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Behavior of Pretilachlor and Dimethametryn in Water of Flooded Rice Fields

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In order to understand the behavior of pretilachlor, a popular rice herbicide in the world, and a synergetic active ingredient, dimethametryn, a monitoring study was conducted in 3 paddy plots in Kyushu region, Japan. The monitoring indicated different behaviors for both pesticides from those reported in the literature. Maximum concentrations of pretilachlor and dimethametryn were 1 order of magnitude lower than the values observed in previous studies. However, the dissipation rates estimated from monitoring data were in agreement with other studies in Japan. The pesticide product was tested and showed good dissolution of pretilachlor and dimethametryn in water, suggesting that another study is needed to explain the low concentrations of the two pesticides in the fields. Besides pesticide behaviors, it was observed from the monitoring that water management in paddy rice cultivation still requires more attention to reduce the environmental risk of rice pesticides.

Keywords: rice pesticide, paddy field, dissolution, water management, drainage

INTRODUCTION

Pesticides have been widely used in agriculture and rice cultivation to ensure a high quality and high yield crop. However, besides the benefit that pesticides bring to us, the publics are now concerned with their potential adverse impact to the environment.

Rice is distinguished from other crops by its flooded condition. As a consequence, pesticides used in rice fields are more prone to runoff than in other agricultural fields and thus will possibly pose their impact on unintended targets. Matsui *et al.* (2002) reported that only pesticides used in rice fields were detected in the river water in Oirase River Basin where the annual consumption of pesticides in rice fields is only about a third of the total agricultural pesticide consumption. And in Japan, it was found that the highest occurrence of pesticides in open waters usually coincides with the application period of pesticides in paddy fields (Ebise and Inoue, 2002; Sudo *et al.*, 2002).

In order to assess the risk posed by those pesticides, regular monitoring programs of different scales are necessary. While national or river basin scale monitoring programs help authorities on their decision making process, farm plot scale monitoring studies provide data base for risk assessment and modeling. The plot scale data are especially useful for the re–approval process of a pesticide when the water quality standard became more stringent (Craven *et al.*, 2008).

Pretilachlor [2–chloro–2,6–diethyl–N–(2–propoxyethyl)acetanilide] is a chloroacetanilide herbicide which is widely used in rice cultivation for the control of several grasses, broad–leaved weeds and sedges. Pretilachlor is used either as a pre–planting or post–emergence application. Despite its popularity, the toxicology data of pretilachlor make its risk non–negligible (Karpouza and Capri, 2006). Dimethametryn (N2–(1,2– dimethylpropyl)–N4–ethyl–6– methylthio–1,3,5–triazine– 2,4–diamine), has been used for a long time in paddy fields in Japan as herbicide (Kawakami *et al.*, 2008). Although dimethametryn possesses physico chemical properties similar to those of pretilachlor (Table 1), no detailed monitoring on the dissipation of dimethametryn and its other behavior in flooded rice fields is reported in the literature.

Therefore, our study aimed to investigate the behavior of pretilachlor and dimethametryn, two herbicides which were applied to flooded rice fields after transplantation.

MATERIALS AND METHODS

Study site and pesticide application

The monitoring was carried out in a paddy block near Kurume City, Fukuoka Prefecture in June and July, 2009. The block lies inside the Chikugo River Basin, a large rice production area in the south of Japan. The layout of the block was shown in Fig. 1. The actual number of cultivating plots was 15 with individual plot size ranging from 0.1 ha to 1.1 ha. The block was consolidated recently with concrete bunds, new irrigation system and sub–surface drainage system. Irrigation canals were separate from the large drainage canal.

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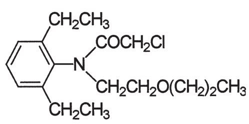
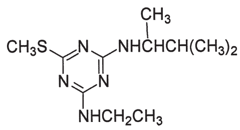
Table 1. Properties of pretilachlor and dimethametryn

	Pretilachlor	Dimethametryn
Chemical structure[1]		
Solubility in water (mg L^{-1}) [1]	50	50
Henry coefficient (Pa m^3 mol^{-1}) [1]	8.1×10^{-4}	9.5×10^{-4}
Octanol–water partition coefficient K_{ow} [1]	$\log K_{ow} = 4.08$	$\log K_{ow} = 4.08$
Soil water partition coefficient K_d [2]	15.8	6.34

[1] Tomlin, 2003; [2] Kawakami *et al.*, 2008

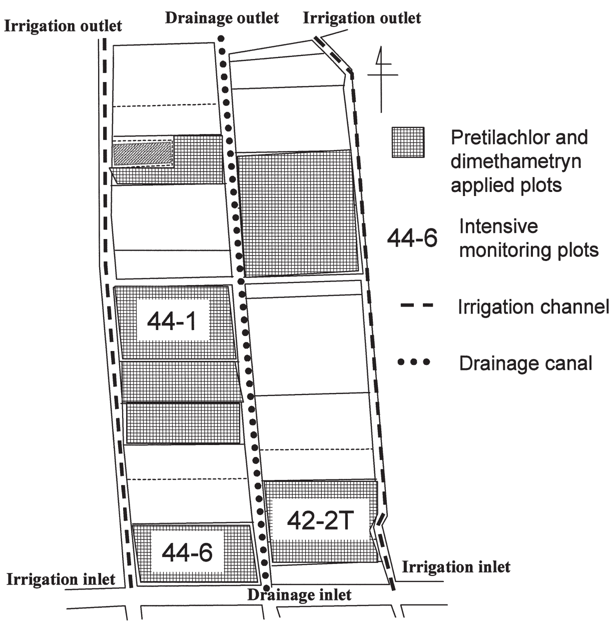


Fig. 1. Layout of the study block.

At the beginning of the study, questionnaires were sent to farmers (15 people) to collect information about their farming schedule and the possible use/application of agrochemicals. After that three plots, to where pretilachlor and dimethametryn were applied, were selected for monitoring (Fig. 1). Water management in each plot including water level, irrigation and drainage practices, was monitored by water level sensors (DL/N, STS Sensor Technik Sirnach AG, Switzerland) and daily observation. Other water balance components including precipitation, evapotranspiration and percolation rate were also monitored during the monitoring period.

Pretilachlor and dimethametryn, as components of the commercial granular herbicide Hokuto® (Syngenta Japan, Tokyo, Japan), were applied from June 4 to 7, 2009. The pesticides were applied about one week after rice transplantation when rice fields were already flooded. The application rates of the active ingredients were 450 g ha^{-1} and 60 g ha^{-1} for pretilachlor and dimethametryn, respectively.

Water sampling

In each paddy plot, water samples of 1–L were taken in the eastern (irrigation side) and western (drainage side) parts of the plots before pesticide application and twice a week after pesticide application starting from 1 day after application. Each sample was composited from several sub–samples taken along the plot sides.

After sampling, the samples were immediately transported back to the laboratory and were filtered before they were stored at 4 °C prior to analysis.

Product dissolution test

0.1 g of the commercial granular herbicide Hokuto® containing pretilachlor and dimethametryn was added to a 1–L brown glass bottle with 1 L of tap water. Then 25–mL samples were taken from the bottle at different intervals (0.5, 1, 2, 4 and 6 hours after application) and diluted to 525 mL with tap water. The samples were then transferred immediately to the laboratory for analysis.

Sample extraction

Water samples were filtered again before extraction. Dilution of 20–folds was performed for the dissolution test samples. And 500 mL of water sample was solid phase extracted using a GL Science Aqusis PLS–3 cartridge (GL Science, Tokyo, Japan). Prior to use, the cartridges were initially conditioned with 10 mL of dichloromethane, 5 mL of methanol, followed by 5 mL of distilled water. The water sample was then loaded into the cartridge at a flow rate of 15 mL min^{-1} using the automated solid phase extraction equipment AutoTrace® SPE Workstation (Caliper Life Science, MA, USA). The cartridges were dried for 10 min by nitrogen gas before the pesticides were eluted by 3 mL of dichloromethane. The dichloromethane extracts were collected and evaporated to approximately 0.4 mL using a Turbo Vap LV Evaporator (Zymark Corporation, MA, USA). The residual solution was made up to 0.5 mL using pure dichloromethane and then transferred to the vial for gas chromatography analysis. Before analysis, 2 μL of a mixture of internal standards (anthracene d10; acenaphthene d10; p–terphenyl d14) at the concentration of 50 mg L^{-1} was added to the vial.

Gas chromatography and mass spectrometry

The pesticides were analyzed using a TRACE GC

Ultra gas chromatograph (Thermo Fisher Scientific, MA, USA) equipped with a TSQ Quantum triple quadrupole mass spectrometer (Thermo Fisher Scientific, MA, USA). The column was a SLB–5MS column (30 m×0.25 μm×0.25 mm) (Supelco, PA, USA). Helium was used as the carrier gas. The temperature was programmed as follows: 60 °C for 1 min, ramped up to 150 °C at 20 °C min^{-1}, then to 280 °C at 10 °C min^{-1}. The temperature was then maintained at 280 °C for 5 min. A splitless injection mode was used, with an injection volume of 1 μl with the injection port hold at 240 °C. The carrier gas was maintained constant at 1.2 mL min^{-1}. The mass spectrometer was set in selective reaction monitoring (SRM) mode. The limits of detection of both pretilachlor and dimethametryn were 0.01 μg L^{-1}. The recovery ratios of both pesticides ranged from 90 to 110%.

RESULTS

General conditions in the study block

All questionnaires were recovered from farmers and information was compiled. The compiled information showed that pretilachlor and dimethametryn were applied in 7 plots, accounting for more than half of the block area (Fig. 1). It means that these two pesticides have a higher potential of polluting the water in canals and rivers. Therefore, monitoring their dissipation behavior in the field is necessary.

Data from the meteorological station in Kurume showed that the average air temperature in Kurume in June and July 2009 was similar to the average temperature in the last 22–year period. But the total precipitation in the monitored paddy block was lower than the average data of June–July in the last 22–year period. Evapotranspiration was a significant water consumption factor with the maximum daily value of about 1.1 cm and the average daily value of 0.45 cm. Monitoring data on percolation rate measured in 3 plots indicated that average percolation rate in the block was low, with value less than 0.1 cm d^{-1}, due to the high clay content in the deep soil layer.

As water balance can greatly affect the fate and transport of rice pesticides, daily water balance of 3 monitored plots were calculated and were presented in Fig. 2. Large fluctuation of actual water depths can be observed in those plots because the farmers adjusted water level according to the condition of the rice plants or following the recommended water management from local agriculture cooperative. Irrigation and runoff amounts are basic data for the calculation of pesticides transport/loss. Those amounts were different from plot to plot as farmers managed their plots according to the condition of rice plants and their own experience.

Dissipation of pretilachlor

Pretilachlor reached its peak concentration in all plots at 1 day after pesticide application (DAPA) as shown in Fig. 3. The maximum concentrations of pretilachlor ranged from 31.5 to 51.5 μg L^{-1}, with similar initial water depths as shown in Fig. 2.

Pretilachlor dissipated rapidly in paddy water and only residual concentrations of 0.1 μg L^{-1} or less were detected at the end of the monitoring period. Using the observed data, estimation of the dissipation rate and half–life of pretilachlor was conducted and the results were shown in Table 2. Values obtained from 3 monitored

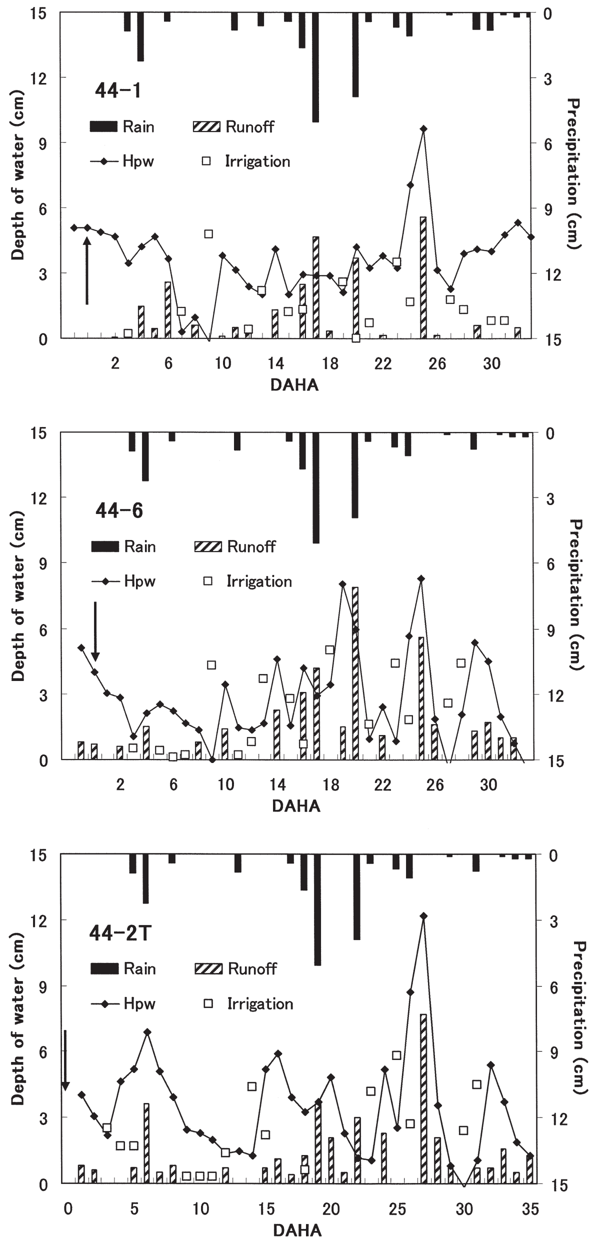


Fig. 2. Water management in 3 monitored plots (↓ application date).

Table 2. Dissipation rates and half lives of pretilachlor and dimethametryn in paddy water

Plot number	Pretilachlor		Dimethametryn	
	k	DT_{50} (d)	k	DT_{50} (d)
44–1	0.2201	3.15	0.1483	4.67
44–6	0.2152	3.22	0.1478	4.69
42–2T	0.2081	3.33	0.1372	5.05

plots were very close to one another.

Dissipation of dimethametryn

Dimethametryn has similar pattern of dissipation with pretilachlor, reaching its peak concentration in all plots 1 DAPA (Fig. 3). However, the maximum concentrations of dimethametryn were only about half those of pretilachlor, ranging from 15.9 to 26.7 μg L^{-1}.

Dimethametryn dissipated exponentially in paddy water similar to pretilachlor. And although having lower maximum concentration, the concentrations of dimethametryn at the end of the monitoring period were higher than those of pretilachlor, standing at about more than 0.2 μg L^{-1}. Consequently, the estimated dissipation rate and half–life of dimethametryn were longer than the corresponding data of pretilachlor (Table 2). Also, good replication was observed between values from 3 monitored plots.

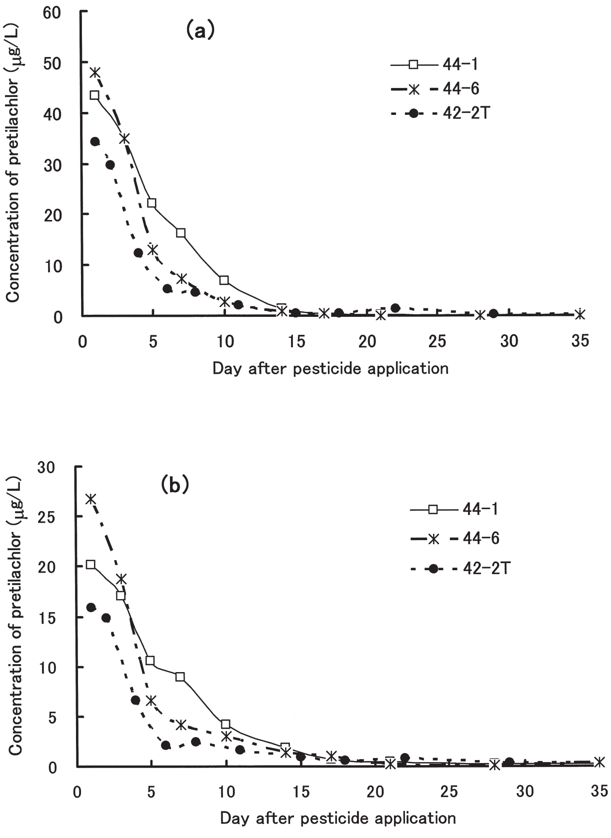


Fig. 3. Concentrations of pretilachlor (a) and dimethametryn (b) in water of 3 monitored plots.

Dissolution of two herbicides in water

Two herbicides also shared similar pattern of dissolution in water as they possess similar physico chemical properties (Table 1) but they had different final maximum concentrations because their contents in the product are different. After a slow dissolution phase at the beginning, probably for water absorption and disintegration of the granule, the two herbicides dissolved in a steady rate from one hour after application onward.

As shown in Fig. 4, pretilachlor, having higher dose in the product (1.5%), reached the level of 1270 μg L^{-1} at the end of the test. This water concentration corresponded to a recovery rate of about 80%. The final concentration of dimethametryn was only 130 μg L^{-1} (Fig. 4), about one tenth of that of pretilachlor although its content in the product is 0.2%. The recovery rate of dimethametryn was also lower, achieving about 62%. It is probably required more than 6 hours (as in this dissolution test) to complete dissolve the product. Blurry water was the observed state of the water in the test bottle at the end of the test.

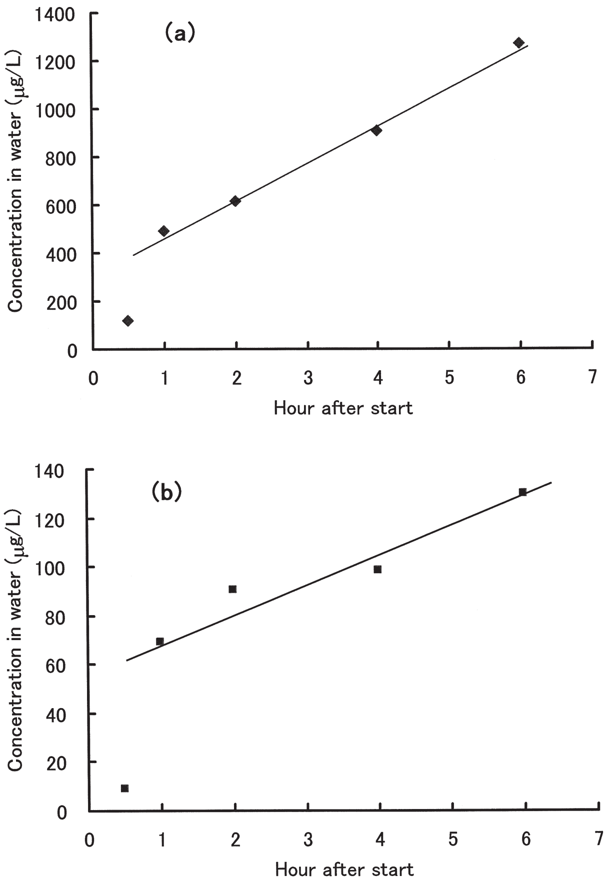


Fig. 4. Dissolution of pretilachlor (a) and dimethametryn (b) in tap water.

Losses of pretilachlor and dimethametryn from paddy plots

It can be observed from Figs. 2 and 3 that there were runoff events from paddy plots when the pesticide concentrations in paddy water were still considerable. As runoff water carried dissolved pesticides out of the plots, there were losses of pretilachlor and dimethametryn from the monitoring plots to the drainage canals. Details about the pesticide contamination in the drainage canal during this period will be presented in another paper.

DISCUSSION

Although the results obtained from this study were comparable and consistent among 3 monitored plots, there are some points worth mentioning about those data:

Table 3. Comparison of pretilachlor fate observed in different studies

	This study	Fajardo *et al.* (2000)	Ishii *et al.* (2004)	Flori *et al.* (2003)	Vidotto *et al.* (2004)
Water depth (cm)	~4	3–4	NA[1]	18	9–12
Application rate (g/ha)	450	600	450	1225	1125
Max. conc. (μg/L)	~50	~1000	~7–800	764	1233–1355
DT_{50} (day)	~3.2	3.0–3.6	NA[1]	>10	4.7–6.8

[1] NA: Not available

1. The peak concentrations of pretilachlor observed in the paddy water of this study were significantly lower than other maximum pretilachlor concentrations observed in flooded rice fields. Those comparisons were presented in Table 3. Application rates in other studies were from 1.3 to 3 folds higher than that of this study but the water depths were higher in case of European paddies. However, the maximum concentrations were 40 to 50 times different, even for the Japanese case (Fajardo *et al.*, 2000; Ishii *et al.*, 2004). In the meantime, the DT_{50} values of pretilachlor were not very much different from those reported previously. Similar DT_{50} values have been estimated by Fajardo *et al.* (2000). The cause of the difference in concentration range and the similarity in DT_{50} values is not available and more study is needed to investigate the processes in detail.
2. Concentrations of dimethametryn observed in this study were also consistent among 3 plots and the concentration ratio between dimethametryn and pretilachlor seems to remain constant at about 0.5 during at least 10 DAPA while the applied mass ratio is about 0.13. And similar to the case of pretilachlor, the maximum concentration of dimethametryn found in this study was also lower than that reported in the literature (Ishii *et al.*, 2004). However, the difference was not as far, estimated to be 3–4 times only.
3. The dissolution test indicated that both herbicides can dissolve relatively quickly in water to reach high concentration, much higher than those found in the field. Probably, adsorption test should be performed for both herbicides in the laboratory in order to find out the cause of low herbicide concentrations in the paddy plots of this study.
4. The losses of those two pesticides through runoff also contributed to the rapid dissipation of them in the paddy plots. Those losses indicated that the water management in the monitoring plots did not comply with the requirement of water holding period of 7 days, proposed by the Ministry of Environment of Japan, to prevent pesticide runoff from paddy plot to the environment. More extension work should be done in order to increase the awareness of farmers about the environmental risk of rice pesticides.

CONCLUSION

The behavior of pretilachlor and dimethametryn applied to 3 paddy plots in Kyushu was monitored. The maximum concentrations of both pesticides were reached within one day but the values were several folds lower than those reported in the literature. Meanwhile, dissolution test showed that those two pesticides can still dissolve to higher concentration in water. More research should be done to clarify the newly observed phenomenon. The water management in the area also needs more attention to reduce the losses of pesticides into the environment and thus posing risk to unintended target organisms.

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REFERENCES

Ebise, S. and T. Inoue 2002 Runoff characteristics of pesticides from paddy fields and reduction of risk to the aquatic environment. *Water Science and Technology*, **45**: 127–131

Fajardo, F. F., K. Takagi, M. Ishizaka and K. Usui 2000 Pattern and rate of dissipation of pretilachlor and mefenacet in plow layer and paddy water under lowland field conditions: A three–year study. *Journal of Pesticide Sciences*, **25**: 94–100

Flori, P., D. Pancaldi, I. Braschi and C. Gessa 2003 Behavior of four herbicides in a paddy field: simulation by a laboratory microcosm. *XII Symposium Pesticide Chemistry: Pesticide in air, plant, soil and water system*, Piacenza, Italy. 223–233

Ishii, Y., K. Inao and Y. Kobara 2004 Dissipation of some herbicide in a flooded rice field and increase of water holding time after application of herbicide. *Bulletin of the National Institution of Agro–Environmental. Sciences* **23**: 15–25 (in Japanese with English summary)

Karpouzas, D. G. and E. Capri 2006 Risk analysis of pesticides applied to rice paddies using RICEWQ 1.6.2v and RIVWQ 2.02. *Paddy and Water Environment*, **4**: 29–38

Kawakami, T., A. Takezawa, I. Nishi, E. Watanabe, M. Ishizaka, H. Eun and S. Onodera 2008 Monitoring of cholinesterase–inhibiting activity in water from the Tone canal, Japan, as a biomarker of ecotoxicity. *Ecotoxicology*, **17**: 221–228

Kawakami, T., H. Eun, M. Ishizaka, S. Endo, K. Tamura and T.

Higashi 2007 Adsorption and desorption characteristics of several herbicides on sediment. *Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes*, **42**: 1–8

Matsui, Y., S. Itoshiro, M. Buma, T. Matsushita, K. Hosogoe, A. Yuasa, S. Shinoda and T. Inoue 2002 Predicting pesticide concentrations in river water with a hydrologically calibrated basin–scale runoff model. *Water Science and Technology*, **45**: 141–148

Tomlin, C. (Ed) 2003 The Pesticide Manual. 13th edition. British Crop Protection Council, Farnham, UK.

Sudo, M., T. Kunimatsu and T. Okubo 2002 Concentration and loading of pesticide residues in Lake Biwa basin (Japan). *Water Research*, **36**: 315–329

Vidotto, F., A. Ferrero, O. Bertoia, M. Gennari and A. Cignetti 2004 Dissipation of pretilachlor in paddy water and sediment. *Agronomie*, **24**: 473–479