Fate of Pesticides in Combined Paddy Rice–Fish Pond Farming Systems in Northern Vietnam

Maria Anyusheva, Marc Lamers,* Nguyen La, Van Vien Nguyen, and Thilo Streck

During the last decades, high population growth and export-oriented economics in Vietnam have led to a tremendous intensification of rice production, which in turn has significantly increased the amount of pesticides applied in rice cropping systems. Since pesticides are toxic by design, there is a natural concern on the impact of their presence in the environment on human health and environmental quality. The present study was designed to examine the water regime and fate of pesticides (fenitrothion, dimethoate) during two consecutive rice crop seasons in combined paddy rice–fish pond farming systems in northern Vietnam. Major results revealed that 5 and 41% (dimethoate), and 1 and 17% (fenitrothion) of the applied mass of pesticides were lost from the paddy field to the adjacent fish pond during spring and summer crop seasons, respectively. The decrease of pesticide concentration in paddy surface water was very rapid with dissipation half-life values of 0.3 to 0.8 and 0.2 d for dimethoate and fenitrothion, respectively. Key factors controlling the transport of pesticides were water solubility and paddy water management parameters, such as hydraulic residence time and water holding period. Risk assessment indicates that the exposure to toxic levels of pesticides for aquaculture (Cyprinus carpio, Daphnia magna) is significant, at least shortly after pesticide application.

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The irrigation practices (continuous or intermittent automatic irrigation), water holding period (WHP), and excess water storage depth were found to control pesticide export from paddy fields in Asia, especially in monsoon rainy season (Inao et al., 2008; Phong et al., 2008; Watanabe et al., 2006, 2007). Other factors, such as solubility, hydrophobicity, and half-life, are related to pesticide properties.

Only a few studies have been published on the fate of pesticides in paddy rice systems in Vietnam. They typically focus on pesticide occurrence and distribution in conventional paddy rice systems in the large lowland areas of the Mekong and Red River deltas (Giger et al., 2003; Hung and Thiemann, 2002; Minh et al., 2007; Toan et al., 2007). In contrast, little information is available about the behavior and transport processes of paddy rice pesticides.

Extended research on pesticide fate is essential because pesticides are increasingly being used in remote areas in which good pesticide management practices have not yet been established. Furthermore, often the rural population directly relies on surface water and groundwater for drinking and domestic water supply (MARD, 2003). Lamers et al. (2011) have recently shown in the same study area that under the current management practices a considerable fraction of applied pesticide mass is lost from paddy fields to surface water and groundwater. Additionally, many rice farming systems there include fish ponds in which farmers raise fish to produce additional food and income. Irrigated water is often first used in the paddy fields, before it flows to fish ponds and further into rivers. A study of Steinbronn et al. (2005) conducted in the same area reported outbreaks of fish disease with symptoms of poisoning by organophosphate pesticides.

Despite the frequent occurrence of combined paddy–rice fish pond farming systems and their importance for the local population, no attempts have been made so far to explore pesticide fate and behavior of pesticides in such systems. To close this gap, we conducted a comprehensive experimental study using two pesticides of different physicochemical properties. While the present paper concentrates on pesticides in paddy water, pesticides in soil and sediments will be addressed in an upcoming paper.

Table 1. Selected studies on pesticide behavior in paddy water and pesticide losses to surface water in paddy rice fields. Solubility in water at 20°C (mg L⁻¹), application rate (AR, g a.i. ha⁻¹), maximum pesticide concentration in paddy water (Max, μg L⁻¹), field half-life (DT50, d⁻¹), cumulative loss to surface water (Loss, % of applied mass). NA = not available.

<table>
<thead>
<tr>
<th>Country</th>
<th>Pesticide</th>
<th>Solubility</th>
<th>AR</th>
<th>Max</th>
<th>DT50</th>
<th>Loss</th>
<th>Reference</th>
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<tr>
<td>Asia</td>
<td>phthalide</td>
<td>2.5</td>
<td>18†</td>
<td>10–25</td>
<td>NA</td>
<td>1.6–1.7</td>
<td>Shiota et al., 2006</td>
</tr>
<tr>
<td></td>
<td>simetryn</td>
<td>450</td>
<td>450</td>
<td>451–496</td>
<td>1.9–2</td>
<td>0.2–6.7</td>
<td>Phong et al., 2006</td>
</tr>
<tr>
<td></td>
<td>thiobencarb</td>
<td>16.7</td>
<td>1500</td>
<td>226–247</td>
<td>2.3–2.4</td>
<td>0.05–1.3</td>
<td>Phong et al., 2006</td>
</tr>
<tr>
<td></td>
<td>simetryn</td>
<td>450</td>
<td>450</td>
<td>950</td>
<td>1.75–1.9</td>
<td>2.4–17.4‡</td>
<td>Watanabe et al., 2006</td>
</tr>
<tr>
<td></td>
<td>bensulfuron-methyl</td>
<td>67</td>
<td>51</td>
<td>108</td>
<td>1.67–2.1</td>
<td>0.1–8.4§</td>
<td>Watanabe et al., 2006</td>
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<td>450</td>
<td>951</td>
<td>1.6–2.0</td>
<td>3.8–37‡</td>
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<td>1500</td>
<td>595</td>
<td>2.2–3.4</td>
<td>1.2–12 ‡</td>
<td>Watanabe et al., 2007</td>
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<td></td>
<td>mefenacet</td>
<td>4</td>
<td>450</td>
<td>498</td>
<td>2.0–2.6</td>
<td>2.7–35‡</td>
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<td>18†</td>
<td>31–34</td>
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<td>1.7–2.4</td>
<td>Maeda et al., 2008</td>
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<td>450</td>
<td>540–595</td>
<td>1.3–14</td>
<td>0.7–18.1</td>
<td>Phong et al., 2008</td>
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<td>thiobencarb</td>
<td>16.7</td>
<td>1500</td>
<td>294–304</td>
<td>2.1–2.2</td>
<td>0.1–3.7</td>
<td>Phong et al., 2008</td>
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<td></td>
<td>tricyclazole</td>
<td>596</td>
<td>400</td>
<td>21–24</td>
<td>11.4–12.1</td>
<td>0.5–0.9</td>
<td>Phong et al., 2009a</td>
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<td></td>
<td>imidacloprid</td>
<td>610</td>
<td>200</td>
<td>59–74</td>
<td>1.9–2.0</td>
<td>0.05–0.1</td>
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<tr>
<td></td>
<td>tricyclazole</td>
<td>596</td>
<td>160, 210</td>
<td>&gt;50</td>
<td>2.1–5</td>
<td>NA</td>
<td>Phong et al., 2009b</td>
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<td>168</td>
<td>4.9–5.6</td>
<td>20–16</td>
<td>NA</td>
<td>Lin et al., 2001</td>
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<td>epoxiconazole</td>
<td>7.1</td>
<td>252</td>
<td>3.7–0.9</td>
<td>11–16</td>
<td>NA</td>
<td>Lin et al., 2001</td>
</tr>
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<td>Europe</td>
<td>cinosulfuron</td>
<td>4000</td>
<td>70</td>
<td>39.5–41.5</td>
<td>NA</td>
<td>NA</td>
<td>Ferrari et al., 2001</td>
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<tr>
<td></td>
<td>pretilachlor</td>
<td>50</td>
<td>1125</td>
<td>936–1233</td>
<td>4.7–6.8</td>
<td>NA</td>
<td>Vidotto et al., 2004</td>
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<td>Portugal</td>
<td>molinate</td>
<td>1100</td>
<td>200–300</td>
<td>1570</td>
<td>NA</td>
<td>NA</td>
<td>Castro et al., 2005</td>
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<td>USA</td>
<td>diazinon</td>
<td>60</td>
<td>2.4§</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Moore et al., 2009</td>
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<tr>
<td>Brazil</td>
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<td>0.11</td>
<td>400</td>
<td>26.3</td>
<td>1</td>
<td>NA</td>
<td>de Melo Plese et al., 2005</td>
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<tr>
<td>Australia</td>
<td>clomazone</td>
<td>1102</td>
<td>-¶</td>
<td>202</td>
<td>7.2</td>
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<td>Quayle et al., 2006</td>
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<tr>
<td></td>
<td>molinate</td>
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<td>-¶</td>
<td>471–1042</td>
<td>2.7–4.7</td>
<td>NA</td>
<td>Quayle et al., 2006</td>
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<tr>
<td></td>
<td>thiobencarb</td>
<td>16.7</td>
<td>-¶</td>
<td>105–148</td>
<td>3.4–3.6</td>
<td>NA</td>
<td>Quayle et al., 2006</td>
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<td></td>
<td>benzofenap</td>
<td>0.13</td>
<td>600</td>
<td>39, NA¶</td>
<td>NA¶ &lt;1</td>
<td>NA¶</td>
<td>Quayle et al., 2007</td>
</tr>
</tbody>
</table>

† In mg m⁻² by aerial application.
‡ Calculated for different irrigation schemes: intermittent automatic irrigation/continuous irrigation
§ mL ha⁻¹ by amendment.
¶ Various treatments; therefore, calculation of single figure not possible.
Material and Methods

Study Site

The field study was performed in the Chieng Khoi Catchment, Yen Chau District, Son La province, northern Vietnam (20°37′00″ N; 106°4′60″ W). The area is mountainous, with elevations ranging from 300 to 1000 m above sea level. The climate is subtropical, with a rainy season from April/May to September/October, and relatively dry cold winters. Annual average temperature and rainfall are 21°C and 1200 mm, respectively. The peripheral upper parts of the study area are dominated by steep hill slopes, mainly covered by tropical monsoon semideciduous forests. In the lower parts of the watershed, hill slopes are cropped with maize and to some extent with cassava, whereas the valley floor is used exclusively for paddy rice cultivation (Oryza sativa L.). Between the upper and lower parts, there is a 26-ha reservoir that provides domestic and irrigation water. An irrigation system distributes the water from the main concrete channel to rice paddies, fish ponds, and further on to a river. There are two paddy rice seasons per year. The spring crop (SC) and summer–autumn crop (SAC) seasons take place in February through June and July through November, respectively.

Our experimental site (paddy field, 550 m²; fish pond, 150 m²) was located at the bottom-most position of a rice field toposequence. During both seasons (SC and SAC), the field was planted with a local sticky rice variety (Oryza sativa L. var. Nep87).

The characteristics of the Ap horizon (0.0–0.19 m) were as follows: pH (H₂O) 8.1; organic carbon content, 1.7%; total carbon content, 2.5%; total nitrogen content, 0.19% (all by mass); stone content, 10% (by volume); bulk density, 0.99 g cm⁻³. Soil texture was sandy loam (US Soil Taxonomy), with clay, silt, and sand mass fractions of 3.2, 41.2, and 55.5%, respectively.

Experimental Setup

Paddy Water Balance

Irrigation water was supplied by an irrigation channel. Paddy water first drained to the adjoining fish pond and later to the adjacent river (Fig. 1). Paddy field and fish pond were surrounded by reinforced high bunds to impede unwanted inflows from or outflows to the surrounding fields. During the experiment, the bunds were checked daily for leakages. Water flow was controlled in close cooperation with the field owner, according to the common local water management practice. To ensure an optimal water level for the rice crop, inflow and outflow were controlled by manually closing or opening the inlet weir (see next paragraph) to ensure continuous water ponding in the optimal range of 3 to 7 cm.

To measure water flow between the system elements (irrigation channel, paddy field, fish pond, and receiving stream), a V-shaped weir (irrigation channel to paddy field) and two HS-flumes (paddy field to fish pond and fish pond to receiving stream) were installed and equipped with automatic pressure sensors (EcoTech, Bonn, Germany). These were linked to an external data logger to record water heads every 5 min, enabling hourly and daily calculations of irrigation and discharge water volumes. The HS-flumes were chosen due to their robustness against siltation (Walkowiak, 2006). A weather station (Campbell Scientific Inc., Logan, UT, USA) was installed next to the experimental field. It provided standard data on air temperature, relative humidity, wind speed, and precipitation.

Conservation of mass for the paddy field requires:

\[ \frac{\Delta \text{PWD}}{\Delta t} = \text{Irr} + \text{Rain} - \text{Drain} - \text{ET}_c - \text{SWR} \]

where \(\Delta \text{PWD}/\Delta t\) denotes the change of paddy water depth (PWD) (mm) over time (d), Irr represents irrigation (mm d⁻¹), Rain denotes rainfall (mm d⁻¹), Drain is drainage flow from the paddy to the fish pond (mm d⁻¹), ET_c is crop evapotranspiration (mm d⁻¹), and SWF stands for the soil water fluxes (mm d⁻¹), comprising matrix infiltration, preferential field flow, and bund flow (Neumann et al., 2009). The PWD was manually measured at several locations in the field and the average value was used in Eq. [1]. Irr and Drain were calculated from characteristic stage–discharge relationships of the weir (installed at the paddy inflow) and flume (installed at the paddy outflow), respectively. The ET_c was calculated according to the FAO–56 method, using the Penman–Monteith equation (Allen et al., 1998). The reference evapotranspiration (ET) was calculated from the weather station data. As recommended by FAO–56, we used a value for the crop coefficient that represents the middle development stage of paddy rice. The SWF term was calculated from Eq. [1]. All terms were evaluated on a daily basis for the monitoring period from −1 to 14 days after application (DAT).

Fig. 1. Diagram of the combined paddy field–fish pond system.
Although we monitored the inflow and outflow of the fish pond, no measurements on the water level in the pond were performed. This does not allow us to provide a full water balance for the fish pond.

The residence time \( \tau \) (d) of the paddy water was calculated as the ratio of the total volume of water \( V_{\text{total}} \) (m\(^3\)) in the paddy field to the average inflow rate \( \vartheta \) (m\(^3\) d\(^{-1}\)):

\[
\tau = \frac{V_{\text{total}}}{\vartheta}
\]

In accordance with Comoretto et al. (2008), \( V_{\text{total}} \) was calculated as the sum of ponding water (avg. PWD times area of paddy field) and soil pore water, assuming a 5-cm active soil layer and average soil gravimetric water contents (measured as 38.5 and 41.8\% during SC and SAC, respectively).

Pesticide Application

We selected two insecticides with contrasting physicochemical properties (Table 2): dimethoate {\( O,O\)-dimethyl-S-[2-(methylamino)-2-oxoethyl]dithiophosphate} and fenitrothion [dimethoxy-(3-methyl-4-nitrophenoxy)-thioxophosphoran]. They were applied as ingredients of the commercial formulations Ofatox 400EC and Dimenat40EC, respectively. These formulations are included in the catalog of pesticides permitted for use in Vietnam (MARD, 2004).

A mixture of the aforementioned insecticides was applied on the paddy field on 6 May (SC) and 28 Aug. (SAC) 2008, 6 to 8 wk after transplanting. The pesticides were applied using a precalibrated backpack sprayer. In both seasons, we applied 400 g a.i. ha\(^{-1}\) dimethoate and 255 g a.i. ha\(^{-1}\) fenitrothion. The application rates were in line with manufacturer recommendations. The respective masses applied in the paddy field were 22 and 14 g of dimethoate and fenitrothion, respectively. They were calculated based on the amount of the formulation sprayed and respective concentrations of the active substances. In the period between transplanting and pesticide application, water was allowed to drain freely through the paddy field. On the day of pesticide application, the flow through the paddy field was stopped. Within the first day of ponding, water was again allowed to flow through the paddy by opening the weir/flume. Due to an insufficient closure of the drainage gates after pesticide application in SAC, pesticides and water briefly drained into the fish pond. Although not intended in this situation, free water drainage at pesticide application is in fact a local practice. Figure 2 depicts the general management scheme of rice cultivation during SC and SAC.

### Table 2. Selected physicochemical characteristics of the pesticides applied to the experimental paddy field: solubility in water (S), vapor pressure (VP), sorption coefficient \( K_{oc} \), degradation half-life (Deg50) due to hydrolysis (hd), photolysis in water (ph), and degradation in soil (s) (Tomlin, 2003). Lethal concentration for 50% of the population (LC50) is reported for 24-h exposure of *Cyprinus carpio* (Cc) and *Daphnia magna* (Dm).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>S (mg L(^{-1}))</th>
<th>VP (mPa)</th>
<th>( K_{oc} ) (cm(^3) g(^{-1}))</th>
<th>Deg50(_{\text{hd}}) (d(^{-1}))</th>
<th>Deg50(_{\text{ph}}) (d(^{-1}))</th>
<th>Deg50(_{\text{s}}) (d(^{-1}))</th>
<th>LC50(_{\text{Cc}}) (\mu)g L(^{-1})</th>
<th>LC50(_{\text{Dm}}) (\mu)g L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethoate</td>
<td>23,300</td>
<td>0.25</td>
<td>16.3–51.9</td>
<td>4.4‡</td>
<td>&gt;175</td>
<td>2–4.1</td>
<td>3680</td>
<td>0.01</td>
</tr>
<tr>
<td>Fenitrothion</td>
<td>14</td>
<td>18</td>
<td>1849</td>
<td>75</td>
<td>0.4–0.5¶</td>
<td>4–28</td>
<td>1500</td>
<td>11</td>
</tr>
</tbody>
</table>

† Derived from USEPA ECOTOX database (http://cfpub.epa.gov/ecotox).
‡ Hydrolyzed at pH 9, relatively stable at pH 7.
¶ Sakellarides et al. (2003).

Fig. 2. Rice development stages and paddy management practices during spring (SC) and summer–autumn (SAC) cropping seasons in 2008.
calculations of MED-Rice (2003). On sampling days, paddy water samples were taken from five spots in the paddy field and mixed together. Irrigation water was sampled weekly, whereas drainage from the paddy field was sampled depending on the opening and closure of the drainage gates during the corresponding sampling event (from 2 DAT and thereafter). Pond water was taken as a grab sample. During SC, the maximum water level of the pond was reached on the fifth day after pesticide application and the pond water was allowed to drain into the stream, initiating sampling from the drainage channel. During the summer season, however, the outflow to the stream was active throughout the monitoring period except on DAT 5 and 7.

**Analytics**

Filtered water samples were analyzed in duplicates, according to Ciglasch et al. (2005). Their procedure was modified as described in detail by Anyushova et al. (2011). In brief, in a first step, pesticides were concentrated by solid phase extraction (SPE) using Envi–Carb cartridges (Supelclean Envi–Carbopack, Supelco). After sorbent activation with a sequence of 8 mL of a mixture of CH$_2$Cl$_2$/CH$_3$OH (9:1, v/v), 3 mL CH$_3$OH, and 25 mL of a solution of ascorbic acid (10 g L$^{-1}$, pH set to 2 by HCl), 400-mL samples were sucked through the SPE cartridges at a flow rate of 5 mL min$^{-1}$. Afterward, the cartridges were rinsed with 2 mL of distilled water and air dried for 2 min. The SPE cartridges were stored frozen until further analysis. To elute pesticides from the cartridges, the 1.4 mL of CH$_3$OH (discarded), 10 mL of acetone, 15 mL of a CH$_3$Cl/CH$_3$OH mixture (9:1, v/v), and 30 mL of tert-buthylmethylether were used sequentially. After adding 10 μL of toluene, the eluates were evaporated almost to dryness. The residues were dissolved in 1 mL of a CH$_3$Cl/CH$_3$OH mixture (9:1, v/v) and used for quantitative analysis, using a matrix-matched calibration technique.

Pesticides were analyzed by capillary gas chromatography using GC HP 6890 (Hewlett-Packard) with a nitrogen–phosphorus detector (NPD) (Agilent Technologies), autosampler (7683 Series; Hewlett-Packard), programmed temperature vaporizer injection system (Unis PTV; JAS), and a capillary column “Rtx–OPesticides” (fused silica, 30 m × 0.25 mm; Restek). The PTV injection conditions were as follows: injection volume 1 μL, pulsed splitless injection at 125°C. After 0.2 min, the temperature was ramped up to 280°C at 250°C min$^{-1}$ and held for 25 min. Pulsed pressure and pulsed time were 207 kPa and 1.5 min, respectively. The oven temperature was initially set to 90°C for 2 min, raised to 300°C at a rate of 15°C min$^{-1}$, and held for 10 min. The total run time was 26 min. Helium was used as carrier gas at a constant flow of 2 mL min$^{-1}$. The conditions of NPD were as follows: temperature 310°C, air flow 60 mL min$^{-1}$, hydrogen flow 3 mL min$^{-1}$, and N$_2$ flow 17.5 mL min$^{-1}$.

Because the paddy water samples taken shortly after application (0–2 DAT) were assumed to be highly loaded with pesticides, the SPE cartridges might have reached the maximum retention capacity. To account for possible breakthrough of the analytes (Poole, 2007), SPE cartridges were linked in these cases (i.e., one cartridge was stacked on top of another, the bottom cartridge serving as a pesticide breakthrough trap) and water samples were sucked through the linked cartridges. In general, high concentrations of highly water soluble dimethoate in water samples caused its breakthrough through the first SPE cartridge. For example, maximum registered loss was 8.5% from the water samples in which dimethoate concentration was 674 μg L$^{-1}$. In contrast, the extraction efficiency for more hydrophobic compound fenitrothion was almost independent of concentration. The maximum breakthrough value was 0.01% at a concentration of 266 μg L$^{-1}$.

At a spiking level of 1 μg L$^{-1}$, the method recoveries of dimethoate and fenitrothion were 72 and 94%, respectively. The detection limit (LOD) was 0.01 μg L$^{-1}$ for both pesticides.

**Aquatic Risk Assessment**

The implemented risk assessment approach for an individual pesticide was based on the ratio concept between measured or predicted environmental concentration (MEC or PEC) to its respective toxicity, expressed as no-observed effect concentration (NOEC) or predicted no-effect concentration (PNEC) (European Commission, 2003):

$$R = \frac{\text{MEC or PEC}}{\text{NOEC or PNEC}} \geq 1$$

An $R$ value below unity indicates no risk. The corresponding ratios for dimethoate ($R_d$) and fenitrothion ($R_f$) were calculated for common carp (Cyprinus carpio) and daphnia (Daphnia magna), as representatives of fish and crustaceans. Because PNEC values are not specified for both pesticides, they were derived from: (i) the minimum values of the short-term acute toxicity endpoints (e.g., lethal concentration for 24-h exposure) (LC50) (Table 2) and (ii) an aquatic risk assessment factor of 1000, as recommended by the European Commission (2003). Therefore, the ratio $R$ was defined as follows:

$$R = \frac{\text{MEC or PEC}}{1000 \times \text{LC50}}$$

For comparison, we used the Vietnamese water quality standard for aquatic culture areas. This standard is 10 μg L$^{-1}$ for the sum of pesticide concentrations in water in areas under aquaculture (Ministry of Transport, 1995). Assigning this value as PEC to calculate $R$ for each individual pesticide can be considered a worst-case scenario.

**Data Processing**

The field water samples were analyzed in duplicates. The mean and standard deviations of the analytical replicates were calculated. This experimental setup, however, impeded any further statistical treatment aiming to provide uncertainty ranges on the results. The pesticide field half-lives (DT50) were derived by numerically fitting a first–order kinetic to measured pesticide concentrations in paddy surface water using the Berkeley Madonna V8.0 software (Macey et al., 2000). The reported DT50 values, therefore, represent the disappearance process and encompass both degradation and transfer processes.

To calculate pesticide loss from the paddy field and fish pond, the volume of respective surface discharge in hourly resolution was multiplied by the corresponding pesticide concentration in the outflow. The hourly pesticide concentrations were estimated by a piecewise linear interpolation as described.
in Potter et al. (2003) and Shih et al. (1998). In a few cases, outflow concentration data were not available and field water concentrations were taken as a surrogate for field outlet concentrations, assuming homogeneous spatial distribution of pesticide concentrations.

Regression analysis was performed with SPSS software V. 18 (PASW Statistics, 2009).

Results

Water Balance of the Paddy field

The water balance components of both monitoring periods are depicted in Fig. 3 and 4. The paddy water residence time was estimated to be 0.7 and 1.3 d in SC and SAC, respectively.

During SC, the major contribution to total paddy influx (190 cm) was irrigation (186 cm). Precipitation was low (4 cm). The fluxes of drainage water to the fish pond, evapotranspiration, and soil water were estimated to be 106, 7, and 78 cm, respectively. Over the monitoring period, the average (± SD) daily paddy irrigation and drainage flow rates were calculated as 12 ± 4 and 7 ± 2 cm d⁻¹, respectively. The average water depth was 7 ± 1 cm (Fig. 4). The calculated average SWF rate during the monitoring period was 5 cm d⁻¹. Average evapotranspiration was 0.5 ± 0.1 cm d⁻¹.

During SAC, the total flux of irrigated and drained water was significantly lower than during SC. Irrigation flux was 60 cm and precipitation 10 cm. Drainage, evapotranspiration, and soil water fluxes were 39, 7, and 22 cm, respectively. Hence, the total outflux in SAC was 68 cm. Over the monitoring period, average daily irrigation, evapotranspiration, drainage, and SWF flow rates (± SD) were estimated to be 4 ± 1, 0.4 ± 0.1, 2 ± 2, and 1 ± 2 cm d⁻¹, respectively. The average water depth of the paddy field was 3.0 ± 0.1 cm.

Pesticide Dynamics

Paddy Surface Water

Both pesticides were not detectable in irrigation water and paddy water before application. During SC, water samples taken shortly after application showed the highest concentrations of dimethoate (614 μg L⁻¹) and fenitrothion (266 μg L⁻¹). These values correspond to 88 and 60% of the total amounts of applied dimethoate (22 g) and fenitrothion (14 g), respectively. Both pesticides disappeared very rapidly from the paddy water. Two weeks after pesticide application (14 DAT), only 0.6% of applied dimethoate and fenitrothion were still measurable. The first-order kinetic was fitted to pesticide concentrations in paddy water (R² > 0.99 for both pesticides) (Fig. 5). Fenitrothion disappeared faster from paddy water than dimethoate. The calculated DT50 value of fenitrothion was 0.2 d, whereas that of dimethoate was 0.3 d.

During SAC, the dynamics of pesticide concentrations in the paddy water showed a pattern similar to that in SC. Shortly after application, the highest concentrations (1074 μg L⁻¹ dimethoate and 405 μg L⁻¹ fenitrothion) were measured in the
paddy water, corresponding to 81 and 48% of the applied mass, respectively. The concentrations of both pesticides then decreased rapidly by more than 98% in 24 h for fenitrothion and 48 h for dimethoate. Thus, 2 wk after application (14 DAT), concentrations of both pesticides were <1 μg L⁻¹. Similar as during SC, fenitrothion concentrations decreased faster than those of dimethoate. The first-order kinetic was fitted to the pesticide concentrations in paddy water, with coefficients of determination of 0.93 (dimethoate) and 0.99 (fenitrothion). Calculated DT50 values of fenitrothion and dimethoate were 0.2 and 0.8 d, respectively.

During SC, dimethoate and fenitrothion concentrations in the drainage water were 5.8 and 0.2 μg L⁻¹, respectively (2 DAT). The concentrations declined rapidly. At 14 DAT, both pesticides were below LOD. Pesticide concentrations in drainage were higher in SAC compared with SC. Dimethoate and fenitrothion concentrations were 50 and 0.8 μg L⁻¹ (2 DAT), and 0.5 and 0.01 μg L⁻¹ (14 DAT), respectively. Generally, concentrations in the drainage water were higher than those in the paddy water. With the exception of dimethoate during SAC, pesticide concentrations in drainage varied linearly with paddy water concentrations (Fig. 6).

In both seasons, considerable amounts of pesticides were transported by drainage water from the paddy to the fish pond (Fig. 5). The cumulative loss of dimethoate was higher than that of fenitrothion. During SC and SAC, respectively, 5 and 41% of applied dimethoate were transported to the fish pond. The respective fractions of fenitrothion were 1 and 17%.

Fish Pond Water

Before pesticide application, dimethoate and fenitrothion were not detected in the pond water. The concentration patterns of both pesticides are shown in Fig. 7. During SC, on the day of application (i.e., at 0 DAT), dimethoate and fenitrothion concentrations were 22 and 0.04 μg L⁻¹, respectively. A drop on 1 DAT was followed by an increase of dimethoate (16 μg L⁻¹) and fenitrothion (0.56 μg L⁻¹) pond concentrations on 2 DAT, after water had been discharged from the paddy field to the fish pond for about 1 d. Thereafter, values in the pond water continuously decreased. Similar patterns were observed during SAC. However, maximum concentrations of dimethoate (101 μg L⁻¹) and fenitrothion (39 μg L⁻¹), measured on the day of application, were higher than during SC (Fig. 7). Two weeks after application, dimethoate and fenitrothion respective concentrations declined to <1 μg L⁻¹ and below LOD during both cropping seasons.

On those days when the outlet from the fish pond to the river was in operation, the measured concentrations in the pond water and pond outlet water were similar (Fig. 7). The pesticide distribution in the pond water was homogeneous because the water was well mixed. This allows calculating the pesticide losses to the river from the measured concentrations in the pond. The losses to the river show pronounced seasonal differences. During SC and SAC, dimethoate losses were 0.1 and 7% of mass applied, respectively. The corresponding losses of fenitrothion were 0.01 and 3%.

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Risk Assessment for Aquaculture

The lower pesticide concentrations in pond water during SC caused shorter risk periods than during SAC. For fish, the PNEC of dimethoate was exceeded during 3 and 7 d in SC and SAC, respectively, whereas the PNEC of fenitrothion was not exceeded (SC) or only for 1 d (SAC). For daphnia, the risk period for fenitrothion was about 6 d in each cropping season, whereas that for dimethoate was equal to the whole monitoring period (R ≫ 1).

The R values associated with the Vietnamese surface water quality standard were significantly higher than unity, indicating risk for all pairs of pesticide and species. For common carp, R values were 3 and 7 for dimethoate and fenitrothion, respectively. For Daphnia magna, R was considerably higher than unity (1 × 10⁶ and 9 × 10², respectively).

Discussion

Water Balance of the Paddy Field

The high irrigation rate ensured an adequate water supply to the paddy field and adjacent fish pond. The average irrigation rates to the paddy during SC and SAC were higher than those reported for continuous irrigation elsewhere (Neumann et al., 2009; Watanabe et al., 2007). In Japan, for example,
Watanabe et al. (2007) measured an average rate of 1.6 cm d\(^{-1}\). The European Commission guidance document “MED–Rice” reports a value of 2.5 cm d\(^{-1}\) for Mediterranean conditions (MED–Rice, 2003). As a consequence of high irrigation rates, the water residence times in the Vietnamese paddy were short. Rainfall during the monitoring periods was slightly lower than (SC) or comparable to (SAC) the values recorded in Yen Chau during the respective periods of the years 2000 to 2006 (data not shown).

Working on paddy rice in Japan, Vu et al. (2005) found that the crop coefficient recommended by the FAO–56 method is appropriate for calculating ET\(_c\) in water budget studies. Our daily ET\(_c\) values are also in the range of values calculated for Thailand (0.3–0.4 cm d\(^{-1}\), Attarod et al., 2009). The total drainage accounted for 56% of the total inflow in both seasons. Similar values were reported from other rice-growing regions with other water regimes (Comoretto et al., 2008; Watanabe et al., 2007).

As studies in France and Italy have shown, the recharge from paddy fields to the aquifer is of minor importance, probably due to the existence of well-formed plow pans (Comoretto et al., 2005). According to MED–Rice (2003), average infiltration rates range from 0.1 to 1.1 cm d\(^{-1}\) in European rice-growing regions. In some regions of Asia, however, infiltration rates are typically higher, ranging between 0.2 and 2.4 cm d\(^{-1}\) (Chen and Liu, 2002; Tabbal et al., 2002; Watanabe et al., 2006, 2007). Bouman and Tuong (2001) reported seepage rates from paddy fields in tropical regions of up to 7 cm d\(^{-1}\). On the study site, average infiltration rates were in the upper range of reported values. The significance of SWF with regard to the water budget can be deduced from the fact that SWF has about the same magnitude as the drainage flux. Pesticide loss with SWF can therefore not be neglected but is beyond the scope of this paper. The results of our measurements with regard to soil water transport will be published in a companion paper.

**Pesticide Dissipation and Losses**

Although applied masses were similar, pesticide concentrations in paddy water on the day of application in SAC were twice as high as in SC. This finding can be explained with the fact that water depth in SAC was about half of that in SC. The fast disappearance of dimethoate from paddy water reflects several factors, besides drainage. The hydrolysis half-life values for dimethoate show that it is rather stable in aqueous media between pH 2 and 7 but hydrolyses under alkaline conditions (Table 2). Accordingly, the high dissipation rate is exclusively explainable neither by chemical nor photocatalytic degradation, which is reported to be minimal (Roberts, 1998). The high water solubility of dimethoate also casts doubt on the importance of sorption to soil as a key process. The rather hydrophilic dimethoate, however, can be transported both laterally with the discharge water and vertically with infiltrating water. Several studies show that it has a high leaching potential (Ciglasch et al., 2005; El Beit et al., 1977). Leaching of dimethoate can be considered the key process explaining the
pronounced differences between concentrations in the paddy surface and drainage water.

The fast disappearance of fenitrothion from paddy water in both cropping seasons partly reflects its low photolysis half-life. Thus, reported dissipation rates in paddy rice waters range from 11 to 19 h (Oubiña et al., 1996). Under laboratory conditions, however, the measured photodegradation rate of fenitrothion is even higher, with half-life values between 2.6 and 3.5 h (Derbalah et al., 2004). Giger et al. (2003) attributed a 100-fold concentration decrease within 2 d after application on paddy fields in Vietnam to high water flow rates and sorption to soil. Since hydrolysis is relatively slow between pH 4 and 9, fast dissipation can be attributed to photodegradation (DT50, 0.4–0.5 d, Maguire and Hale, 1980), sorption to soil (Table 2), and volatilization from surface water (DT50, 18 min, Sakellarides et al., 2003). Despite its hydrophobicity, losses to groundwater cannot be excluded entirely if a preferential flow in paddy fields is taken into account.

The pesticide losses in our study are in agreement with those reported by Watanabe et al. (2006), with a continuous irrigation scheme. In their work, short water residence time in paddies caused high pesticide losses via drainage water. The studies reported in Table 1 clearly indicate that the fraction of pesticides lost by drainage strongly depends on pesticide solubility. Our data from both cropping seasons are in line with these findings. The postapplication period, during which no water was discharged from the rice fields, strongly affects the pesticide amounts transported with the drainage water. Thus, in SAC, the incomplete turnoff of the outflow during application resulted in the discharge of highly polluted water to the fish pond. This period is referred to as “WHP” or “field closure period.” In Japan, Watanabe et al. (2007) recommended a WHP of 10 d after pesticide application. Under South European conditions, WHP varies from 2 to 7 d, depending on local management practices (MED-Rice, 2003). Quayle et al. (2007) reported a WHP of 28 d for the pesticide thiobencarb in Australian paddies.

Besides surface discharge, subsurface drainage may also have caused pesticide loss to the fish pond because high concentrations of pesticides were detected in pond water shortly after application also in SC. Another possible pathway of pond water contamination is spray drift.

Higher pesticide losses from the fish pond to the river in SAC compared with SC were partly caused by higher pesticide loads drained from the paddy water to the fish pond during respective periods. Another control, of course, was the period of no drainage from the fish pond to the river. A longer no drainage period in SC, i.e., smaller water fluxes due to lower water volumes (Fig. 1), resulted in lower pesticide loads to the river. The tradeoff, however, is a longer period of pesticide exposure in the pond.

Based on our data, it cannot be resolved to what extent the reduction of the pesticide loads within the sequence paddy–fish pond–river is due to sorption to the pond sediments or degradation in soil and surface water.

Risk Assessment

Pesticide concentrations in fish ponds connected to paddy fields depend mainly on pesticide solubility and water management scheme. In view of the second factor, the risk to species with relatively high PNEC (e.g., common carp, Table 2) can be significantly reduced by extending the WHP.

Cong et al. (2009) reported adverse effects for snakehead fish, a common fish species in paddy fields in Vietnam exposed to the organophosphorus pesticide diazinon. In their experiment, exposure to realistic environmental pesticide concentrations (16–350 μg L⁻¹) resulted in long-term inhibition of brain cholinesterase. Moreover, exposure at the highest concentration level resulted in 30% growth inhibition. Klemick and Lichtenberg (2008) reported that fish harvests in the Mekong Delta were affected by pesticide use in the paddy fields, although the harvest losses were economically insignificant.

To date, there are three legislative water standards in Vietnam concerning surface, coastal (recreation and aquaculture), and groundwater quality. However, only the first two standards provide maximum allowable pesticide concentration limits. Regarding aquaculture, an individual standard is set only for DDT. Other pesticides are referred to as “total pesticides.” In view of the differences in pesticides and their effects

![Fig. 7. Measured concentrations of dimethoate (D) and fenitrothion (F) in the pond water and pond outlet water (μg L⁻¹) in spring (SC) and summer–autumn (SAC) seasons. The error bars represent the standard deviations of analytical replicates. Corresponding predicted no effect concentration (PNEC) values for each pesticide are represented by dashed lines: PNEC(Dm)–dimethoate/fish, PNEC(Cc)–fenitrothion/fish, PNEC(Dm)–fenitrothion/Daphnia. Note: PNEC dimethoate/Daphnia is very low and therefore not shown. The arrows show the period when the drainage from the paddy field to the fish pond was turned on.](image-url)
on aquatic organisms, a fundamental improvement of the current standard is required.

It is important to note that the PNEC-based risk assessment procedure of the European Commission (2003) does not consider several specific pesticide effects, such as neurotoxicity, behavioral, and endocrine disrupting effects. Consequently, for substances exhibiting such effects (e.g., some insecticides), the estimates are likely to be too low; the risks may therefore be underestimated.

Conclusion

The persistence of both pesticides in paddy water was found to be short, despite their different chemical properties. The transport of rice pesticides to surface water is largely controlled by their solubility and paddy water management practice expressed by hydraulic residence time and water holding period. Consequently, pesticides with low water solubility should be preferred and WHP extended.

Under current management conditions, however, the pesticides in drainage water are the main source of surface water pollution in paddy rice areas.

The risk imposed on carp and crustacean species cannot be neglected. Moreover, our risk assessment procedure can only consider several specific pesticide effects, such as neurotoxicity, behavioral, and endocrine disrupting effects.

The high SWF observed suggests that pesticides leaching with soil water is another important loss pathway in the investigation system. However, to arrive at a complete balance, pesticide sorption to paddy and soil sediment must also be considered. Measured data and a discussion of the related processes will be presented in an upcoming paper.

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References


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