56 DAA (Table 2). This is likely due to higher adsorption of metsulfuron-methyl by the clay fraction than by silt and sand fractions in the soils. Abdullah *et al.*[11] noted that a high soil clay content resulted in limited leaching of metsulfuron-methyl owing to stronger adsorption by soil. In fact, the soil clay fraction is known to be associated with much of the organic matter in soils. The adsorption of metsulfuron-methyl by the clay fraction is actually the result of adsorption by both organic matter and clay minerals. This was further supported by the observation that the silt contents of soils correlated positively with ERs and negatively with NERs at some sampling dates (Table 2).

## 4 CONCLUSIONS

The findings from this study indicate considerable variation in ERs and NERs of $^{14}$C-metsulfuron-methyl among different paddy soils. At the end of the experiment, ERs and NERs comprised 10.1–67.9% and 5.6–28.7% of applied radioactivity respectively, which suggested a potential risk of carryover of both soil ERs and NERs of $^{14}$C-metsulfuron-methyl to rice grown in the follow-up season. Soil pH, MBC and clay/silt fractions are the predominant factors governing the amounts of both ERs and NERs of $^{14}$C-metsulfuron-methyl in paddy soils. There was a statistically significant positive correlation between soil pH and ERs, which indicates that there may be higher bioreactivity and greater transport potential of metsulfuron-methyl residues in soils with higher pH. In southeastern China, and other similar regions, widespread use of lime has been adopted because liming of acidic soil can improve crop yield. Results from this study suggest that liming would increase the potential risk of mobilizing metsulfuron-methyl residues and harming rice grown in typically acidic paddy soils owing to increase in soil pH.

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