

Short Communication

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Photodegradation of Butachlor and Pyrazosulfuron-ethyl in Rice Paddy Water under Natural Sunlight

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Abstract

BACKGROUND: Dissipation of herbicides in paddy water varies significantly, being dependent on environmental conditions such as sunlight. The photodegradation under natural sunlight may be one of natural degradation routes of herbicides dissipation. Therefore, the aim of this study was to monitor the degradation of butachlor and pyrazosulfuron-ethyl in paddy water under natural sunlight.

METHODS AND RESULTS: The 12 water sample bottles of treatment were covered by quart glass plates, which allow about 90% of UV radiation (280-2000 nm) to pass through, to minimize the UV attenuation. The other 12 water sample bottles of the control were covered by glass lids and wrapped with aluminum foils to prevent the sunlight. The concentration of butachlor and pyrazosulfuron-ethyl in paddy water samples bottles was monitored under ambient conditions with and without natural sunlight. The concentration of butachlor and pyrazosulfuron-ethyl for treatment decreased from 355.3 µg/L to 37.8 µg/L and from 10.5 µg/L to 3.9 µg/L, respectively, during consecutive 21 days after herbicide application under natural sunlight.

CONCLUSION: The concentration of butachlor in paddy

water decreased quickly under ambient conditions with natural sunlight. The degradation of butachlor in paddy water was enhanced by the natural sunlight. However, the degradation of pyrazosulfuron-ethyl was insignificant under natural sunlight.

Key words: Butachlor, Natural sunlight, Paddy water, Photodegradation, Pyrazosulfuron-ethyl

Introduction

Herbicides are widely used in rice paddies, golf courses and other types of fields. The acetanilide herbicide butachlor and the sulfonyleurea herbicide pyrazosulfuron-ethyl are pre-emergence herbicide to control weeds of transplanted rice paddy fields (Chen and Chen, 1979; Zheng *et al.*, 2008). Previous study investigated herbicide behavior and its dissipation in rice paddy environment (Ok *et al.*, 2012), however, the influence factor on herbicide degradation in paddy water was imprecise. Many environment factors related to the degradation and dissipation of herbicides including temperature, pH, sunlight, microbe, and soil properties (Chen and Chen, 1979; Samanta *et al.*, 1999; Sarmah and Sabadie, 2002; Vulliet *et al.*, 2004; Zheng *et al.*, 2008). Degradation of herbicides in paddy

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water also varies significantly, being dependent on environmental conditions such as sunlight (Chen and Chen, 1979; Sarmah *et al.*, 2000). The photodegradation under natural sunlight may be one of natural degradation routes of herbicides dissipation. Several studies reported that photodegradation of butachlor were the major routes of herbicides dissipation from paddy fields in summer days (Chen and Chen, 1979). Chen and Chen (1979) reported that the half-life of butachlor in aqueous solution were 5.4 hr after exposure to sunlight. In addition, the photolysis of pyrazosulfuron-ethyl was observed to enhance in aqueous condition (Zheng *et al.*, 2008). However, the photodegradation of butachlor have been investigated solely under controlled laboratory conditions, and only few studies for pyrazosulfuron-ethyl has been referred to their photochemical degradation in paddy water. Therefore, the aim of this study was to monitor the degradation of butachlor and pyrazosulfuron-ethyl in paddy water under natural sunlight.

Materials and Methods

All analytical grade solvents (acetonitrile, acetone, acetic acid, methanol, phosphoric acid) were purchased from Wako Chemicals (2011, Tokyo, Japan). Deionized water used for sample preparation and mobile phase was produced with a Milli-Q water purification system (Millipore, Billerica, MA, USA). Analytical standard grade butachlor (98%) and pyrazosulfuron-ethyl (98%) were also purchased from Wako Chemicals. The primary individual stock solutions (50 mg/L) of each analytical standard were prepared in 100 mL volumetric flask with pure acetonitrile. These stock standard solutions were diluted with acetonitrile to obtain a final concentration of 10 mg/L and kept in fridge at 4°C. The 10 mg/L standard stock solutions were appropriately diluted in acetonitrile:water (20:80, v/v) to prepare working standards 0.5 mg/L and 0.01 mg/L of butachlor and pyrazosulfuron-ethyl, respectively.

The paddy water was collected from the experimental paddy field at FM Honmachi of Tokyo University of Agriculture and Technology (TUAT), Japan. Paddy water samples were filtered through 1.2 µm glass fiber filters and sterilized by autoclave at 120°C for 20 minutes for the experiments. These solutions were divided into 24 sample bottles of 250 mL and the standard solution was spiked in water sample bottles. The 12 bottles for treatment were covered by quart

glass plates, which allow about 90% of UV radiation (280-2000 nm) to pass through, to minimize the UV attenuation. The other 12 bottles for the control were covered by glass lids and wrapped with aluminum foils to prevent the sunlight. The concentration of butachlor and pyrazosulfuron-ethyl in water sample bottles at initial, 1, 3, 7, 14 and 21 days was monitored under ambient conditions with and without sunlight from May 5 to May 26 in 2011 at the university farm of TUAT. The solar radiation was monitored by pyrhelimeter placed next experimental field. The water temperature was also monitored by temperature sensors placed in the water samples.

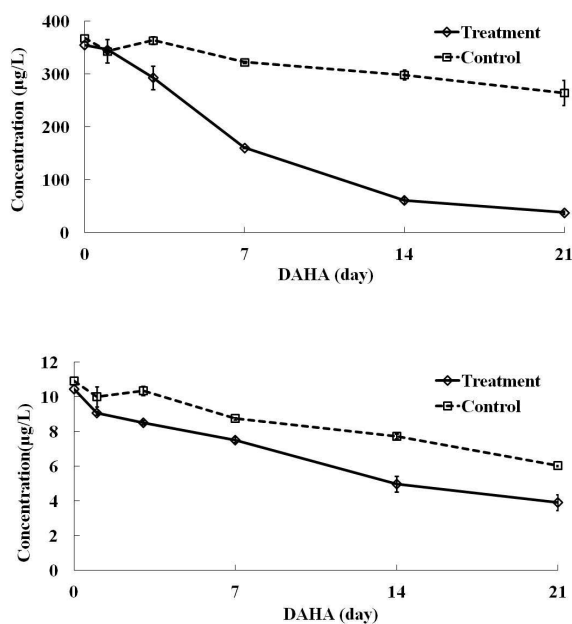
Prior to the extraction, water samples were filtered by 1.2 µm glass fiber filter paper (GC/C-Whatman). The water samples of pyrazosulfuron-ethyl were adjusted to pH 2.5 by acid phosphoric and then both sample of butachlor and pyrazosulfuron-ethyl were extracted by solid phase extraction method using the Superclean ENVI-18 as previous study by Ok *et al.* (2012). All water samples were analyzed by high performance liquid chromatography (HPLC) within 1 day after the sampling. The Separations Module was equipped with a Shimadzu HPLC column C-18 which was kept at 40°C during the analytical operation. The pump was set in isocratic mode at the flow rate of 1 mL/min with the mobile phase of acetonitrile: 0.01% acetic acid (30:70 and 50:50, v/v) for butachlor and pyrazosulfuron-ethyl, respectively. The HPLC detection wavelength of 215 nm and 242 nm were selected for all measurements for butachlor and pyrazosulfuron-ethyl, respectively. Sample injection volume was 20 µL.

Results and discussion

Monitored average temperatures of tested paddy water sample in the treatment and control in this experiment were 20.9 ± 7.8 and 19.5 ± 5.8 °C, respectively. The temperature at noon of the treatment seems to be higher than the control due to the heat supplied by the sunlight. However, over the course of experiment, the difference of mean temperature between control and treatment in this experiment was insignificant. The cumulative ultraviolet B(UVB) radiation energy of the natural sunlight during 21 days after herbicide application was 321.4 kJ/m² in this experiment. The pH values in paddy water was 7.4 ± 0.1 for treatment and 7.6 ± 0.2 for

control, which were in similar range to monitored data in micro paddy lysimeter experiment (Ok *et al.*, 2012).

The concentrations of butachlor and pyrazosulfuron-ethyl during consecutive 21 days after herbicide application under natural sunlight are shown in Fig. 1. The average concentration of butachlor at initial day was 355.3 $\mu\text{g/L}$ for treatment and 367.9 $\mu\text{g/L}$ for control, and the corresponding values for pyrazosulfuron-ethyl was 10.5 $\mu\text{g/L}$ for treatment and 10.9 $\mu\text{g/L}$ for control. The average concentration of both herbicides was similar as the concentration range in the actual paddy field and micro paddy lysimeter experiment (Ok *et al.*, 2012). The concentration of butachlor and pyrazosulfuron-ethyl for treatment decreased to $37.8 \pm 3.3 \mu\text{g/L}$ and $3.9 \pm 0.5 \mu\text{g/L}$ during 21 days after herbicide application under natural sunlight (Fig. 1). These conditions of control and treatment were assumed that herbicide dissipation under the dark condition was due to the abiotic degradation such as hydrolysis, and that dissipation under natural sunlight was due to the total effect of hydrolysis and photochemical degradation. Therefore, the herbicide decay solely due to photodegradation was determined by subtracting the herbicide concentration obtained in the experiments without light from that obtained under the natural sunlight condition. The concentration



DAHA is the days after herbicide application
Fig. 1. Concentrations of butachlor and pyrazosulfuron-ethyl in paddy water under natural sunlight.

of butachlor in paddy water was degraded quickly under natural sunlight. However, there was slight difference between treatment and control for pyrazosulfuron-ethyl under natural sunlight.

The half-life (DT_{50}) during 21 days after herbicide application was determined using first-order kinetics. The DT_{50} was obtained as the slope of natural logarithm of pesticide concentrations ($\mu\text{g/L}$), $\ln(c)$, versus the exposure period (hour, hr). The results are summarized in Table 1. The estimated DT_{50} of butachlor in paddy water during 21 days after herbicide application were 6.0 days for treatment and 46.5 days for control, respectively. The butachlor were very sensitive to sunlight that the half-life of butachlor was about 5.4 hr in aqueous solution (Chen and Chen, 1979) and 58.2 ± 4.5 hr in filtered river water under sunlight (Lin *et al.*, 2000).

On the other hand, the estimated DT_{50} of pyrazosulfuron-ethyl in paddy water during 21 days after herbicide application were 15.5 days for treatment and 26.1 days for control. The sulfonylurea herbicides class indicated that photodegradation is an alternative pathway to chemical hydrolysis (Samanta *et al.*, 1999; Vulliet *et al.*, 2004; Pusino *et al.*, 1999). In addition, the photochemical behavior of sulfonylurea herbicides depends on the pH (Vulliet *et al.*, 2004). Scrano *et al.* (1999) reported the whole reaction (photolysis + hydrolysis) under sunlight is faster in acidic and alkaline conditions than in neutral solutions. The pH value was in neutral range of 7.4

Table 1. The half-life(DT_{50}) (day) of butachlor and pyrazosulfuron-ethyl in paddy water under natural sunlight

Temperature (C)	Treatment	Control
Butachlor		
Ln(c) versus time		
Equations	$y = -0.1147t + 5.92$	$y = -0.0149t + 5.90$
R^2	0.98	0.95
DT_{50} (day)	6.0	46.5
Pyrazosulfuron-ethyl		
Ln(c) versus time		
Equations	$y = -0.0457t + 2.30$	$y = -0.0266t + 2.38$
R^2	0.99	0.97
DT_{50} (day)	15.5	26.1

Ln(c) is natural logarithm of pesticide concentration
 y is a natural logarithm of pesticide concentration
 t is the time after experiment was started (hour)
 R^2 is the square of the correlation coefficient of y and t

and 7.6 for treatment and control in this study. Thus, the photodegradation of pyrazosulfuron-ethyl in paddy water under natural sunlight was insignificant in this study.

Conclusion

The degradation processes of herbicides, butachlor and pyrazosulfuron-ethyl, in rice paddy water under natural sunlight were investigated. The concentration of butachlor in paddy water decreased quickly under ambient conditions with natural sunlight. The degradation of butachlor in paddy water was enhanced by the natural sunlight. However, the degradation of pyrazosulfuron-ethyl was insignificant under natural sunlight.

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