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Mineralization of metsulfuron-methyl in Chinese paddy soils

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ABSTRACT

A laboratory study was conducted to investigate the mineralization of metsulfuron-methyl (MSM) in paddy soils in response to soil moisture, temperature and soil properties. The results indicated that MSM mineralization was relatively limited in the paddy soils when soil temperature was low. Only 2.2–6.0% of the applied ^{14}C mineralized after 84 d of incubation at 15 °C. The mineralization of MSM was enhanced by increasing soil moisture and soil temperature. Soil moisture would have different impact on the response of MSM mineralization to variation in soil temperature. An increase of 10 °C accelerated the average rate of MSM mineralization by 2.3 times at 50% water-holding capacity (WHC) and 1.9 times at 40% WHC. Regression analysis showed that soil pH, organic carbon contents, microbial biomass carbon contents, and silt/clay fractions were the dominant factors affecting MSM mineralization, with pH as the most important factor. The relatively slow mineralization rate of MSM suggested long persistence of this herbicide in soil, thus increasing its potential ecological risk, especially when applied in alkaline soils and in cold areas.

1. Introduction

Metsulfuron-methyl (MSM), a member of the sulfonylurea herbicide family, is one of the most widely used herbicides in fields around the world because of its broad spectrum for controlling weeds while used at low rates. However, there are several environmental concerns on the use of MSM. Previous studies have shown that the extremely low levels of MSM residues have phytotoxicity to sensitive crops in crop-rotation systems (Yao et al., 1997; Ye et al., 2003; Li et al., 2005; Hollaway et al., 2006). Studies also have revealed MSM residues contaminate surface and ground waters (Perkova and Donkova, 2003; Cessna et al., 2006), and have unintended side effects on non-target organisms (Ismail et al., 1998; Wang et al., 2003; Zhang and Yin, 2007). Therefore, it is important to obtain a better understanding of the fate of MSM in soil, and to find strategies to minimize the environmental impacts of its residues.

Many studies have provided useful information relating to MSM degradation rates and pathways. The degradation of MSM in the environment may be caused by both chemical hydrolysis and microbial transformations (Brown, 1990). Degradation pathways include the cleavage of sulfonylurea bridge, *O*-demethylation of the methoxy-triazine moiety and triazine ring opening after *O*-demethylation (Pons and Barriuso, 1998; Li et al., 1999; Sarmah and Sabadie, 2002). Rates of MSM degradation are influenced by edaphic factors and environmental conditions (Brown, 1990). Different authors have shown that soil pH is the most important factor in affecting both sorption behavior and chemical degradation of MSM because of its ability to influence the ionization state of the herbicide (Brown, 1990; Pons and Barriuso, 1998; Zhu et al., 2007; Wang et al., 2008; Zanini et al., 2009).

Degradation of organic contaminants in soil so far has been evaluated mostly by considering the extractable parent compound. Bound or non-extractable residues of the contaminant are usually excluded in risk assessment. However, recent studies have shown the subsequent toxicities from the release of bound or non-extractable residues in soil (Wang et al., 2003; Ye et al., 2003; Li et al., 2005). Thus, the half-lives and the risk assessment of the contaminant will be biased if calculated only from the extractable parent compound. Furthermore, partial degradation of xenobiotic organic compounds may lead to accumulation of metabolites in the environment, either serving as end products or as intermediates for further degradation (Pons and Barriuso, 1998; Johannesen et al.,

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2003; Li et al., 2005; Hollaway et al., 2006). In contrast, mineralization is a process to describe a complete breakdown of an organic compound to CO_2, H_2O, and other simple inorganic compounds. Therefore, mineralization represents the complete removal of all toxic byproducts and is therefore the ultimate measure of degradation. Complete mineralization is also the terminal point for environmental concern. Hence, knowledge of the mineralization of xenobiotic organic compounds is important for accurately assessing the risk of contamination.

Although the roles for biotic and abiotic transformations in the mineralization of xenobiotic organic compounds differ, both degradation pathways generally contribute toward the mineralization process. Therefore, mineralization of xenobiotic organic compounds in soil may be affected by soil physico-chemical properties, biological properties, and environmental conditions. In fact, soil moisture, temperature, and other environmental conditions vary significantly around the world or change greatly with time. For example, paddy soils typically undergo several drying-wetting cycles during a rice growing season. The results of our previous studies suggested that MSM mineralization in the paddy soils at 35 °C was enhanced by increasing soil moisture contents from 20% to 50% water-holding capacity (WHC) (Wang et al., 2007). However, MSM mineralization under different moisture and temperature regimes for paddy soils is still poorly understood. Moreover, it is interesting to note that there were different effects of soil moisture variations on the distribution of MSM residues between extractable and bound fractions at 35 °C and 15 °C (Wang et al., 2007, 2009). Therefore, the present study was conducted to investigate the mineralization dynamics of MSM in six Chinese paddy soils with different moisture regimes at 15 °C, and to evaluate the effect of soil temperature and soil properties on MSM mineralization. The findings will provide a more complete picture for understanding the fate of MSM in soil under different environmental conditions, and also give more information about the potential risk of MSM on the soil ecosystem. When investigating the complete degradation of xenobiotic organic contaminants, the evolution of CO_2 is often used as an indicator for mineralization (Levanon, 1993). Using ^{14}C-labelled MSM as a tracer in this study, the ^{14}C-evolved as CO_2 was determined in NaOH solution which entrapped $^{14}CO_2$ during the incubation periods.

2. Materials and methods

2.1. Chemicals

^{14}C-labelled MSM (triazine-4-^{14}C; specific radioactivity, 4.55×10^4 Bq mg^{-1}; radiochemical purity and chemical purity >97.3%) used in this study was purchased from 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-oxazoyl-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-oxazoyl-2)-benzene (0.4 g) in a mixture of ethanolamine (175 mL), glycol-ether (350 mL) and dimethylbenzene (475 mL). All chemicals including solvents used were analytical grade.

2.2. Soils

Six paddy soils with different properties were sampled from Zhejiang Province in southeastern China. All soil samples were collected from the surface soil layer (0–20 cm) and transported to the laboratory immediately. After plant residues were removed, the soil samples were ground, sieved through a 2-mm plastic mesh, thoroughly homogenized, and then stored in the dark at 4 °C until use in the incubation experiments. Aliquots were air-dried, ground and sieved to pass through a 0.149 mm plastic mesh, followed by analysis of physical and chemical properties. Table 1 shows the selected properties of the test soils. The soils were classified using the USDA seventh edition of the Keys to Soil Taxonomy (Soil Survey Staff, 1996). Soil pH was determined in suspension of 1:2.5 soil/water (w/w) after shaking for 1 h, soil organic carbon and total nitrogen contents were measured by Walkley–Black procedure and Kjeldahl method, respectively, soil texture was determined using the pipette method (Anderson and Ingram, 1993). Soil moisture contents of the fresh soil samples were adjusted to 50%, 40%, and 20% WHC, and then incubated at 15 °C in the dark for 5 d. Soil microbial biomass carbon (MBC) of the soil samples 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).

2.3. Incubation experiments

The six soil samples were removed from 4 °C storage and kept at 25 ± 1 °C for 5 d in the dark to restore soil microbial activity prior to chemical treatment. A spiking solution was prepared by dissolving ^{14}C-MSM in a 1:1 methanol:water mixture to give a solution concentration of 1000 μg mL^{-1}. The samples, which consisted of 60 g oven-dried weight equivalent soil, were placed in 250 mL Erlenmeyer flasks followed by the addition of 0.6 mL of the spiking solution. This gave an initial ^{14}C-MSM concentration of 10 μg g^{-1} soil. After spiking, each sample was thoroughly mixed in a fume hood, and was kept in the fume hood for 24 h to remove methanol. The moisture contents of each soil sample were further adjusted to 20%, 40%, and 50% WHC by the addition of autoclaved distilled water. Preliminary experiments indicated that the residual methanol from the spiking solution did not influence the microbial biomass size. The 20% WHC treatment was not included for soil No. 3 and soil No. 4 because the water contents were higher than 20% WHC when the soils were collected. All treated flasks were incubated in the dark at 15 ± 1 °C in the incubator and aerated weekly in a fume hood for 30 min, at which time the soil moisture contents were readjusted by weighing. Throughout the incubation, no obvious soil humidity and temperature variation occurred in the experimental systems. Three replicates were used in each treatment.

2.4. Measurement of mineralization and mass balance

To collect $^{14}CO_2$ that was generated during the mineralization of ^{14}C-MSM, each flask was equipped with a vial containing 10 mL 0.5 M NaOH. The vials containing the NaOH solution were suspended from the rubber stopper, and were replaced weekly throughout the 84-d incubation period. A 0.5-mL aliquot of the NaOH traps was mixed vigorously with 10 mL of scintillation cocktail I and kept for 24 h in the dark prior to measurement on a liquid scintillation counter (Winspectral-1414; Wallac, Turku, Finland). Mineralization of MSM was calculated as percent of $^{14}CO_2$ evolved over the initially applied ^{14}C-MSM. Cumulative mineralization curves were plotted as the percent $^{14}CO_2$ evolved as a function of time.

The mass balance of ^{14}C recovery was computed based on the accumulated $^{14}CO_2$ evolution and the amounts of ^{14}C-residues in soils. To determine ^{14}C-residues in soil, 1.0-g soil aliquots (oven-dry basis) were removed from each flask at time intervals of 7, 14, 28, 56, and 84 d after ^{14}C-MSM application and were combusted for 5 min in a biological oxidizer (OX-600; Harvey

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

Soil no.	Soil taxonomy	pH (H_2O)	OC[a] (g kg^{-1})	WHC (%)	MBC[b]			TN (g kg^{-1})	Clay (%)	Silt (%)
					A (mg kg^{-1})	B (mg kg^{-1})	C (mg kg^{-1})			
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

[a] MBC: microbial biomass carbon; n.d.: not determined; OC: organic carbon; TN: total nitrogen; WHC: field water-holding capacity.
[b] MBC was measured 5 d after incubating soil at moisture levels of (A) 50%, (B) 40% and (C) 20% WHC and 15 ± 1 °C in the dark.

Instruments, Hillsdale, NJ, USA). The $^{14}CO_2$ evolved from the combustion was trapped in 15 mL of scintillation cocktail II, and the radioactivity was determined by the liquid scintillation counter. The recovery of ^{14}C for this combustion procedure was >92.3%. The total mass balance of ^{14}C activity was found to be 97.4 ± 3.5% throughout the incubation period.

2.5. Data analysis

The dissipation kinetics of MSM in soil under laboratory conditions was accurately described using the first order model (Wang et al., 2007),

$$C = C_0 e^{-kt}, \quad (1)$$

where C is the amount of MSM remaining at time t, C_0 is the initial amount of MSM, and k is the first-order rate constant. Theoretically, the mineralization rate of xenobiotic organic compounds can be expressed as

$$dP/dt = -dC/dt, \quad (2)$$

where P is the percentage of $^{14}CO_2$ released. Integration of Eq. (2) gives

$$P = C_0 - C, \quad (3)$$

so that substitution of Eq. (1) into Eq. (3) gives

$$P = C_0(1 - e^{-kt}). \quad (4)$$

It should be noted that although C_0 is the amount of the xenobiotic organic compound added at time zero, it can also be redefined to represent the maximal amount of xenobiotic organic compounds that may be converted into the product CO_2. Fifty percentage mineralization time ($t_{1/2}$) was further calculated from the formula $t_{1/2} = \ln 2/k$. In addition, backward multiple-linear regression and path analysis were used to study the relationship between the $^{14}CO_2$ production and soil properties. All the statistical analyses were carried out using SPSS 10.0 for Windows.

3. Results and discussion

3.1. Mineralization of ^{14}C-metsulfuron-methyl in soils

Fig. 1 shows the cumulative $^{14}CO_2$ production in the different soils through the 84-d incubation of MSM at 15 °C. Comparison of the 16 curves shown in Fig. 1 demonstrates the influence of soil properties and moisture contents on the mineralization of MSM. The data indicated that the percentage of $^{14}CO_2$ varied little during the early incubation period. At 7 d after the application of MSM, only about 0.3–0.8% of the applied ^{14}C was mineralized to $^{14}CO_2$. Upon the termination of the incubation experiment after 84 d, the cumulative $^{14}CO_2$ production in the tested acid soils increased

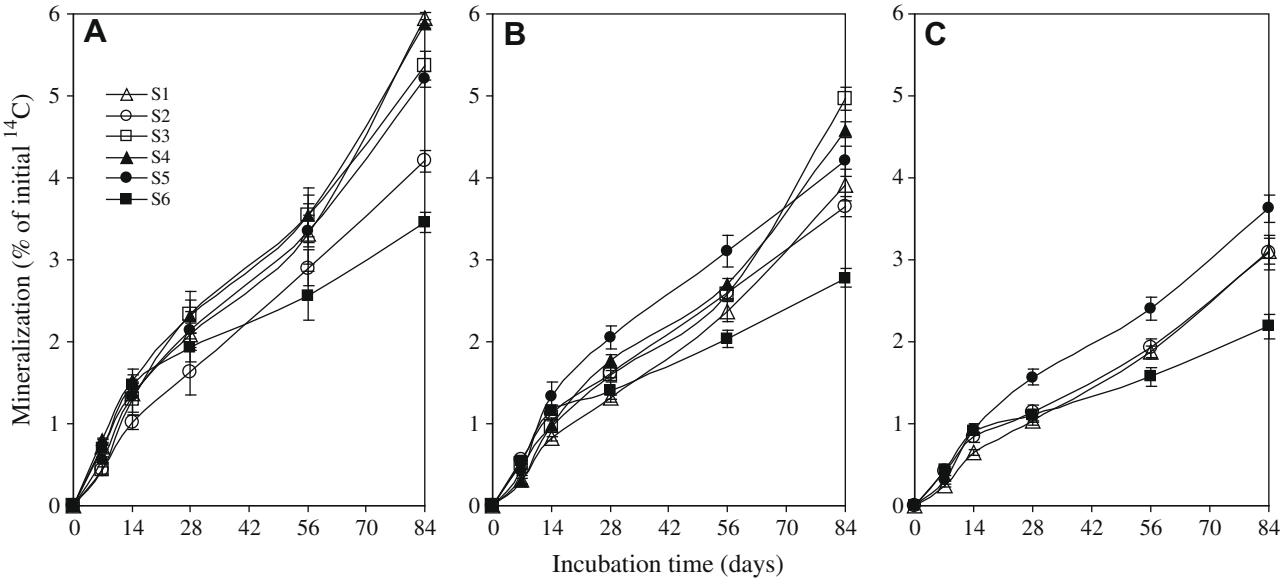

Fig. 1. Mineralization of ^{14}C-metsulfuron-methyl in soils incubated at (A) 50%, (B) 40% and (C) 20% water-holding capacity (WHC). Error bars represent the standard deviation of three replicates. Soil labels are the same as in Table 1.

to 3.1–6.0%, and about 2.2–3.5% in the alkaline soil (soil No. 6). The much lower mineralization of MSM was also found in the alkaline soil than in the acid soil at 35 °C in our earlier study, and the higher pH and lower MBC of soil No. 6 were attributed as the reasons for the lower mineralization of MSM (Wang et al., 2007). It should be mentioned that some MSM mineralization rates determined at several time points, especially in soil No. 6, were close to or lower than the impurity level (<2.7%) of the radiolabelled MSM used in the study. This phenomenon indicated that the potential for MSM mineralization was rather limited under conditions tested in the present study. Nevertheless, a higher mineralization of MSM was observed in the soils held at 35 °C compared to 15 °C. The cumulative $^{14}CO_2$ production was about 12–48% of the applied ^{14}C amount in the same soils incubated at 20%, 40%, and 50% WHC after incubation at 35 °C for 84 d (Wang et al., 2007).

Moreover, given the specific labeling position, $^{14}CO_2$ measured in our study was derived from mineralization of the triazine ring of MSM. The rates reported herein may not reflect complete mineralization of the parent MSM if other pathways were significant, but is an accurate assessment of MSM mineralization via the ^{14}C-labelled triazine ring. MSM may break down to sulfonamide and triazine ring through irreversible hydrolysis of the sulfonylurea bridge. Sulfonamide is generally considered to be mineralized rapidly in soil, whereas the mineralization of triazine ring is fairly slow (Pons and Barriuso, 1998; Li et al., 1999). Therefore, the investigation of MSM mineralization via triazine ring may provide a more accurate means for evaluating the terminal point for environmental concern.

The results also indicated that MSM mineralization increased with the increase of soil moisture content (Fig. 1). For example, at the end of the incubation, 3.5–6.0% of the applied ^{14}C was recovered as $^{14}CO_2$ in the soils with 50% WHC, whereas 2.8–5.0% and 2.2–3.6% were recovered as $^{14}CO_2$ from the treatments with 40% and 20% WHC, respectively. The lower MSM mineralization rates in soils with less soil moisture may be contributed to the lower soil microbial activity. Previous studies showed that increasing soil moisture content generally increased soil microbial activity and pesticide mineralization (Wang et al., 2007). Thus, an increase in MBC with increased soil moisture contents (Table 1) likely results in increased mineralization of ^{14}C-MSM residues through biological degradation in all soils. Furthermore, lower moisture conditions could increase the sorption of pesticide onto soil components, making the pesticide less available for microbial degradation (Johannesen et al., 2003). Similarly, our previous study showed that more bound residues and less extractable residues of MSM were formed in soils with lower soil moisture contents (Wang et al., 2009).

Fitting the data to Eq. (4) showed that MSM mineralization in all treatments was well described by the exponential equation, with correlation coefficients ranging from 0.97 to 1.00. As shown in Table 2, the rate constants (k) of MSM mineralization for the soils maintained at 50% WHC were generally larger than those at 40% WHC or 20% WHC, and 50% mineralization time ($t_{1/2}$) decreased when the soil water contents were increased from 20% WHC to 50% WHC. The $t_{1/2}$ values varied between 365 and 1925 d, which were much longer than the half-lives of MSM degradation previously reported (Pons and Barriuso, 1998; Sarmah and Sabadie, 2002). This may be attributed to the difference between mineralization and degradation. The 50% mineralization time ($t_{1/2}$) was calculated from the degradation of both the parent compound and all of the associated metabolites. In published studies, MSM degradation half-lives were mostly estimated from the dissipation of the parent compound, which often lack information on mineralization dynamics. In addition to mineralization, other pathways such as formation of intermediates and bound residues could also contribute to the disappearance of the parent compound. The much longer 50% mineralization time might highlight that the mineralization of MSM and its degradation intermediates was much slower for the conditions used in the present study. Andersen et al. (2001) reported that the degradation products of MSM may be mineralized more slowly than their formation. Thus, additional research is needed to study the MSM degradation products and their impact on environmental safety.

3.2. Effect of soil temperature on mineralization of ^{14}C-metsulfuron-methyl

It has been reported that both MSM hydrolysis and biological transformations were highly dependent on the soil temperature (Pons and Barriuso, 1998; Sarmah and Sabadie, 2002). These degradation processes can be drastically enhanced by increasing soil temperature. The results showed that less MSM residues were found under higher soil temperature conditions (Wang et al., 2007, 2008, 2009). The average rate constants (k) of MSM mineralization for different soil moisture regimes were 6.1, 2.9 and 1.3 ($d^{-1} \times 10^{-3}$) in 35 °C, 25 °C and 15 °C, respectively. The data of

Table 2
The rate constants (k) of metsulfuron-methyl mineralization and 50% mineralization time ($t_{1/2}$) in the soils incubated at 50%, 40% and 20% water-holding capacity (WHC).

Soil no.[A]	Soil moisture (% WHC)	k ($d^{-1} \times 10^{-3}$)	r	$t_{1/2}$ (days)
S1	50	1.90 ± 0.03 a[B]	0.991**	365
	40	1.21 ± 0.02 b	0.969**	573
	20	0.88 ± 0.00 c	0.996**	788
S2	50	0.86 ± 0.01 a	0.966**	806
	40	0.83 ± 0.00 b	0.969**	835
	20	0.77 ± 0.02 c	0.993**	900
S3	50	1.80 ± 0.01 a	0.997**	385
	40	1.61 ± 0.01 b	0.988**	431
S4	50	1.87 ± 0.02 a	0.976**	371
	40	1.55 ± 0.05 b	0.986**	447
S5	50	1.64 ± 0.06 a	0.986**	423
	40	1.42 ± 0.03 b	0.995**	488
	20	1.05 ± 0.04 c	0.992**	660
S6	50	0.49 ± 0.00 a	0.982**	1415
	40	0.40 ± 0.01 b	0.971**	1733
	20	0.36 ± 0.00 c	0.967**	1925

[A] Soil labels are the same as in Table 1.
[B] The different lower-case letters indicate significant difference at the 5% level between moisture contents for the same soil.
** Significant at the 1% probability level.

MSM mineralization at 25 °C were not listed, and MSM mineralization rate constants (k) at 35 °C were obtained from the literature (Wang et al., 2007). Fig. 2 shows the k values of MSM mineralization at two moistures (50% and 40% WHC) and three temperatures (15, 25, and 35 °C) in the same soils. The effects of temperature on the rate constant (k) were described directly by the Arrhenius equation ($R^2 \geqslant 0.99$, $P \leqslant 0.05$), $k = Ae^{-E_a/RT}$, where A is the pre-exponential Arrhenius factor, E_a the activation energy, R the universal gas constant and T the absolute temperature. The activation energy E_a was calculated by plotting ln k versus $1/T$. The E_a values were 45.7–82.4 and 43.9–75.1 (kJ mol^{-1}) in the soils under 50% and 40% WHC respectively. The sensitivity of the rate of a reaction to changes in temperature depends on the E_a value. High E_a values indicate that MSM mineralization is highly sensitive to temperature change (Dungan et al., 2001). For an increase of 10 °C, the average rate of MSM mineralization would increase by 2.3 times at 50% WHC and 1.9 times at 40% WHC. On the other hand, the data suggest that the response of MSM mineralization to variation in soil temperature depends on the soil moisture content. Increasing soil temperature may stimulate MSM mineralization more significantly in a moist soil than in a dry soil. This knowledge can be useful for finding ways to minimize the hazardous effects of MSM residues on the environment.

It is important to note that presence of herbicide residues in the soil not only cause damages to succeeding crops, non-target organisms or human health, but also increase the potential risk for contamination of water resources due to the leaching of residues through soil. The results indicated that MSM and its metabolites may have a long persistence in the soil under dry and low temperature conditions due to limited mineralization. In fact, sulfonylurea herbicides, including MSM, are widely used for winter wheat field weeding (Brown, 1990; Yao et al., 1997; Zanini et al., 2009). Furthermore, soil temperature and soil water content are generally low during the growth of winter wheat, especially in northern China. Thus, the impact of MSM residues on crops sown in the following season is of valid concern. Yao et al. (1997) reported that the phytotoxicity of MSM residues in soils may become a particular concern in the Chinese continuous rotation systems of wheat–rice or wheat–rice–rice because MSM used during the wheat growing season was found to inhibit the growth of rice seedlings in the follow-up cropping season. Therefore, special attention should be given to the use and management of MSM during the dry and cold seasons. In addition, more efforts should be made to better understand the behavior of MSM and similar herbicides in soil for ensuring the ecological safety issues.

3.3. Effect of soil properties on mineralization of ^{14}C-metsulfuron-methyl

Backward multiple-linear regression analysis was performed to understand the effect of soil properties on MSM mineralization. The regression equations obtained for the three moisture contents produced a good fit of the accumulated $^{14}CO_2$ values for the 84–d experiment. Both coefficients of the multivariate regression and the partial regression reached at least the 0.05 significance level (Table 3). According to the obtained regression relationships, soil pH, OC, MBC, and silt fractions were significantly related to the cumulative $^{14}CO_2$ production in soils at 50% WHC. A highly significant relationship with soil pH, MBC, and clay fractions was also observed for the accumulated $^{14}CO_2$ production in soils at 40% WHC. In the soils at 20% WHC, however, only soil pH was found to be related to the $^{14}CO_2$ evolution.

Overall, the regression analysis suggested that MSM mineralization was negatively correlated with soil pH, OC content, and clay content, and positively correlated with soil MBC and silt content. With a pK_a of 3.3, MSM may dissociate over the range of soil pH tested (5.36–9.04) and be present in the anionic form. It has been reported that the sulfonylurea linkage is susceptible to hydrolysis through the attack of the neutral bridge carbonyl-carbon by water, while for the negatively-charged dissociated molecule, the nucleophilic attack by water has lower sensitivity compared to the unionized MSM (Brown, 1990). Sarmah and Sabadie (2002) noted that the hydrolysis and abiotic degradation rate of the undissociated neutral form of MSM was hundreds of times faster than that of the ionic form. Therefore, a decrease in soil pH could lead to an increase in MSM degradation or mineralization due to the increasing predominance of the neutral chemical form. In addition, MSM is known to bind to soil organic and clay fractions through different sorption mechanisms (Brown, 1990; Zhu et al., 2007; Zanini et al., 2009). As a result, the sorption may also have a significant impact on MSM mineralization. The potential inhibition of degradation due to sorption may explain the negative influence of soil

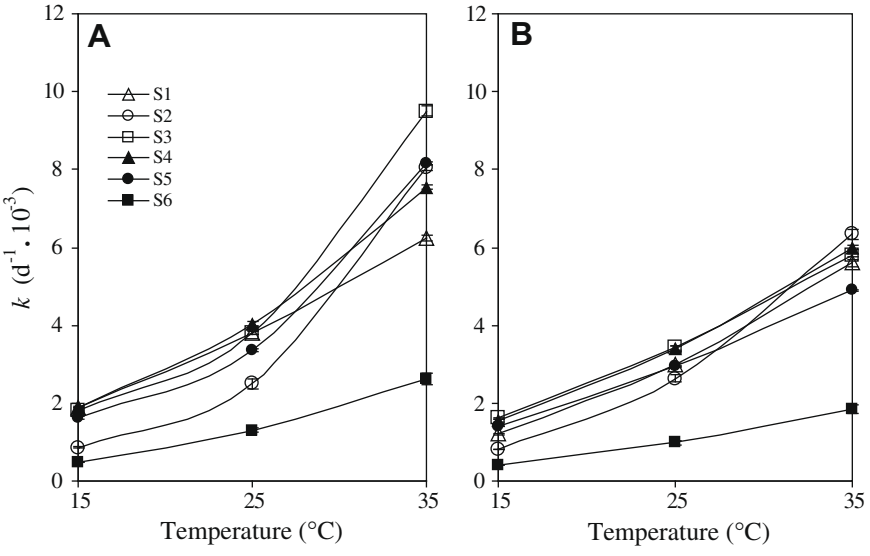

Fig. 2. The rate constants (k) of metsulfuron-methyl mineralization in soils incubated at (A) 50% and (B) 40% water-holding capacity (WHC) with different temperatures. Error bars represent the standard deviation of three replicates. Soil labels are the same as in Table 1. The k values for 35 °C were from the literature (Wang et al., 2007. Geoderma, 142, 325–333), and the k values for 25 °C were calculated from cumulative mineralization curves (data not listed).

Table 3
Multiple-regression models for predicting the accumulated $^{14}CO_2$ based on soil properties.

Soil moisture	Regression equations	R^2	F value	T value of the partial regression coefficient	
					T value
50% WHC[a]	$Y_1 = 6.915 - 1.436X_1 - 0.821X_2 + 6.754 \times 10^{-3}X_4 + 0.145X_6$	0.969	468.84*	X_1	35.3*
				X_2	20.4*
				X_4	16.2*
				X_6	20.7*
40% WHC	$Y_2 = 9.489 - 0.609X_1 + 1.347 \times 10^{-3}X_4 - 0.0553X_5$	0.978	595.97**	X_1	19.7**
				X_4	5.9*
				X_5	16.4**
20% WHC	$Y_3 = 5.722 - 0.395X_1$	0.940	31.492*	X_1	5.6*

[a] WHC: field water-holding capacity; X_1: pH, X_2: organic carbon, X_4: microbial biomass carbon, X_5: clay content, X_6: silt content; Y_1, Y_2, and Y_3 represent the accumulated $^{14}CO_2$ at day 84 incubated under moisture contents of 50%, 40% and 20% WHC, respectively.
* Correlation is significant at the 0.05 probability level.
** Correlation is significant at the 0.01 probability level.

Table 4
Path analysis for the effects of soil properties on metsulfuron-methyl mineralization at 50% water-holding capacity.

	Direct effects	Indirect effects			
		X_1	X_2	X_4	X_6
X_1[b]	−1.6931 (38.9)[a]		0.377 (8.7)	−0.9097 (20.9)	1.3731 (31.5)
X_2	−0.8558 (29.7)	0.7459 (25.9)		0.7746 (26.9)	−0.5081 (17.6)
X_4	1.2842 (28.8)	1.1993 (26.9)	−0.5162 (11.6)		−1.4651 (32.8)
X_6	1.6782 (37.8)	−1.3853 (31.2)	0.2591 (5.8)	−1.1212 (25.2)	

[a] The data in the parentheses show percentage, and the other values in the tables represent path coefficients.
[b] X_1: pH; X_2: organic carbon; X_4: microbial biomass carbon; X_6: silt content.

OC content and clay content on the mineralization rate, and a positive influence from the silt content, when the soil water content was 40% or 50% WHC (Table 3).

Path analysis is a straightforward extension of the multiple regression analysis. The goal of path analysis is to understand the relative importance of direct and indirect effects of independent variables on the dependent variable. Also, path analysis may be used to elucidate the interactions between the independent variables on the dependent variable. In this study, soil properties, e.g. soil pH, MBC, OC, etc., were the independent variables, and the accumulated $^{14}CO_2$ at day 84 was considered the dependent variable. The results of path analysis revealed that soil pH and soil texture had significant direct effects on MSM mineralization at 50% or 40% WHC (Tables 4 and 5). The order of importance of the direct effects was pH (X_1) > silt content (X_6) > MBC (X_4) > OC (X_2) in the soils at 50% WHC, and pH (X_1) > clay content (X_5) > MBC (X_4) in the soils at 40% WHC. Although MBC (X_4) had relatively small positive direct effects in the equation Y_1 and Y_2 with 28.8% and 19.4%, respectively (Y_1 and Y_2 indicate the accumulated $^{14}CO_2$ at day 84 incubated at 50% and 40% WHC, respectively), the effect was greater via soil silt content (32.8%) at 50% WHC and through soil pH (64.4%) at 40% WHC. Additionally, the indirect effects of soil pH were larger than the direct effects of clay content on MSM mineralization at 40% WHC. These analyses indicated that soil properties appeared to function in a relatively complex way, resulting in the observed differences in the mineralization rate among the different soils and conditions tested. There was a strong interaction of soil pH with MBC, silt content, and clay content to influence MSM mineralization in the selected soils. The importance of the direct and indirect effects of soil pH on MSM mineralization indicated that pH-dependent hydrolysis of MSM could be significant for MSM degradation in soils at low temperatures. However, the principal component analysis showed that microbial decomposition played an important role than pH-dependent hydrolysis for MSM mineralization at 35 °C (Wang et al., 2007). Those phenomena imply that increase of soil temperature has a greater impact on microbial activity than that on soil pH for MSM mineralization.

Table 5
Path analysis for the effects of soil properties on metsulfuron-methyl mineralization at 40% water-holding capacity.

	Direct effects	Indirect effects		
		X_1	X_4	X_5
X_1[b]	−1.0425 (64.4)[a]		−0.2022 (12.5)	0.3731 (23.1)
X_4	0.2518 (19.4)	0.8373 (64.4)		−0.2107 (16.2)
X_5	−0.5579 (41.3)	0.6973 (51.6)	0.0951 (7.0)	

[a] The data in the parentheses show percentage, and the other values in the tables represent path coefficients.
[b] X_1: pH; X_4: microbial biomass carbon; X_5: clay content.

4. Conclusions

MSM mineralization in paddy soils is relatively limited at 15 ± 1 °C. Fifty percentage mineralization time ($t_{1/2}$) of ^{14}C-MSM residues was estimated to be 365–1925 d. The results suggest that MSM residues may have long persistence during low-temperature seasons or in cold-climate areas. MSM mineralization was enhanced with increasing soil moisture content and soil temperature. A significant finding of this research is that soil moisture content would have different effects on the response of MSM mineralization to variation in soil temperature. An increase of 10 °C would accelerate MSM mineralization rate by 2.3 times at 50% WHC but only 1.9 times at 40% WHC. The mineralization rate was negatively correlated with soil pH, organic carbon contents, and clay contents, while it was positively correlated with soil MBC and silt contents. Regression analyses suggested that these soil properties did not act separately but in an interactive manner in influencing the overall MSM mineralization in soils. Soil pH was the dominant factor in affecting MSM mineralization in the soils tested. Moreover, the pH-dependent hydrolysis may

have played a greater role in MSM degradation at lower soil temperature.

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