

# Kinetic Distribution of $^{14}\text{C}$ -Metsulfuron-methyl Residues in Paddy Soils under Different Moisture Conditions

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Rice paddy soils undergo several cycles of drying and wetting during a growing season. A laboratory study was conducted to determine the effect of soil moisture conditions on the distribution and kinetics of extractable and bound residues of  $^{14}\text{C}$ -metsulfuron-methyl in six Chinese paddy soils during 84 d of incubation at 15°C with moisture contents varying from 20 to 50% of the field water-holding capacity. The amount of extractable residues consistently increased and bound residues decreased with increasing soil moisture content. At the end of the incubation experiments, extractable residues and bound residues accounted for 34.5 to 84.4% and 11.6 to 53.3% of applied radioactivity in soils, respectively. Soil pH and soil microbial biomass carbon were the most predominant factors affecting the formation and relative distribution of herbicide residues between extractable and bound residue forms. In high-pH soils, bound residues decreased and extractable residues increased, suggesting an increased leaching risk for metsulfuron-methyl in alkaline soils. High precipitation rates, along with the common practice of liming in southeastern China, may lead to enhanced herbicide leaching as well as phytotoxicity to rotation plants and should be considered in overall pest management practices.

**M**ETSULFURON-METHYL (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate;  $\text{C}_{14}\text{H}_{15}\text{N}_5\text{O}_6\text{S}$ ) is a sulfonylurea herbicide with a molecular weight of 381.4 g mol<sup>-1</sup>, a melting point 158°C, and a vapor pressure of  $2.5 \times 10^{-12}$  mm Hg (25°C) (Beyer et al., 1988; Brown, 1990). Its water solubility is 270 and 2790 mg L<sup>-1</sup> at pH 4.6 and 7, respectively (Beyer et al., 1988). Metsulfuron-methyl inhibits the enzyme acetolactate synthase, which stops plant cell division by inhibiting biosynthesis of the essential amino acids valine and isoleucine (Beyer et al., 1988; Brown, 1990). It is widely used for pre- and post-emergence control of many annual grasses and broadleaf weeds in cereal, pasture, and plantation crops because metsulfuron-methyl is effective even at low application doses and is easy to use (Brown, 1990). Wang et al. (2003) reported that the application area of metsulfuron-methyl in China was about  $4.2 \times 10^6$  h<sup>-2</sup>.

Metsulfuron-methyl has been shown to persist in the environment for many months (Pons and Barriuso, 1998; Wang et al., 2001; Hollaway et al., 2006). Occasionally, even extremely low concentrations of metsulfuron-methyl residues remaining in soil caused phytotoxicity (Moyer, 1995; Yao et al., 1997; Ye et al., 2003; Li et al., 2005; Hollaway et al., 2006). It is clear, then, that the occurrence of metsulfuron-methyl residues in the soil is an important problem and must be given due attention.

The principal degradation pathways of metsulfuron-methyl in soil include chemical hydrolysis and microbial degradation (Brown, 1990; Sarmah and Sabadie, 2002). The half-lives and the sorption

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**Abbreviations:** MBC, microbial biomass carbon; WHC, field water-holding capacity.

distribution coefficients of metsulfuron-methyl are variable and are dependent on soil properties and environmental factors (Pons and Barriuso, 1998; Wang et al., 2001; Oliveira et al., 2001; Berglöf et al., 2003; Kah and Brown, 2007). It has been reported that pH seems to be the most important soil property controlling metsulfuron-methyl behavior. It influences the ionization state, which in turn can affect the herbicide's residual form, sorption, and chemical degradation (Brown, 1990; Pons and Barriuso, 1998; Wang et al., 2001; Sarmah and Sabadie, 2002). In the cereal-growing area of southeastern China, the pH of paddy soils ranges from 5 to 9 in the top 20-cm layer. As a weak acid with a pKa of 3.3, metsulfuron-methyl is predominantly anionic in this pH range, especially at the higher pH values. The anionic form is soluble in water and is less susceptible to hydrolysis, which may increase its persistence and leaching potential. Yao et al. (1997) noted that the phytotoxicity of metsulfuron-methyl residues in soils may become a particular concern in the Chinese continuous rotation systems of wheat-rice or wheat-rice-rice because metsulfuron-methyl used during the wheat growing season was found to inhibit the growth of rice seedlings in the follow-up cropping season. Therefore, knowledge about the behavior and fate of metsulfuron-methyl in Chinese paddy soils is of great regional importance for sustaining the agronomic systems and protecting the environment.

The potential risk of pesticides in the environment depends not only on the residual amount but also on its distribution among the different residual forms. The residual form has a direct influence on the persistence, mobility, and bioavailability of pesticide residues in the environment (Navarro et al., 2007). Pesticide residues in soils can be divided into extractable and bound (non-extractable) forms. Extractable residues are readily available for ecological receptors and are easily leached, whereas there is a significant decline in the rates of desorption, degradation, or environmental mobility of bound residues with a concurrent increase of persistence in soils (Chung and Alexander, 1998). Several environmental and agricultural factors are capable of influencing the degradation and binding of herbicide residues in soils (Navarro et al., 2007). Soil moisture often plays an important role in herbicide fate. Studies show that increasing soil water content within the field water-holding capacity (WHC) can stimulate microbial degradation of several sulfonylurea herbicides (Fuesler and Hanafey, 1990; Pons and Barriuso, 1998; Hollaway et al., 2006). Change in soil moisture contents can alter the ratio of soil to solution, which can directly affect the degradation, sorption, and leachability of pesticides. Sulfonylurea herbicide residuals that remain in the soils are one of the most important factors affecting the environmental safety of sulfonylurea herbicides in soil (García-Valcárcel and Tadeo, 1999; Kah and Brown, 2007). Little quantitative information is available concerning effects of soil moisture on dynamics of sulfonylurea herbicide residuals in soil.

The objectives of this study were to determine the kinetics of extractable and bound residues of  $^{14}\text{C}$ -metsulfuron-methyl in six Chinese paddy soils under different moisture conditions and to better understand the role of soil moisture content and soil properties in affecting the retentive binding and dissipation

of pesticide residues in soils. The findings will provide needed information for its safe use and reducing its negative environmental impacts.

## Material and Methods

### Chemicals

Metsulfuron-methyl (chemical purity, >98%) was purchased from Chem Service (West Chester, PA).  $^{14}\text{C}$ -Labeled metsulfuron-methyl (triazine-4- $^{14}\text{C}$ ), with a specific radioactivity of  $4.55 \times 10^4 \text{ Bq mg}^{-1}$  and radiochemical purity and chemical purity >97.3%, was synthesized by the Institute for Application of Atomic Energy, Chinese Academy of Agricultural Sciences (Beijing, China). Liquid scintillation cocktail I was prepared by dissolving 2'5-diphenyloxazole (5 g) and 1'4-bis-(5-phenyl-oxazolyl-2)-benzene (0.4 g) in a mixture of dimethylbenzene (600 mL) and glycol-ether (400 mL). Liquid scintillation cocktail II was prepared by dissolving 2'5-diphenyloxazole (5 g) and 1'4-bis-(5-phenyl-oxazolyl-2)-benzene (0.4 g) in a mixture of ethanolamine (175 mL), glycol-ether (350 mL), and dimethylbenzene (475 mL). Other chemicals, including solvents, used in this study were of analytical grade or better.

### Soils

Six paddy soils were sampled from the top 20 cm in Zhejiang Province, which is located in southeastern region of China. Fresh soil samples were taken to the laboratory immediately after sampling, hand-picked to remove discrete plant residues, sieved through a 2-mm screen, and stored in dark at 4°C until use. Aliquots were air-dried, ground, and sieved to pass through a <0.149-mm plastic mesh. Analysis of physical and chemical properties was performed using standard methods. Selected soil properties are presented in Table 1. Soil pH was determined in suspension of 1:2.5 soil/water (w/w) after shaking for 1 h. Soil texture was measured using the pipette method. Soil organic carbon and total nitrogen contents were determined by the Walkley-Black procedure and by the Kjeldahl method, respectively (Anderson and Ingram, 1993). The fresh soil samples with soil moisture contents of 50, 40, and 20% WHC were incubated at  $15 \pm 1^\circ\text{C}$  in the dark for 5 d. Soil microbial biomass carbon (MBC) was extracted by the chloroform-fumigation-extraction method, and total organic carbon in the extracts was measured using a total organic carbon analyzer (TOC-500; Shimadzu Corp., Kyoto, Japan) (Vance et al., 1987).

### Incubation Experiments

Soil samples were retrieved from storage at 4°C and kept at  $25 \pm 1^\circ\text{C}$  for 5 d in the dark before the treatment. The herbicide spiking solution was prepared by dissolving  $^{14}\text{C}$ -metsulfuron-methyl in a 1:1 methanol/water mixture to give a concentration of  $1000 \mu\text{g mL}^{-1}$ . A 60-g portion of soil (oven-dry basis) was placed in 250-mL Erlenmeyer flasks and treated with 0.6 mL of the spiking solution, giving an initial metsulfuron-methyl concentration of  $10 \mu\text{g g}^{-1}$  soil. After methanol was completely evaporated in a fume hood after 24 h, treated soil was thoroughly mixed, and soil moisture was adjusted to 20, 40, and 50%

**Table 1. Basic properties of the soils used in this study.**

Soil no.	Soil taxonomy	pH (H <sub>2</sub> O)	OC†	WHC	MBC‡			TN	Clay	Silt
					A	B	C			
S1	clayey illitic thermic typic umbraqualfs	6.22	18.3	71.3	403.6	327.1	226.0	3.7	40.0	57.0
S2	clayey montmorillonitic thermic typic endoaquolls	6.50	24.3	72.6	491.5	403.4	272.8	4.2	44.3	46.4
S3	loamy mixed active thermic aeric endoaqualfs	6.00	13.5	55.8	621.6	540.7	n.d.	2.2	29.0	32.3
S4	clayey kaolinitic thermic plinthaqualfs	5.36	9.1	72.4	354.8	360.0	n.d.	2.1	39.0	41.1
S5	loamy mixed superactive thermic typic endoaquolls	5.78	17.9	68.5	375.9	381.5	307.1	3.5	40.4	48.0
S6	calcareous loamy mixed active thermic mollic endoaquepts	9.04	5.5	53.6	102.4	101.3	98.4	1.8	24.3	71.1

† MBC, microbial biomass carbon; n.d., not determined; OC, organic carbon; TN, total nitrogen; WHC, field water-holding capacity.

‡ MBC was measured 5 d after incubating soil at moisture levels of 50 (A), 40 (B), and 20%WHC (C) and 15 ± 1°C in the dark.

WHC by adding autoclaved distilled water. Preliminary experiments indicated that the use of methanol did not significantly affect soil microbial biomass size. The 20% WHC treatment for soils S3 and S4 were not conducted because the water content of these two natural soils was higher than this treatment. Pesticide application rate (10 µg g<sup>-1</sup>) used in the present study was higher than normal agronomic doses (about 1.5 µg g<sup>-1</sup>) (Pons and Barriuso, 1998) to facilitate chemical analysis.

All flasks were incubated at 15 ± 1°C in an incubator and aerated weekly in a fume hood for 30 min, at which time the soil moisture content was readjusted by weighing. Flasks were kept in the dark until they were removed for sampling or watering. After given time intervals (0, 7, 14, 28, 56, and 84 d after treatment), 6.0-g aliquots of soil (oven-dry basis) were taken from each flask and subjected to extraction and analysis as described below. Three flasks were run for each treatment, and one sample was taken from each flask.

### Extraction and Analysis

The soil sample was shaken with 40 mL methanol for 2 h and centrifuged (955 g for 10 min at 20°C). The extraction procedure was repeated five times for each sample, and the supernatants were combined, followed by addition of methanol to make up the volume to 200 mL. Previous experiments showed that the radioactivity in the extracts from the sixth time extraction was nearly undetectable and that this extraction procedure was more exhaustive in removing extractable <sup>14</sup>C-residues than 24-h Soxhlet extraction (Wang et al., 2001). One milliliter of the extract was mixed with 10 mL of scintillation cocktail I, and radioactivity was measured on a liquid scintillation counter (Winspectral-1414; Wallac, Turku, Finland) after the vials were kept in the dark for 24 h.

After the extraction, the residual soil was left in a fume hood to remove the solvent, and a 1.0-g aliquot (oven-dry basis) was combusted for 5 min on a biological oxidizer (OX-600; Harvey Instrument, Hillsdale, NJ). The <sup>14</sup>CO<sub>2</sub> evolved from the combustion was trapped in 15 mL of scintillation cocktail II, and radioactivity was determined by a liquid scintillation counter. The combustion efficiency (>92%) for each soil was measured of known activity immediately before combustion.

### Statistical Analyses

Statistical analysis consisted of determination of means, SDs, one-way ANOVA (*P* ≤ 0.05), and simple correlation

analysis. All the statistical analyses were performed using SPSS 10.0 for Windows.

## Results and Discussion

### Kinetics of Extractable Residues

Changes in extractable <sup>14</sup>C-metsulfuron-methyl residues with time and soil moisture contents in the paddy soils are shown in Fig. 1. The level of extractable <sup>14</sup>C-residues decreased substantially from 0 to 56 d after <sup>14</sup>C-metsulfuron-methyl application except for the alkaline soil tested (soil S6). Extractable radioactivity ranged from 60.5 to 82.8% of applied radioactivity in the five acidic soils at Day 7 and fell to 32.9 to 57.6% of applied radioactivity after Day 56. From Day 56 to 84, extractable radioactivity in the soils did not change significantly with time. At Day 84, extractable residues ranged from 34.5 to 59.0% of applied radioactivity in the five acidic soils. Compared with the acidic soils, the percentage of extractable residues in the alkaline soil (S6) was much higher. At the end of the incubation, the extractable radioactivity ranged from 65.6 to 84.4% of applied radioactivity in S6. It is well known that the metsulfuron-methyl degradation/hydrolysis processes in soil and aqueous solution are pH dependent (Brown, 1990; Sarmah and Sabadie, 2002). The abiotic hydrolysis of the anionic metsulfuron-methyl at high pH was slower when compared with the hydrolysis of the neutral form of metsulfuron-methyl at low pH. Sarmah et al. (2000) reported that the rate of hydrolysis was at least 100 times faster in the acidic pH range than under neutral and moderately alkaline conditions.

During the same time interval, the amount of extractable residues always increased with increasing moisture content in all six soils tested. Analysis of variance showed a significant effect of soil moisture on the concentrations of metsulfuron-methyl-extractable residues (*P* = 0.002). When the soil moisture content increased from 20 to 50% WHC, the amount of extractable residues increased from 39.4 to 65.6% to 48.3 to 84.4% of applied radioactivity at Day 84 in S1, S2, S5, and S6. Several studies have indicated that the amount of the extractable pesticide residues decreases with decreasing soil moisture (Walker and Jurado-Exposito, 1998; García-Valcárcel and Tadeo, 1999; Hultgren et al., 2002). This may be explained by the variation in diffusion and/or the competitive adsorption of herbicide in soil under different environmental conditions. At lower soil moisture, the reduction in soil microbial activity could increase the

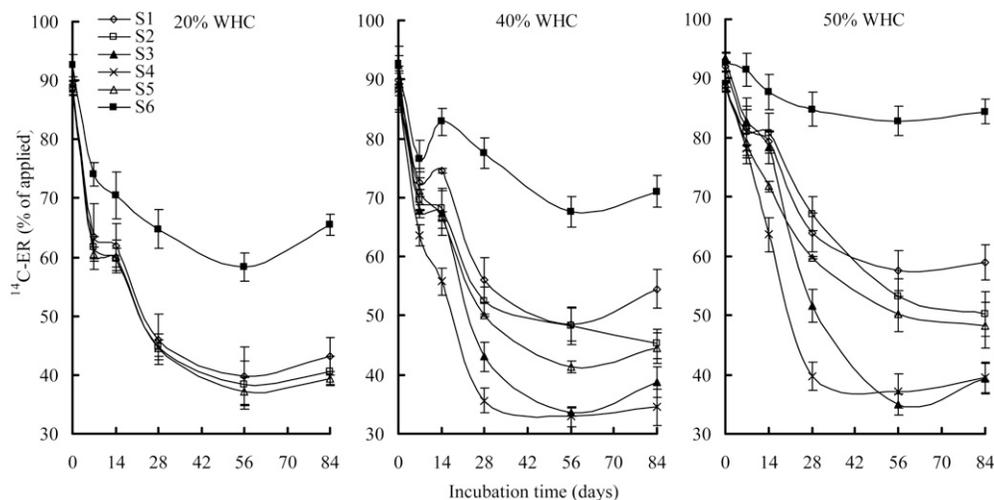


Fig. 1. Kinetics of extractable  $^{14}\text{C}$ -metsulfuron-methyl residues ( $^{14}\text{C}$ -ER) in the paddy soils incubated under moisture contents of 20, 40, and 50% water-holding capacity (WHC). Bars are  $\pm$ SE of three analyses. The soil number in this figure is the same as stated in Table 1.

herbicide persistence and therefore may increase the possibility of the herbicide bound to the soil sorption sites. Moreover, the increase in extractable residues with increasing soil water content could result from a solubility effect; the compound partitioning to the sorbed phase decreases as its concentration in soil solution decreases with increasing water content.

The losses of extractable radioactivity over time can be attributed to  $^{14}\text{CO}_2$  produced from the mineralization of  $^{14}\text{C}$ -metsulfuron-methyl and metabolites and the formation of non-extractable or bound residues. Although metabolites were not identified in the present study, several metsulfuron-methyl metabolites have been reported in previous studies. Pons and Barriuso (1998) found that hydroxyl-metsulfuron-methyl and amino-triazine, referred to as methyl-2-(4-hydroxy-6-methyl-1,3,5-triazine-2-yl carbamoylsulfamoyl) benzoate, and 4-hydroxy-6-methoxy-2-amino-1,3,5-triazine, respectively, were the main intermediates from the two metabolic pathways involved in the degradation of metsulfuron-methyl: *O*-demethylation and cleavage of sulfonyleurea bridge of the methoxy-triazine moiety. Sarmah et al. (2000) noted that 2-[(*N*-acetylcarbamoyl)carbamoylsulfamoyl] benzoic acid was the hydrolysis product with opened triazine ring for metsulfuron-methyl. However, the complete degradation of triazine amine went slower than that of metsulfuron-methyl in soil (Pons and Barriuso, 1998; Bossi et al., 1999), which may constitute an ever-present and cumulative risk of metabolites to the environment and, eventually, to non-target organisms. Despite this, the adverse effects caused by the metabolites of metsulfuron-methyl along with the parent compound in soil have been presented (Boldt and Jacobsen, 1998; Li et al., 2005; Hollaway et al., 2006). Therefore, the research of extractable  $^{14}\text{C}$ -residues, including  $^{14}\text{C}$ -metsulfuron-methyl and its  $^{14}\text{C}$ -metabolites, may complete a more comprehensive assessment of its integral environmental impacts. Indeed, the behavior of degradation products as a function of soil moisture conditions should be studied in future research to fully understand the toxicological effects of metsulfuron-methyl and similar herbicides.

### Kinetics of Bound Residues

Rapid formation of bound  $^{14}\text{C}$ -metsulfuron-methyl residues was observed in all soils (Fig. 2). The bound residues were 2.7 to 11.8% of applied radioactivity at Day 0 and increased to peak values at Day 56 in all soils, varying from 14.2 to 61.0% of applied radioactivity. During the initial 56 d, the sharp increase in bound residues with time coincided with the rapid decrease in the extractable form in the acidic soils, indicating an increase in binding of the extractable residues to the soil matrix over this period. From Day 56 to Day 84, the amount of the bound residues gradually decreased, which indicated that the initially bound residues of  $^{14}\text{C}$ -metsulfuron-methyl in soil were being released and subsequently mineralized. Approximately 2.8 to 20.1% of the bound radioactivity observed at Day 56 disappeared through degradation by Day 84. The bound residues at Day 84 ranged from 11.6 to 53.3% of applied radioactivity. These results showed that the bound residues of metsulfuron-methyl constituted a substantial part of the total herbicide residues in the tested soils, particularly in the acidic soils. Ye et al. (2003) demonstrated that the main components of bound residues formed during the degradation of metsulfuron-methyl in soils were 2-amino-4-hydroxyl-6-methyl-1,3,5-triazine; 2-amino-4-methoxyl-6-methyl-1,3,5-triazine; metsulfuron-methyl; and 2-methylformate-benzenesulfonyl-isocyanate. The same researchers also suggested that a major part of the bound metsulfuron-methyl residues in soil were comprised of the parent compound and that the phytotoxicity induced by the bound metsulfuron-methyl residues to oil rape could be attributed to the fact that the metsulfuron-methyl parent compound was released from the bound residue form and became available during plant growth (Ye et al., 2003). Therefore, special attention should be given to the release of the bound residues of metsulfuron-methyl into soil solution when assessing the impact of this herbicide on the growth of sensitive plants.

Over the incubation period, the amount of bound residues was significantly less ( $P < 0.001$ ) in the same soil with a higher moisture content than with a lower moisture content. When

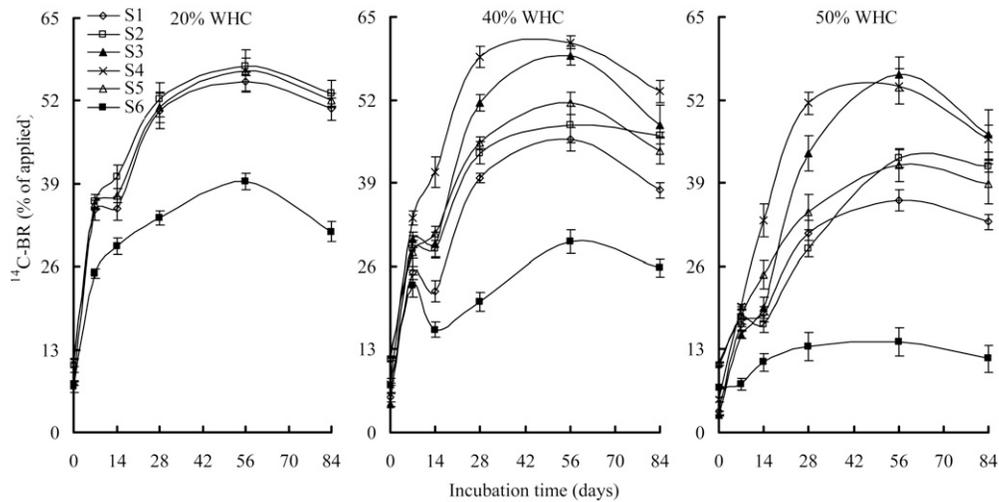


Fig. 2. Kinetics of bound  $^{14}\text{C}$ -metsulfuron-methyl residues ( $^{14}\text{C}$ -BR) in the paddy soils incubated under moisture contents of 20, 40, and 50% water-holding capacity (WHC). Bars are  $\pm$ SE of three analyses. The soil number in this figure is the same as stated in Table 1.

the soil moisture content decreased from 50 to 20% WHC, the bound residues increased from 11.6 to 46.6% to 31.5 to 53.1%, respectively, of applied radioactivity at Day 84. Similar trends have been reported in earlier studies for other soil types, where the formation of bound residues of metsulfuron-methyl was also found to decrease with increasing soil water content (Pons and Barriuso, 1998). It was suggested that greater microbial activity may have contributed to an increased release or degradation of bound residues at higher soil moisture content (Pons and Barriuso, 1998). Furthermore, soil particles were covered by multiple layers of water molecules in moist soils, which decreased the affinity of hydrophobic organic compounds to the surfaces of soil particles. Reduced binding of a herbicide to soil may make its residues more available for microbial and chemical degradation (Kah and Brown, 2007). At the end of the experiment, 4.1 to 14.6% of applied radioactivity was lost in the soils incubated at 50% WHC, whereas 3.2 to 13.0% and 3.0 to 8.5% losses were observed for the 40 and 20% WHC treatments, respectively (data not listed).

### Influence of Soil Properties

Results in Tables 2 and 3 show that the formation of extractable and bound residues of metsulfuron-methyl depended closely on the soil properties. The dependence of sulfonylurea degradation in soil on soil properties is well documented (Brown, 1990; Pons and Barriuso, 1998; Wang et al., 2001; Hultgren et al., 2002). Increasing soil pH significantly decreased the level of bound residues and increased the level of extractable residues in the selected soils. Brown (1990) reported that metsulfuron-methyl existed primarily in the anionic species in neutral to alkaline soil, and the anions would be repelled by soil colloids that carry net negative charges. Therefore, in neutral and alkaline soils, less adsorption of metsulfuron-methyl may be expected. Ye et al. (2005) indicated that metsulfuron-methyl was easily protonated in acidic soils and that the protonated metsulfuron-methyl was strongly bound to humic substances through ion exchange. These interactions resulted

in the formation of more extractable and less bound residues of  $^{14}\text{C}$ -metsulfuron-methyl in high-pH soils and less extractable and more bound residues in low-pH soils. In addition, the anionic species of sulfonylurea herbicides were highly soluble in water and degraded at a slow rate in alkaline soils, which may significantly increase the potential for leaching (Sarmah et al., 2000; Delgado-Moreno et al., 2007).

Metabolism of metsulfuron-methyl in soil is also known to depend on soil microbial populations (Yu et al., 2005). In the present study, negative correlations ( $P < 0.05$ ) between soil MBC and extractable  $^{14}\text{C}$ -metsulfuron-methyl residues were observed for most of the incubation time intervals (Table 2). This relationship is generally seen as a reflection of an enhanced biotic transformation of xenobiotics in soils with a higher microbial activity (Yu et al., 2005). The decrease in the extractable residues may be attributed to a combined effect of an enhanced mineralization and an increased incorporation of the extractable residues into the bound residues through microbial actions. Moreover, somewhat positive correlations ( $P < 0.05$ ) between bound metsulfuron-methyl residues and soil MBC were found in the present study (Table 3), reinforcing the positive effect of soil microbial biomass and activity on degradation of the extractable residues. Previous studies showed that incorporation into soil microbial biomass was an important route in the formation of non-extractable or bound residues for pesticides (Kaufman and Blake, 1970; Charney et al., 2004).

No apparent relationship was found between the level of extractable or bound residues and soil organic C or total N, except at 20% WHC (Tables 2 and 3). The organic C and total N levels varied considerably among the six paddy soils in the present study, but these variations apparently did not induce any detectable effect on the different forms of metsulfuron-methyl residues. In a study of six Brazilian soils with organic carbon levels ranging from 3.5 to 74.5 g kg<sup>-1</sup>, Oliveira et al. (2001) found that the sorption coefficient of metsulfuron-methyl by soils was correlated with soil organic carbon, but the magnitude of influence was very small. It is likely that soil organic C

**Table 2. Correlation coefficients between <sup>14</sup>C-metsulfuron-methyl–extractable residues and soil properties.**

Soil moisture	DAA†	pH	OC	MBC	TN	Clay	Silt
20% WHC	7	0.979*	-0.917	-0.985*	-0.933	-0.966*	0.965*
	14	0.959*	-0.953*	-0.973*	-0.962*	-0.987*	0.974*
	28	0.980*	-0.936	-0.952*	-0.960*	-0.981*	0.935
	56	0.985*	-0.926	-0.965*	-0.949	-0.975*	0.944
	84	0.983*	-0.928	-0.970*	-0.948	-0.975*	0.950*
40% WHC	7	0.817*	-0.088	-0.691	0.074	-0.403	0.858*
	14	0.900*	-0.230	-0.694	-0.104	-0.574	0.833*
	28	0.943**	-0.248	-0.817*	-0.087	-0.498	0.914*
	56	0.935**	-0.216	-0.864*	-0.037	-0.396	0.938**
	84	0.921**	-0.313	-0.854*	-0.131	-0.510	0.945**
50% WHC	7	0.967**	-0.539	-0.609	-0.475	-0.821*	0.715
	14	0.826*	0.009	-0.252	0.038	-0.492	0.601
	28	0.897*	-0.044	-0.580	0.093	-0.373	0.843*
	56	0.913*	-0.263	-0.812*	-0.061	-0.392	0.970**
	84	0.939**	-0.378	-0.817*	-0.188	-0.511	0.962**

\* Significant at the 0.05 probability level.

\*\* Significant at the 0.01 probability level.

† DAA, days after metsulfuron-methyl application; MBC, microbial biomass carbon; OC, organic carbon; TN, total nitrogen; WHC, field water-holding capacity.

content affected degradation and sorption and that the interaction of these processes rendered the effect on the formation of extractable or bound residues imperceptible.

In the present study, especially at 20% WHC, extractable metsulfuron-methyl residues demonstrated a negative relationship with soil clay contents (Table 2), and bound residues showed a positive relationship with soil clay contents (Table 3). This may be attributed to the hydrophobic interaction as discussed previously for explaining the effect of moisture content on the formation of bound residues. When the soil moisture content was relatively low, metsulfuron-methyl residues may be bound to clay fractions through competitive adsorption processes between the herbicide and water molecules by ion exchange, H bonds, or covalent bonding mechanisms. For instance, other researchers have observed an increase in sorption of herbicides with decreasing soil size fractions (Benoit et al., 2000; Hang et al., 2003). This phenomenon was further corroborated by the observation that the silt contents of soils were positively correlated with extractable residues and nega-

tively correlated with bound residues for some sampling dates in the present study (Tables 2 and 3).

## Conclusions

Results from the present study showed that soil moisture conditions influenced the distribution of metsulfuron-methyl residues between extractable and bound fractions and indirectly affect the overall herbicide degradation in paddy soils. The amount of extractable residues increased, but the bound residues decreased, as the soil moisture content increased from 20 to 50% WHC. These data suggest that a relatively high proportion of the extractable residues may be available under high soil water content conditions. Given the high precipitation rates and intensive rainfall patterns in regions such as southeast China, the use of metsulfuron-methyl during the rainy season may result in leaching of this and other similar herbicides through the soil profile. Soil pH and MBC were the predominant factors affecting the dynamics of <sup>14</sup>C-metsulfuron-methyl

**Table 3. Correlation coefficients between <sup>14</sup>C-metsulfuron-methyl–bound residues and soil properties.**

Soil moisture	DAA†	pH	OC	MBC	TN	Clay	Silt
20% WHC	7	-0.970*	0.951*	0.956*	0.969*	0.988*	-0.950*
	14	-0.938	0.801	0.992**	0.808	0.868	-0.946
	28	-0.966*	0.954*	0.941	0.975*	0.990**	-0.937
	56	-0.970*	0.951*	0.958*	0.968*	0.988*	-0.953*
	84	-0.970*	0.952*	0.950*	0.971*	0.989*	-0.945
40% WHC	7	-0.791	0.064	0.677	-0.102	0.376	-0.861*
	14	-0.880*	0.198	0.670	0.075	0.552	-0.821*
	28	-0.941**	0.251	0.815*	0.090	0.504	-0.913*
	56	-0.926**	0.182	0.843*	0.005	0.389	-0.934**
	84	-0.891*	0.384	0.823*	0.209	0.587	-0.915*
50% WHC	7	-0.948**	0.592	0.619	0.530	0.862*	-0.696
	14	-0.820*	-0.036	0.251	-0.069	0.471	-0.603
	28	-0.891*	0.045	0.616	-0.106	0.341	-0.867*
	56	-0.908*	0.284	0.824*	0.078	0.408	-0.974**
	84	-0.922**	0.489	0.857*	0.296	0.584	-0.950**

\* Significant at the 0.05 probability level.

\*\* Significant at the 0.01 probability level.

† DAA, days after metsulfuron-methyl application; MBC, microbial biomass carbon; OC, organic carbon; TN, total nitrogen; WHC: field water-holding capacity.

residue formation in the studied soils. The significantly positive correlation between soil pH and extractable residues indicated that there would be an increased potential for the movement of metsulfuron-methyl residues in high-pH soils. In southeastern China and other regions in the world, there is a widespread use of lime in acidic soils to improve crop yields. This practice may further increase the risk for metsulfuron-methyl to leach to ground water or cause phytotoxicity to plants in the subsequent season.

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