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# The fate of agrochemicals in paddy rice – aquaculture systems in Northern Vietnam

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## Abstract

In Northern Vietnam, many irrigated paddy rice farming systems include ponds in which farmers raise fish to produce additional income and food. The transport of agrochemicals applied in the paddy fields to adjacent ponds and/or receiving streams raises concern about pesticide pollution of water bodies and related fish malfunctions.

Hence, the quantification and forecast of pesticide losses to ground and surface water from paddy rice fields is of indispensable concern and a prerequisite for assessing the potential environmental exposure and risk of water pollution across vulnerable landscapes.A representative farming system based on a paddy field connected to a fish pond was chosen in 2008 to study the environmental fate of agrochemicals. A mixture of two pesticides (dimethoate and fenitrothion) was applied in two consecutive rice growing seasons. The results indicated that, under the conditions studied, both pesticides dissipated rapidly from paddy water. A significant fraction of dimethoate was transported with the outflow while the losses of fenitrothion were lower during both seasons. Simultaneous appearance of both pesticides in soil water at two depths indicated transport along prefe-rential flow paths.

## Introduction

The intensive use of pesticides in Vientam's agricultural sector and related environmental, health, and marketing aspects have been addressed during the last decade (Dasgupta et al., 2007, Kleimick and Lichtenberg, 2008, Toan et al., 2007). The pesticides found in the environment were identified to originate from agriculture, the main sources being vegetable and paddy rice production.

Due to the prerequisites of the paddy rice production such as continuous water logging, agrochemicals applied in paddy fields represent a threat to the environment as they are transported with outflow water in dissolved and/or sediment-bound phases towards receiving waters. Recent studies conducted in the Mediterranean rice growing regions (Spain, Italy and Greece) as well as in Japan indicate that losses from paddy fields to receiving water

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bodies can reach up to 18% of the applied pesticide (Phong et al., 2008). Additionally, high infiltration capacity of paddy fields tremendously increases the risk of pesticide transport towards ground water (Janssen and Lennartz, 2007).

The correlation between the pesticide use on paddy fields and its negative effect on fish health/harvest in integrated paddy-fish production systems in Vietnam was studied less intensively. The economical assessment made by Kleimick and Lichtenberg (2008) revealed a positive correlation between pesticide use and harm to the fish population in rice-fish cultures. Studies on physiological changes in fish revealed long-lasting effects of organophosphate pesticides on the fish health population in Vietnam (Cong et al., 2006). Therefore, the quantification and forecast of pesticide losses to surface and ground water from paddy fields is a prerequisite for assessing the risk of pollution of water bodies and for aquatic life.

## Material and Methods

### *Study site*

The study site is located in the Chieng Khoi catchment in Northern Vietnam (Yen Chau district, Son La province). This highland area is characterised by elevations ranging from 300 to 1000 m a.s.l. and tropical monsoon climate with rainy season in summer (May-October) and relatively dry, cold winters (November-April). Annual average temperature and rainfall are 21 °C and 1200 mm, respectively. A representative paddy field – fish pond system was chosen as experimental plot (Figure 1). Irrigation water was taken from an adjacent irrigation channel and discharged to the paddy field through a supply pipe. The paddy water first drained to the adjacent fish pond before it further flew to the receiving stream. To measure the water flow between the system elements (Irrigation channel - paddy field – fish pond – receiving stream), a V-shaped weir and two HS-flumes were installed and equipped with automatic pressure sensors linked to an external data logger to record water heads. Both the paddy field and the fish pond were surrounded by bunds to impede any diffuse and unwanted in- or outflows. During the rice growing season, the water level in the paddy field was measured manually about daily

### *Agrochemicals*

Two organophosphate insecticides, dimethoate (o,o-dimethyl S-methylcarbamoylmethyl phosphorodithioate) and fenitrothion (o,o-dimethyl o-(3-methyl-4-nitrophenyl) phosphorothiolate) (Table 1), were applied on the paddy field as a mixture of commercial insecticides “DiMENAT”™ and “OFATOX”™, respectively, in two rice growing seasons (spring and summer 2008) at the tillering stage of the rice crop. The application rates were kept at 400 g $ha^{-1}$ and 255 g $ha^{-1}$ for dimethoate and fenitrothion, respectively. Directly after application, inflow and outflow of the paddy field were closed for one day.

### *Sampling*

In total, two sampling series were scheduled in 2008 to monitor the fate of pesticides in the integrated paddy rice-aquaculture system. Pesticide concentrations were regularly monitored in the paddy field, fish pond and irrigation and drainage channels.

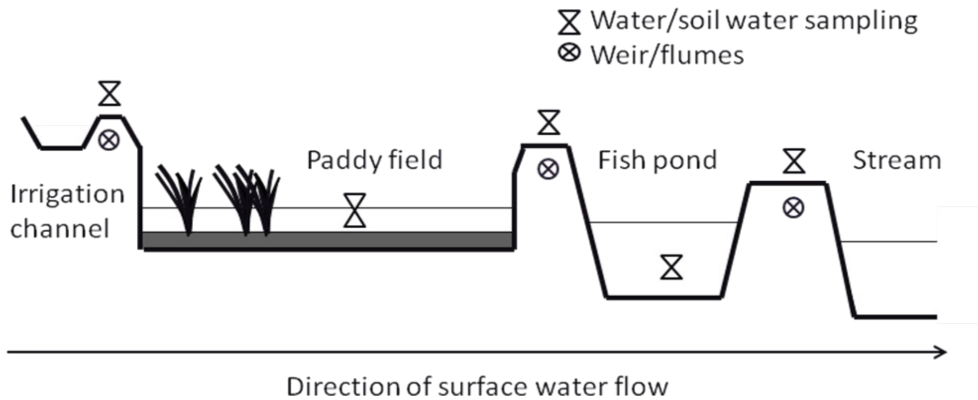


Figure 1. The schematic representation of the experimental setup.

Table 1. Key physico-chemical properties of applied agrochemicals

| Substance | S (mg $L^{-1}$) | Lg $K_{o/w}$ | DT50 (days) |
|---|---|---|---|
| Dimethoate | 23 300 | 0.704 | 4.4* |
| Fenitrothion | 14 | 3.430 | 84.3 |

S – solubility in water, Lg $K_{o/w}$ – $\log_{10}$ of *n*-octanol--water partition coefficient, DT50 – half-life in water. * Hydrolysis half-life is determined at pH 9. Source: Tomlin, 2003.

The sampling protocol has been set up in a way to allow for variable sampling that is, water samples were taken about daily during the first week after pesticide application and weekly towards the end of the sampling period. On sampling days, composite paddy water samples were taken from five spots in order to represent average concentrations in the paddy water. The samples were merged and subsequently split in two sub-samples. Irrigation water was sampled only weekly. The fish pond water samples were the grab samples. Soil water was extracted using porous suction cups installed in triplicates at depths of 20 cm and 40 cm. Seven hours before sampling a suction of 50 kPa was manually applied using a hand vacuum pump. Soil solution extracted within the first hour was discarded. Overall, the samples were taken at -1, 0, 1, 2, 3, 4, 5, 7, 9, 14 days after treatment (DAT).

*Analytical procedure*

Water samples were processed according to the procedure developed and tested by Ciglasch et al. (2005). Water samples were brought to the field laboratory in Yen Chau and poured through a 0.45 µm filter. Pesticides were concentrated from the water sample by solid phase extraction (SPE) using cartridges filled with graphitized nonporous carbon (Supleclean Envi-Carbopack, Supelco, USA). To activate the sorbent the cartridge was rinsed by 8 ml of methylene chloride/methanol (90:10 v/v), followed by 3 ml of methanol and 25 ml of 10 g $L^{-1}$ ascorbic acid (pH adjusted to 2 with HCL). Subsequently, 400 ml of filtered water samples were sucked through the SPE cartridges at a flow of 5 ml $min^{-1}$ using a vacuum pump to ensure a pressure difference of 7 hPa. After concentration, the cartridges were kept frozen at -18 °C until further analysis.

The pesticides were eluted from the cartridges and analysed at State Institute for Agricultural Chemistry, Stuttgart. Before eluting the pesticides the cartridges were dried for 5 minutes to remove remaining water. In a next step, 10 ml of acetone, 15 ml of a 90:10 (by volume) mixture of methylene chloride/ methanol and 30 ml of TBME (tert-butyl methyl ether) were used to elute the pesticides from the sorbent. The effluents were collected in pear-shaped flasks and spiked with two drops of toluene as a keeper. To remove methylene chloride and methanol samples were evaporated almost to dryness using a rotary evaporator. The residues were re-dissolved with 1 ml of a mixture of cyclohexane and toluene (90:10 v/v). The solutions were then washed into a gas chromatograph vial and used for quantitative analysis by employing matrix-matched calibrations.

## Results

Before pesticide application dimethoate and fenitrothion were not detectable in the paddy water. However, during the spring season highest concentrations of 614 and 266 µg $L^{-1}$ of dimethoate and fenitrothion, respectively, were measured 30 minutes after application (Fig. 2). These concentrations correspond to fractions of 88% and 60% of the total amount of applied dimethoate and fenitrothion, respectively. During the first day after application, the concentration of both pesticides in paddy water rapidly decreased by more than 90%. The high losses of fenitrothion could be explained by its susceptibility to photodegradation while this process is not significant for dimethoate (Oubina et al. 1996). A comparable pattern of pesticide concentration behavior was observed during the summer rice crop season (Data not shown). Directly after application the highest pesticide concentration of 1074 and 405 µg $L^{-1}$ of dimethoate and fenitrothion was observed in the paddy water (81% and 48% of the total amount of applied pesticides, accordingly). The observed difference in initial pesticide concentrations could be explained by the reduced paddy water level during the summer rice crop season. The respective pesticide losses with the outflow to the fish pond were higher for dimethoate than for fenitrothion during both monitoring periods, reaching a maximum of 13% during the summer rice season.

Neither of the pesticides was detectable in the soil water collected at -1 DAT during spring and summer sampling seasons. Nevertheless, both pesticides were found in the soil water at 20 and 40 cm depth on the days of pesticide application, respectively. Higher concentrations of both pesticides were measured during the summer rice season which corresponds to the higher concentrations in the paddy water (Fig. 3). Fenitrothion concentrations peaked at both sampling depths on the day of application followed by a significant decrease towards the end of the monitoring period. On the contrary, dimethoate concentrations exhibited a significantly slower decrease. Therefore, the vertical transport with percolating water can be considered an important transport pathway for this pesticide.

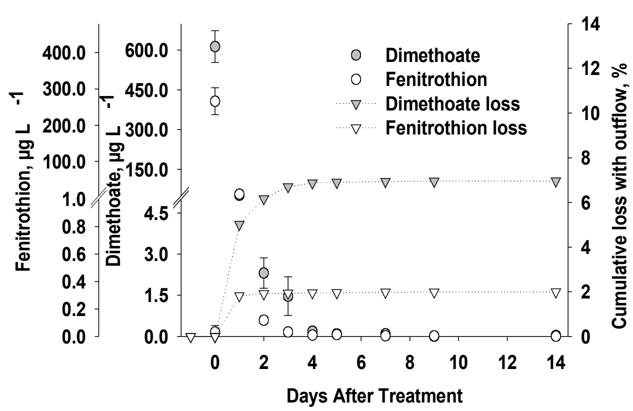


Figure 2. Pesticide concentrations in paddy water and respective cumulative losses with outflow during spring season.

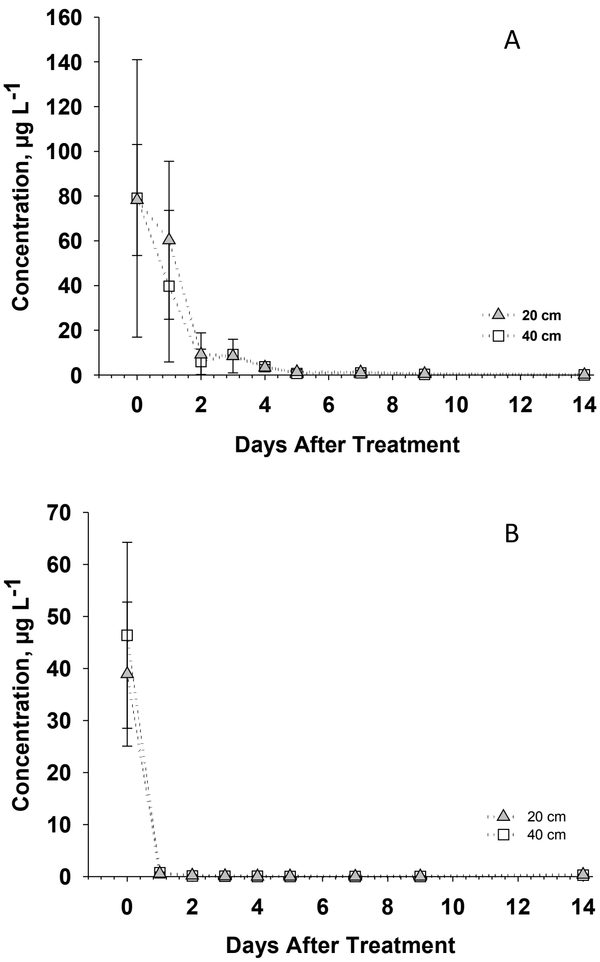


Figure 3. Pesticide concentrations of soil water extracted from 20 and 40 cm depth (data are shown for the summer season): dimethoate (A) and fenitrothion (B).

The measured concentrations of the pesticides in the fish pond water during the summer season are shown in Figure 4. The highest concentrations were observed during the day of application which indicates a potential breakthrough of pesticides through the paddy bunds and/or the deposition with spray drift. However, the maximum pesticide concentration observed in the pond water was lower than the acute toxicity criteria (LC50 of 40 and 2-10 mg $L^{-1}$) for the (here representative) Common Carp fish species.

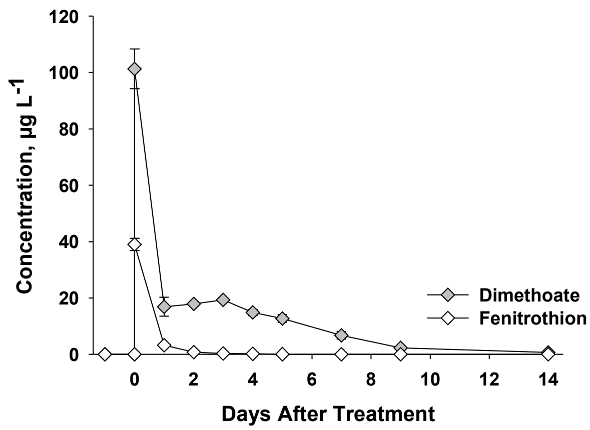


Figure 4. Concentration of dimethoate and fenitrothion in the fish pond.

## Summary and conclusion

The present study aimed at gaining knowledge of processes and key factors that govern the environmental fate of selected pesticides in the paddy field. Dimethoate and fenitrothion concentrations decreased rapidly in paddy water during two consecutive rice seasons. For dimethoate, transport with outflow and percolation were shown to be important processes in paddy fields. Considerable concentrations (>> 0.1 µg $L^{-1}$) were detected in the soil water during the first days of the monitoring period. Other important processes such as sorption to paddy sediments will be addressed in upcoming work.

Concentrations of pesticides in the pond water did not exceed acute toxicological endpoints for some fish species but could nevertheless pose a threat to the environment.

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