Behavior of Simetryn and Thiobencarb in the Plough Zone of Rice Fields

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Abstract The behavior of simetryn and thiobencarb in flooded rice soil was investigated in a 2-year study. The concentrations of simetryn and thiobencarb were in the hundreds of $\mu g\ kg^{-1}$ in the top soil layer (0–5 cm) and became significantly lower in tens of $\mu g\ kg^{-1}$ in the deeper soil layers (5–10 and 10–15 cm). The half-lives of the two herbicides were also shorter (36 and 17 days for simetryn and thiobencarb, respectively) in the top soil layer, as they were most affected by environmental conditions, compared with corresponding values of 82 and 69 days in the 5–10 cm soil layer. Simetryn concentration was stable, while thiobencarb's half-life was 165 days in the 10–15 cm layer. About 35% of the applied mass of simetryn and thiobencarb were found in the rice soil compartment.

Keywords Herbicide · Rice · Paddy soil · Leaching

Rice production has continuously increased over the years to meet the rising food demand. Rice yield depends heavily on the use of agrochemicals, including pesticides. Rice production in developed countries such as Australia, Japan, and the US relies on herbicides to protect the crop and to save on labor cost. However, rice pesticide residues can spill to the environment and affect human and animal health.

Rice fields are considered a flood control and a groundwater-charging area; therefore, the risk of rice pesticides contaminating the groundwater cannot be neglected. Studies about the potential leaching of rice pesticides to deeper soil layers were mainly conducted using undisturbed lysimeters with radioactive-labeled compounds (Park et al. 2005). Model simulations were also a popular alternative for assessing the leaching potential of rice pesticides (Karpouzas et al. 2005). However, real-field studies should also be conducted to obtain concrete data about the behavior of rice pesticides in the soil compartment.

Simetryn [N^2,N^4-diethyl-6-methylthio-1,3,5-triazine-2,4-diamine] and thiobencarb (S-4-chlorobenzyl diethylthiocarbamate) are among the most popular herbicides in Japan. These two compounds are usually combined in one product, but simetryn is more soluble and has a smaller K_d than thiobencarb. Therefore, their leaching potentials are supposed to be different.

Our study aimed to investigate the behavior of simetryn and thiobencarb in the shallow soil layer of the rice field to gather preliminary data for risk assessment and model validation purposes.

Materials and Methods

The study was conducted in the experimental farm of the Tokyo University of Agriculture and Technology (TUAT) in Fuchu, Tokyo. A paddy plot of 1,500 m^2 (half of the Japanese standard plot of 3,000 m^2) was used in 2004. In 2005, a smaller paddy plot of 138 m^2 was used, which was set up inside a neighboring standard paddy plot. The soil in all plots is light clay, with an organic carbon content of

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about 4%. The detailed description of the field setup can be found in Phong et al. (2006, 2008). Following the general paddy field preparation and water ponding, the paddy soil was puddled and leveled by several passes of a rotary tiller under a few centimeter-ponding water condition. After soil preparation, 20-day-old rice seedlings were transplanted at a spacing of 16 cm × 30 cm.

The granular herbicide KumishotSM® (Kumiai Chemical Industry, Tokyo, Japan) containing simetryn and thiobencarb was applied on June 24, 2004 and on June 20, 2005. The application rates of the active ingredients were 450 and 1,500 g ha^{-1} for simetryn and thiobencarb, respectively.

Composite samples from five spots (four corners and the center) were taken from the plot. At each spot, a 30-cm-diameter PVC ring was driven into the muddy layer, and inner water was removed by an aspirator. The soil was sampled by a stainless steel core (5 cm diameter × 5 cm length) for three layers (0–5, 5–10, and 10–15 cm). Care was taken to avoid cross contamination among layers, especially under the wet condition of the field. Sampling was carried out at 7, 14, 22, and 35 days after herbicide application (DAHA) in 2004 and samples of 3, 50, 70, and 80 DAHA were added in 2005. All samples were kept frozen until chemical analysis.

The soil samples were centrifuged at 12,000 rpm for 15 min and then ground in a ceramic mortar. Final moisture content was measured. A 20 g soil sample was weighed into a 200 mL Erlenmeyer flask containing 100 mL of acetone. The mixture was sonicated for 10 min and then shaken for 2 h. The soil was then removed from the solution by filtering the slurry solution. The residual soil was washed twice with 20 mL of acetone. All filtrates were combined and the acetone solution was evaporated to 10 mL with a rotary evaporator. The remaining solution mixed with 30 mL of saline water (NaCl 10%) was extracted twice with 30 mL of dichloromethane in a separatory funnel. In 2005, diatomaceous earth cartridges (ChemElut, Varian) were used instead of the separatory funnel to increase reproducibility. The two dichloromethane extracts were combined and dried with 20 g of anhydrous sodium sulfate. The extract was then filtered through silicone-treated filter paper (1PS, Whatman). Dichloromethane was rotor-evaporated from the filtered solution at 35°C. The residue was dissolved in 5 mL of acetone using ultrasonication. The final samples were kept at 4°C before gas chromatography analysis.

In 2004, samples were analyzed using a Shimazu (Osaka, Japan) 2010 gas chromatograph equipped with a flame thermoionic detector (FTD) and a DB-17 capillary column (J&W Scientific, CA, USA). The limit of detection is 10 µg kg^{-1}. The recovery values (n = 3) were 108.8 ± 4.5% and 98.7 ± 1.8%, respectively, for simetryn and thiobencarb. In 2005, samples were analyzed using an Agilent (CA, USA) 6890N gas chromatograph equipped with an Agilent 5973 MSN mass spectrometer and a fused-silica DB-5 MS capillary column (J&W Scientific, CA, USA). The detection limits for soil samples were 10 µg kg^{-1} for both herbicides and recoveries (n = 3) were 83.0 ± 5.6% and 60.7 ± 2.2% for simetryn and thiobencarb, respectively.

Results and Discussion

The concentrations of simetryn in the soil layers in 2004 and 2005 are shown in Fig. 1. In 2004, the highest concentration of simetryn was 251 µg kg^{-1} at 14 DAHA in the 0–5 cm soil layer; it decreased gradually to 147 µg kg^{-1} at 35 DAHA. Simetryn concentrations in the deeper soil layers were low at the beginning but tended to increase toward the end of the monitoring period. Inao et al. (2001) reported a similar concentration of simetryn in the top 0–5 cm but no data are available for the deeper soils. Simetryn concentrations in the 5–10 cm and 10–15 cm depths peaked at 35
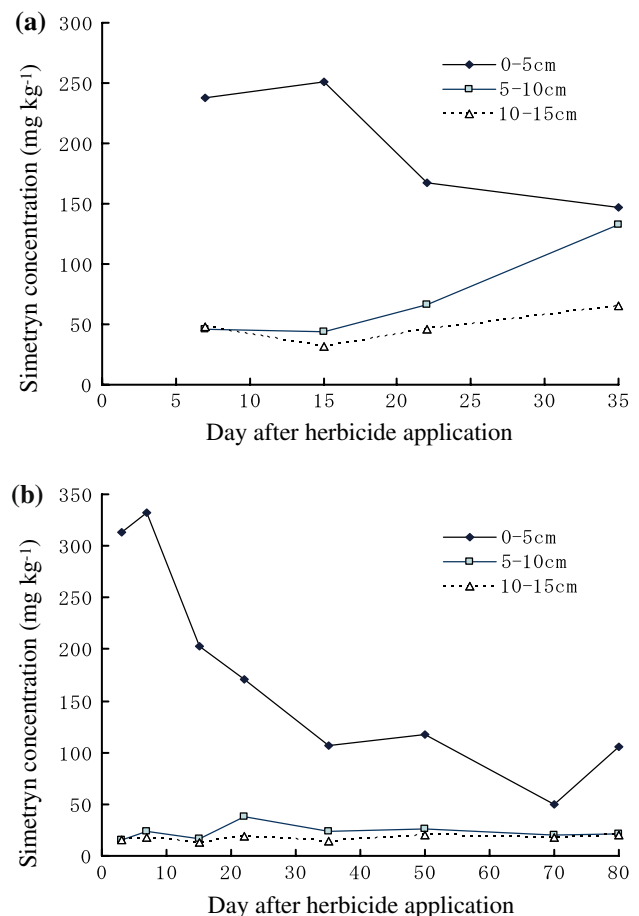

Fig. 1 Simetryn concentrations in soil layers in 2004 (**a**) and 2005 (**b**)

DAHA. However, the closeness of simetryn concentration in the three layers suggested that there may be cross contamination during sampling on this date (35 DAHA), but the monitoring period may be too short for a confirmative conclusion. In 2005, the concentrations of simetryn in the top layer were higher than the corresponding data of 2004, with the maximum concentration of 332 μg kg^{-1} at 7 DAHA. Concentrations at the deeper layers of 2005 were lower than those of 2004, but the evolution of concentration was similar. There was a clear peak of simetryn concentration at 22 DAHA in the 5–10 cm soil layer. But in the 10–15 cm soil layer, simetryn concentration just slightly increased and fluctuated around the 20 μg kg^{-1}. A lysimeter study by Nhung (unpublished data) also found similar simetryn concentrations in these deeper soil layers at 22 DAHA.

Dissipation of simetryn may be different between 2004 and 2005. However, the 2005 data were used to estimate the half-life of simetryn in the rice soil as the 2004 data have less statistical value. First-order kinetics was applied in the estimation. The calculated values of DT$_{50}$ of simetryn are presented in Table 1. The estimation of DT$_{50}$ for the 10–15 cm soil layer was not possible because there was no clear trend in the concentrations. The dissipation rate was lower in the deeper soil layer as there was a supply from the upper layer and it was less affected by environmental factors such as sunlight.

The distribution of simetryn mass in paddy soil in 2004 and 2005 is shown in Fig. 2. As it corresponded with the concentration profile, more simetryn remained in the top layer in 2005 than in 2004. However, the total mass of simetryn deposited in the soil compartment at the beginning of the monitoring period was similar between the 2 years. Simetryn moved faster to the deeper soil layers in 2004 than in 2005, which means that environmental conditions, especially soil condition, can strongly influence the movement of pesticide in the paddy soil compartment. The situation in 2005 is considered appropriate for sustainable agriculture as pesticide dissipated quickly in the surface soil layer and less pesticide moved down to the deeper soil layers, reducing the risk of contamination for both surface and groundwater sources.

For thiobencarb, there were clear differences between concentrations in the top 0–5 cm layer and the other soil layers in both 2004 and 2005 (Fig. 3). The highest

Table 1 Calculated half-lives of simetryn and thiobencarb in soil layers in 2005

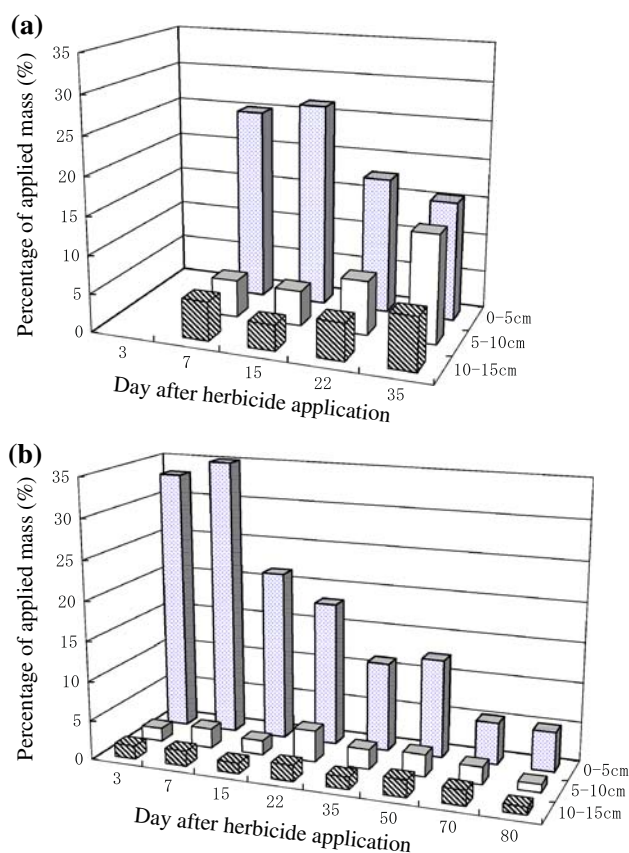| Soil layer	Period	Simetryn	Thiobencarb
0–5 cm	3–80 DAHA	36	17
5–10 cm	22–80 DAHA	82	69
10–15 cm	22–80 DAHA	Not determined	165

Fig. 2 Distribution of simetryn in soil layers in 2004 (**a**) and 2005 (**b**)

concentration of thiobencarb in 2004 was 906 μg kg^{-1} at 7 DAHA in the 0–5 cm soil layer, and the lowest concentration was 491 μg kg^{-1} at 22 DAHA. In 2004, thiobencarb concentrations in the 5–10 cm soil layer were <10% of the concentration in the top layer at 7 DAHA but increased to be about 35% at 35 DAHA. The sudden increase of thiobencarb concentration in this layer at 35 DAHA may confirm the assumption mentioned earlier that there was an error in this sampling date. Meanwhile, thiobencarb concentrations at the 10–15 cm soil layer remained stable throughout the monitoring period. In 2005, the peak concentration of thiobencarb in the top layer was 1,118 μg kg^{-1} at 7 DAHA, which was higher than the corresponding data of 2004. But the concentrations in this layer decreased quickly in the following days. Concentrations of thiobencarb in two deeper soil layers in 2005 were low, and relatively stable during the monitoring period. The data of 2005 were more comparable with results from a lysimeter study by Nhung (unpublished data), which reported similar concentrations of thiobencarb in this soil profile at 22 DAHA.

As in the simetryn case, thiobencarb was observed to dissipate more rapidly in 2005 than in 2004. But only the data of 2005 were used to estimate the half-life of thiobencarb as the data of 2004 have less statistical value. All
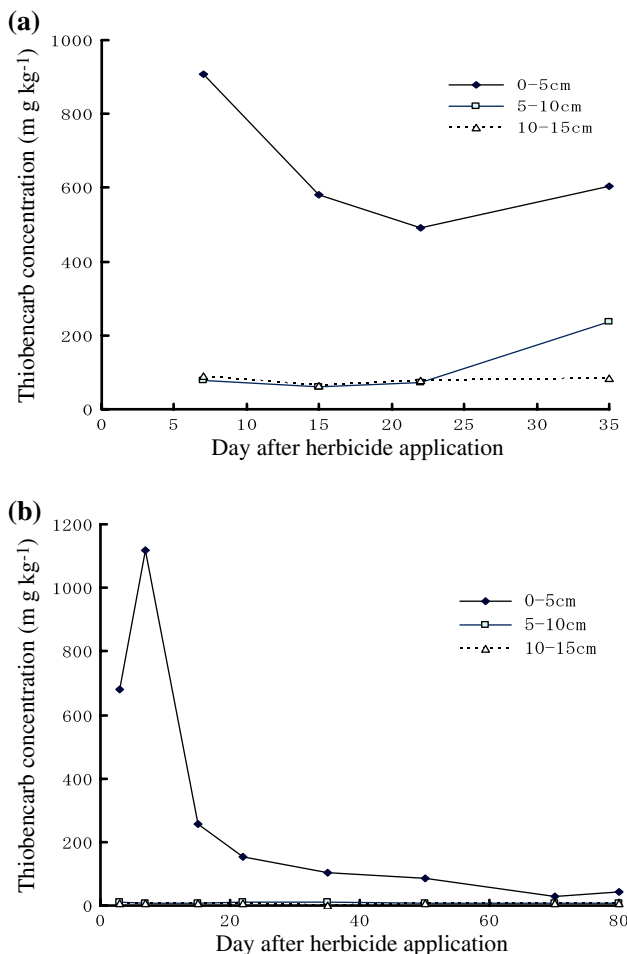
(a)

(b)

Fig. 3 Thiobencarb concentrations in soil layers in 2004 (**a**) and 2005 (**b**)

(a)

(b)

Fig. 4 Distribution of thiobencarb in soil layers in 2004 (**a**) and 2005 (**b**)

the data were fitted with the first-order kinetics. The calculated DT_{50} values of thiobencarb are also presented in Table 1. With high concentration of thiobencarb available for dissipation, the DT_{50} value of the top soil layer was the shortest. In the deeper soil layers of 5–10 and 10–15 cm, the dissipation rate was lower and they are comparable with thiobencarb half-lives in a variety of soils (Quayle et al. 2006). Supplement of thiobencarb from the upper soil layer, no effect of sunlight, and soil redox potential are among the factors that supposedly make the DT_{50} of thiobencarb in the deeper soil longer than that in the upper soil layer.

The distribution of thiobencarb mass in paddy soil in 2004 and 2005 is shown in Fig. 4. The maximum total mass (at 7 DAHA) was similar between 2 years, being 34% and 36% of total applied mass in 2004 and 2005, respectively. Most of thiobencarb mass remained in the top soil layer. It reflects the high K_d (soil-water distribution coefficient) value of thiobencarb. The same pattern of distribution was reported for thiobencarb in a flooded soil column experiment (Doran et al. 2008), but the percentage of thiobe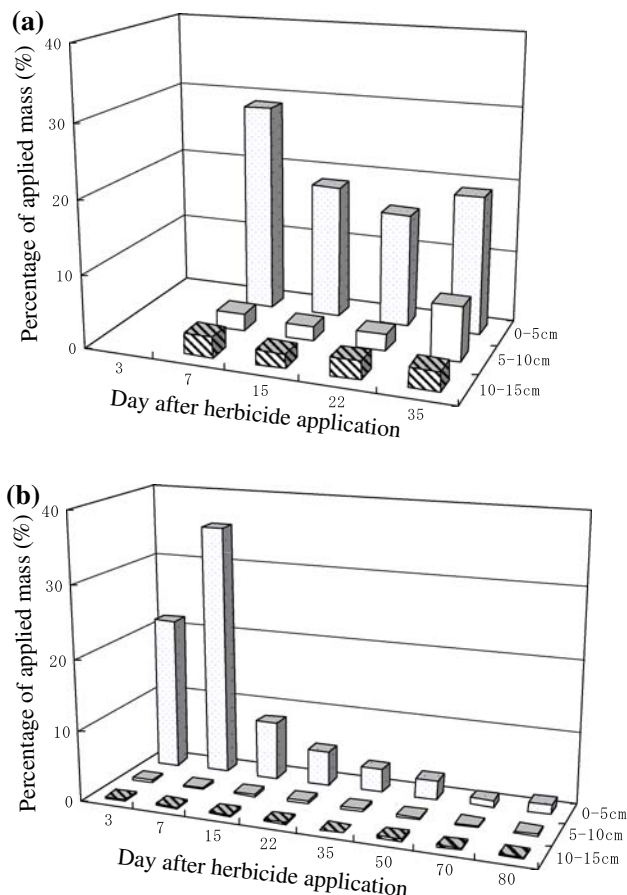ncarb mass in the soil in their study was greater (more than 70%). The cause of this phenomenon was the difference in depth of floodwater (~ 4 cm in this study and 1 cm in the study of Doran et al. 2008). Aktar et al. (2007) reported that no residue of thiobencarb was found in the 30 cm (12″) soil layer during a 60-day monitoring period in an Indian transplanted paddy, irrespective of thiobencarb application rates and meteorological conditions. Thiobencarb poses less risk for groundwater than simetryn when applied to the rice field.

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