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ARTICLE

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Prediction of the environmental concentration of pesticide in paddy field and surrounding surface water bodies

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Abstract Pesticides are very important in European rice production. For appropriate environmental protection, it is useful to predict the potential impact of pesticides after application, in paddy fields, in paddy runoff, and in the surrounding water, by calculating predicted environmental concentrations (PECs). In this paper, a joint simulation is described, coupling a field-scale pesticide fate model (RICEWQ) and a transportation model (RIVWQ) to evaluate the potential for predicting environmental concentrations of pesticides in the paddy field and adjacent surface water bodies and comparing the predicted values with the monitoring data. The results demonstrate that the application of the calibrated field-scale RICEWQ model is a conservative method to predict the PEC at the watershed level, overestimating the observed data; the coupled RICEWQ and RIVWQ models could be adequately used to predict PECs in the surrounding water at watershed level and in the higher tier risk assessment procedure.

Keywords Pesticide fate model · Predicted environmental concentration · Tryciclazole · Rice field · Pesticide risk assessment

Introduction

At present, each year an estimated 2.5 million tons of pesticides are applied to agricultural crops worldwide. Pesticides generate large benefits in increased food production and pest-control. However, the proportion of pesticides applied reaching the target pest and/or weed has been found to be less than 0.3 and 99.7% went "somewhere else" in the environment (Pimentel and Levitan 1986; Pimentel 1995; van der Werf 1996). Therefore, increasing attention has been paid to the adverse impacts of pesticides on the environment, human health, and life-support systems.

Contamination of surface waters (SWs) and groundwater (GWs) by pesticides has been detected at various sites in Europe. The potential for contamination of water bodies is high in areas where rice is cultivated under flooded conditions. Irrigation increases the likelihood of transport of pesticides via runoff/drainage to surface water and via leaching to groundwater if the aquifers are not confined by impermeable soil layers (Boesten and van der Linden 1991).

Some rice-growing areas are in zones of high ecological value, including important natural areas in Spain, Portugal, and France, and others are close to towns and villages in countries such as Italy, Portugal, and Greece. Concentrations of some active substances in excess of 0.1×10^{-9} kg L^{-1} in SWs and in GWs (maximum residue level allowed for drinking uses) that are also used for drinking water supplies have been reported in Italy, Greece, Spain, and Portugal (Capri et al. 1999; Charizopoulos and Papadopoulou-Mourkidou 1999; Gomez de Barreda 1999; Cerejra 2000). Both represent a potential risk for non-target organisms including humans.

In such ecosystems measuring the water quality is very difficult and expensive. Models can significantly help in planning sampling and risk assessment. In fact, monitoring studies have shown that the water quality in paddy rice should be evaluated at a larger scale, e.g., the hydrographic basin. In these conditions, the variability in rainfall, topography, vegetative cover, and farming practice further complicates the problems of accurately predicting water runoff, soil erosion, and ultimately pesticide off-field transport into surface water (Wauchope 1978; Bobba et al. 2000). Therefore, for a correct risk

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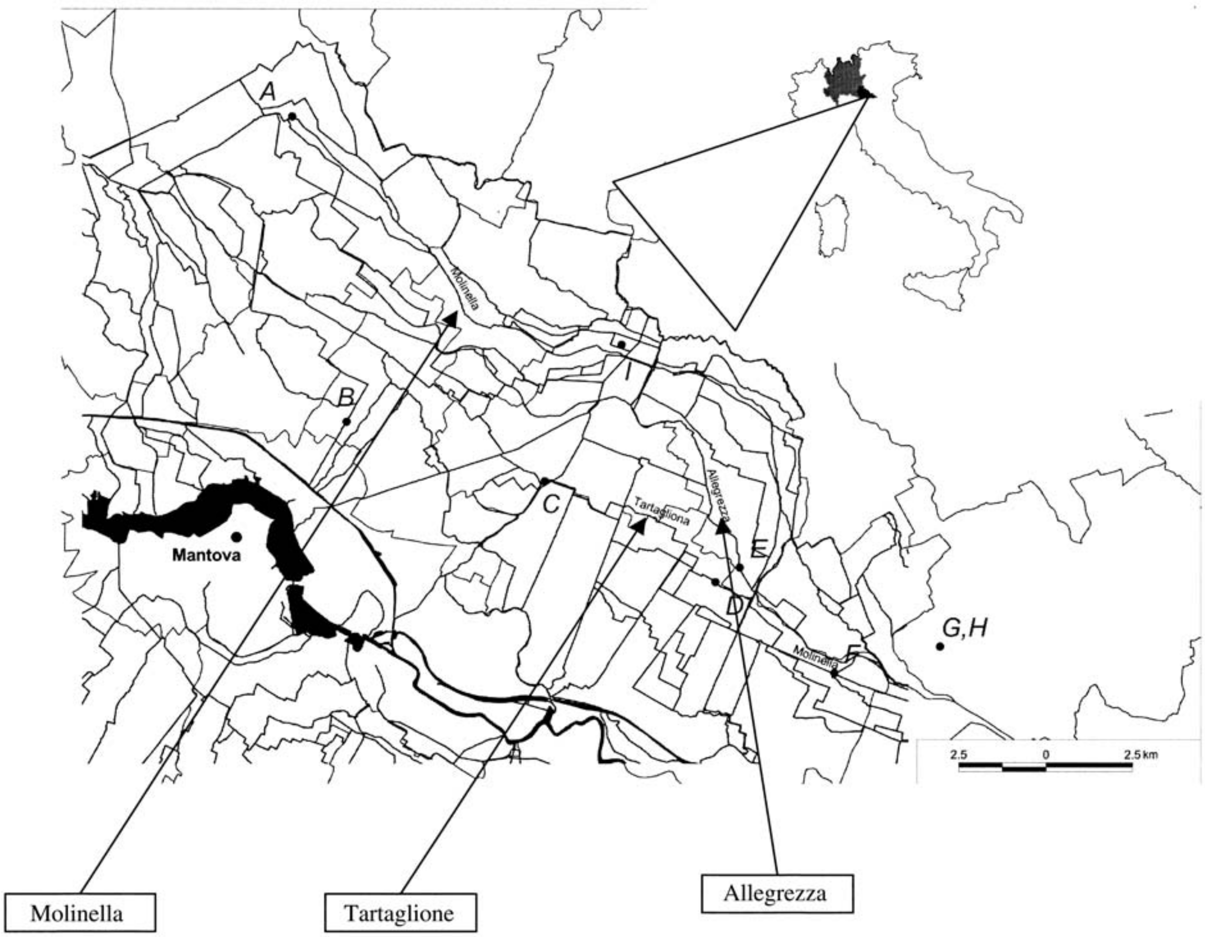

Fig. 1 Location of Mantova province (Lombardia region, northern Italy) with the main irrigation/drainage canals (*lines*) and sampling sites (*points*) of the study area: the paddy field scale are *G* and *H* (Rovigo province, Veneto region), the catchment scale (*A*, *B*, *C*, *D*, *E*, *F*, *I*). Sampling point at large scale (*L*, Po River) out of the figure on the *right side*

assessment in rice areas, a model for the prediction of pesticide concentrations in surrounding water body is desirable.

For rice crops, the most suitable model for predicting the pesticide concentration in surface water (PECsw) is RICEWQ, already tested in Italy in paddy conditions (Capri and Miao 2002; Miao et al. 2003a). However, RICEWQ has generally been used for simulating pesticide fate only under small-scale and edge-of-field conditions (e.g., paddy), where physical features, such as soil hydrological properties and slope, are relatively homogeneous.

The major objective of this study is to evaluate tools, e.g., mathematical models, for predicting environmental concentrations of pesticides in the paddy field and neighboring basin, including adjacent surface water bodies such as irrigation channels and streams.

Materials and methods

Field data and measurements

Field data were based upon a monitoring study carried out in Mantova Province (45°09′N, 10°12′E, altitude: 20 m), in northern Italy (Fig. 1). This study area is intensively cropped with rice mostly within the Fissaro Tartaro basin that covers 30,895 ha (Ente Nazionale Riso 2003). Three main streams, the Allegrezza, the Molinella, and the Tartaglione cross the entire drainage basin from northwest to southeast, and they collect water from minor irrigation streams which flow mainly from northeast to southwest, crossing the larger waterways. The White Water Canal (Canale delle Acque Bianche) runs horizontally along the southern part of the province from west to east, collecting water from streams coming from overlying land. This stream crosses through Veneto, flowing into the Adriatic Sea near the mouth of the Po River.

This basin is covered by 62 soil types. The soil properties (top horizon) in the basin strongly vary. The percent clay ranges from 1–47% (average 22%), the sand varies from 6–82% (average 38%), organic carbon ranges from 0–12.2% (average 3%) and pH varies from 6.0–8.3 (average 7.95). The sediment properties of the paddies and water bodies were slightly different and varying from silty-clay and 1.5% organic carbon in the paddy to sandy and less than 0.5% organic carbon in the water bodies.

In this basin covered by 62 soil types, sediment and water were sampled at three scale levels: (1) the small-scale sampling was performed in the inlet and outlet of a paddy field at two sampling locations (sites G and H in the basin); (2) the medium scale sampling was performed at seven sampling locations in a secondary drainage basin consisting of minor irrigation streams which flow into major irrigation channels or streams (sites A, B, C, D, E, F, I) (Fig. 1); and (3) large-scale sampling was performed at an intersection of the main streams before the waterways flow into the Po River (site L). At all these sampling points, surface waters were sampled twice, three days after pesticide application and after the paddy harvesting (3 months later) of the whole basin area in both 1999 and 2000. Water samples (2 L) were analyzed after liquid-liquid partition in methanol via GLC-ECD and confirmation of a positive sample in GLC-MS. The limit of detection (LOD) of tricyclazole in water was 0.1×10^{9} kg L^{-1} The pesticide used as the test compound was tricyclazole (5-methyl-1,2,4-triazolo[3,4-b]benzothiazole) as the commercial formulation Beam® applied by airplane on the 25 July (1999 and 2000). An application at the rate of 0.6 kg/a.i. ha (label dose) was estimated after a survey of the whole basin. Due to the crop sensitivity to fungus enemies the whole watershed was covered in one day by the aerial application of tryciclazole.

An average value of paddy water level in the basin was considered as well with an initial depth of around 5 cm, rising to 10 cm in June, 20 cm in July, and 30 cm in August. The estimated drainage rate was 2.59 cm day^{-1} ha^{-1}. Rice emerged on 20 May, matured on 20 July and was harvested on 3 September.

Scenario assumptions for the model applications

The model application in this paper is a good example of higher tier assessment in realistic agronomic conditions for Italian paddy management but under worst conditions for pesticide use (highest use dose, application in 1 day in all the fields). In the framework of the European registration procedures for pesticides, uniform principles have been established that describe in detail the decision-making criteria (Annex VI of Council Directive 91/414/EC). The uniform principles put great emphasis on the estimation of the exposure of groundwater resources and of non-target organisms to pesticides and the follow-up risk assessment based on exposure and toxicity. The use of validated models to calculate Predicted Environmental Concentrations (PECs) in SWs is the basis for assessing the potential environmental exposure also in the paddy field basin. Calculations are carried out following a tiered approach form unrealistic conservative scenario (tier 1) to realistic worst case scenario (tier 4).

Based on the realistic scenario (5-m stream size and 200-ha paddy area), the testing scenario-sets for the model simulations were developed to represent, as much as possible, the different scales monitored (small, medium and large). As the monitoring study was not performed for model validation purposes, the scenarios developed are similar and representative to the observed ones and they include the variability of the most important parameters influencing the model output.

The small-scale of the monitoring study (sites G and H) was used as the realistic scenario for the calculation of the PECsw running off from the edge paddy field scale. At this scale the RICEWQ model was suitable for the calculation. Two exercises were used: the first with a two-year simulation (1999 and 2000) at the two sampling points measured (sites G, H); the second one simulating the pesticide fate in the different soils available in the basin, totaling 62 soil types available in the basin (Figs. 2 and 3). When the model was applied using the different soils present in the basin, the simulated runoff concentrations were plotted as frequency distributions (Fig. 4). The output variables were the pesticide concentration in the first paddy runoff event after application (1st-concentration); the cumulative chemical concentration in paddy runoff during the first 28 DATs (days after treatment) (C-concentration); and the time-weighted average pesticide concentration in paddy runoff over the first 28 DATs (T-concentration).

At the medium and large scale, the RIVWQ model was used for the calculation of the PECsw in the stream. In the model exercise

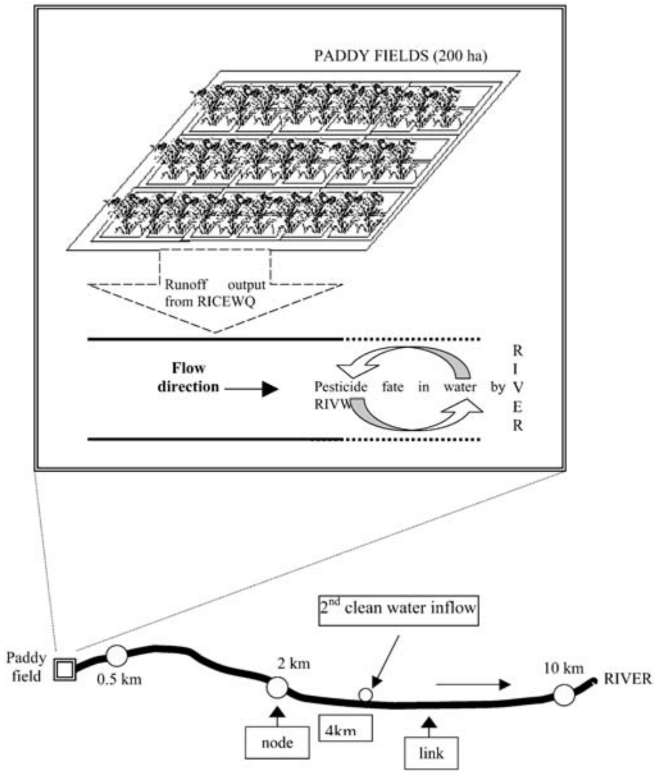

Fig. 2 Schematic representation of the coupled RIVWQ-RICEWQ models. The runoff output of RICEWQ from the paddy field is the pesticide input to RIVWQ that calculates PECsw in each node along the stream

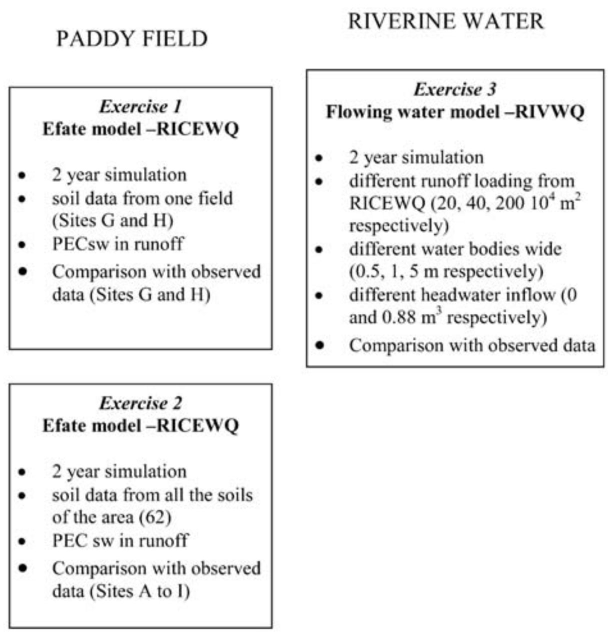

Fig. 3 The joint simulation strategies and scenario development. Scenarios developed are realistic representations of the monitoring studies

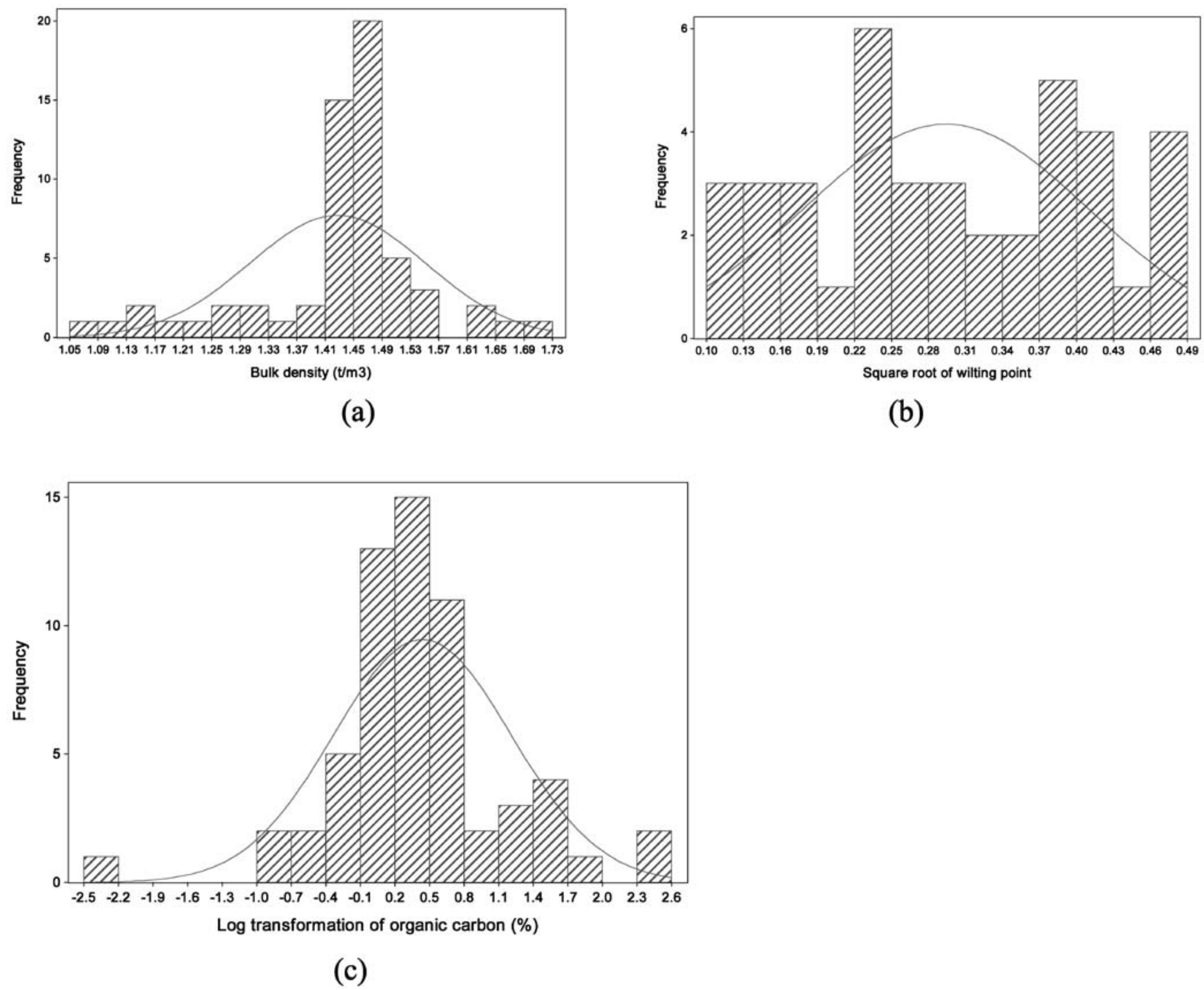

Fig. 4 The frequency distribution of **a** bulk density, **b** square root of Wilting Point, and **c** log-transformation of organic carbon% of 62 soil samples of the study area

(exercise 3) the main parameters of the stream (width, flow, loading) were varied stochastically (Figs. 2 and 3). The scenarios simulated 20, 40 and 200 ha paddy fields loading runoff water into an assumed stream, which was set to 0.5, 1 and 5 m wide, respectively. These scenarios were developed to calculate the PECsw at different distances along the water body (0.5, 2, and 10×10^3 m, respectively). The scenario reflects the field situation monitored in the field although the 200 ha paddy field with a 5-m-wide stream is closer to the larger scale monitored (Fig. 2). It is worth noting that the monitoring sites (A to L) for the medium and large scale are not exactly distributed along with the stream but relative to the position from the monitoring study (Sites G and H). A graphic representation of how the models work at basin level is presented in Fig. 3.

The prediction of each model scenario was compared against the observed data of small scale (paddy scale) and medium scales (basin level) for evaluating the accuracy of the models of RICEWQ and the coupling between RICEWQ and RIVWQ, respectively. Model simulations involved a linkage of two models. Pesticide application and dissipation in rice fields were simulated using RICEWQ version 1.61. Pesticide simulated by RICEWQ from paddy overflow or drainage, were stored as a daily time-series record. These pesticide masses and water volumes from RICEWQ simulations were converted into time-series input files that were read by RIVWQ and assigned to a node in RIVWQ. The pesticide loadings and water volume in the input files account for the area planted with rice and treated with the chemical draining to a particular node.

Model description

RICEWQ 1.6.1 simulates the water and chemical mass balance associated with the unique flooding conditions, overflows, and controlled water releases that are typical in a rice cropping system (Williams et al. 1999a). The model applies the principle of mass balance to simulate water volume changes in the paddy and chemical residues in three media of the rice paddy (rice foliage, water column and benthic sediments) from the point of chemical application. The equation is expressed as follows:

$$V\frac{\partial C}{\partial t} = \sum M_{influx} - \sum M_{outflux} - \sum M_{react} \qquad (1)$$

where V is the volume (m^3) of paddy water (i.e., the rice paddy (ha) multiplied by the depth of paddy water), ∂C is the change in concentration (10^{-6} kg m^{-3}) over time ∂t (s), $\sum M_{influx}$ and $\sum M_{outflux}$ are cumulative influx and outflow of chemical mass (10^{-6} kg) from the control volume, and $\sum M_{react}$ is the mass (10^{-6} kg m^{-2}) transformed from all processes. RICEWQ operates at a sub-daily time step, and integrates the hourly pesticide fate to provide daily outputs and mass balance of the chemical in three media: paddy rice foliage, water body and benthic sediments. The pesticide mass balance equations in water, sediment and foliage subecosystems are listed below:

$$\frac{\partial M_W}{\partial t} = M_{Wapp} + M_{wash} - M_{W\deg} + M_{Wtran} - M_{volat} - M_{out} \\ -M_{seep} - M_{bed} - M_{setl} + M_{resus} \pm M_{difu}$$

$$\frac{\partial M_S}{\partial t} = -M_{S\deg} + M_{Stran} + M_{bed} + M_{setl} - M_{resus} \pm M_{difus} \quad (3)$$

$$\frac{\partial M_F}{\partial t} = +M_{Fapp} - M_{F\deg} + M_{Ftran} - M_{wash} - M_{harv} \quad (4)$$

in which $\partial M_W, \partial M_S, \partial M_F$ are the change in chemical mass in water (10^{-6} kg 10^{-3} m^{-3}), sediment and foliage over time ∂t (s), M_{Wapp} is the mass of the applied pesticide not lost to drift and arriving at the water surface (10^{-6} kg m^{-2}), M_{Fapp} is the mass of the applied pesticide intercepted by foliage, M_{wash} is the mass washed off from foliage, $M_{W\deg}$, $M_{S\deg}$, $M_{F\deg}$ are the masses of pesticide degraded in water, sediment and foliage separately, M_{Wtran}, M_{Stran}, M_{Ftran} are the masses of metabolite formed by transformation of parent compound in water, sediment and foliage, M_{volat} is the mass volatilized across the air-water interface, M_{out} is the mass lost in overflow or drainage, M_{seep} is the mass lost in seepage, M_{bed} is the mass transfer to bed sediment by direct partitioning, M_{setl} is the mass transfer to sediment by particulate settling, M_{resus} is resuspended mass, M_{difus} is the mass diffusion between the water and sediment, and M_{harv} is the mass of pesticide removed after harvest (this mass may be removed from the ecosystem, left alone and available for wash off, or be applied to bed sediment) (all in units 10^{-6} kg).

RIVWQ 2.02 simulates the transport of organic chemicals in tributary stream systems based on the theory of constituent mass balance. Each simulation involves mathematically tracking the total mass of chemical residues in the tributary systems from the loading points. The mass balance is calculated along each link of the node defined in the scenario (Fig. 2) and governing equation applied to a control volume takes the following general form:

$$V\frac{\partial c}{\partial t} = \sum_{i=1}^{NC} (Q * c) + \sum_{i=1}^{NC} \left(E_L * A\frac{\partial c}{\partial x}\right) + \Delta s \quad (5)$$

in which V is the nodal volume (m^3) of a stream, c is chemical concentration (kg m^{-3}), t is the time step(s), i is the counter for links entering a node, NC is the number of links or channels entering a node, Q is the flow in a link (m^3 s^{-1}), E_L is the dispersion coefficient (m^2 s^{-1}), A is the link cross-sectional area (m^2), x is longitudinal distance (m), and Δs represents the rate of net addition of the constituent mass due to external input (e.g., paddy runoff) or internal transformation processes (e.g., backwater of the stream) (kg s^{-1}). Within each nodal volume, RIVWQ simulates transformation processes and simultaneously tracks the mass balance of each chemical in two media: the stream water column and benthic sediments.

RIVWQ can accommodate trapezoidal or rectangular cross-sections. Geometric rating curves are used to calculate cross-sectional areas and water depths as function of flow for several of the processes discussed above.

$$D = cQ^d \quad (6)$$

$$A = B \times D \quad (7)$$

$$Q = v \times A \quad (8)$$

in which v is stream water flow velocity (m s^{-1}), Q is stream water flow (m^3 s^{-1}), D water depth (m), c and d are the empirical and exponent coefficients of channel depth which can be estimated by user, B top width (m), and A cross-sectional area (m^2) (Williams et al. 1999b).

For solution scheme of stream water, an explicit upwind technique was employed to simulate chemical solution schemes. At a node i of stream, the chemical concentration equation is written:

$$c_i^{n+1} = c_i^n + \frac{\Delta t}{V}\left[\sum_{j=1}^{NC}\left(Q * c_{j2}^n\right) + \sum_{j=1}^{NC}\left(E_L * A * \frac{c_{j1}^n - c_{j2}^n}{\Delta x}\right)\right] \quad (9)$$

where n and n+1 are old and new time steps respectively, $\triangle t$ is the time step (s), Q is stream water flow (m^3 s^{-1}), c_i is the constituent concentration (kg m^{-3})at node i, c_{j1} and c_{j2} are the constituent concentrations at downstream and upstream nodes in a link respectively, j is the counter for links entering a node, and $\triangle x$ is the length (m) of a link.

Boundary conditions for the RIVWQ model are: optional inflow at the paddy runoff inflow nodes; optional concentrations at the paddy runoff inflow nodes; optional incremental inflows and stream features such as bed sediment sorption, dead storage, and base water flow along the nodal network. Here base flow is a constant water flow in a stream regardless of paddy runoff.

As for water balance, both RICEWQ and RIVWQ use a storage accounting model to calculate the water balance in the paddy or one node:

$$\frac{\partial S}{\partial t} = \sum I - \sum O \quad (10)$$

in which the water change in storage (m^3), ∂S, over time (s), ∂t, is equal to the cumulative sum of inflow water sources (m^3 s^{-1}), $\sum I$, minus the cumulative sum of outflow (m^3 s^{-1}), $\sum O$.

For a detailed description of the models of RICEWQ and RIVWQ, the reader is referred to Williams et al. (1999a, 1999b), Capri and Miao (2002), and Miao et al. (2003a).

Model parameterization

Tables 1 and 2 summarize the input variables/parameters required by the RICEWQ and RIVWQ models. Crop practice parameters (e.g., crop emergence and harvest date, pesticide application date and rate, maximum area of coverage of crop), water management parameters (the paddy water depth of initial and terminal irrigation, the depth of paddy outlet, the maximum irrigation and drainage rate, the depth of the active sediment layer), and pesticide properties (sediment partition coefficient, the pesticide degradation half-life in water) were obtained from field and laboratory measurements. For RIVWQ, the bed sediment physical texture, the organic carbon content (%), stream cross-section and flow velocity were determined with samples in the laboratory or monitored on the spot. Additional parameters were estimated from literature (Cheng 1990; Tomlin 1994; Williams et al. 1999a, 1999b; Villholth et al. 2000; Capri and Miao 2002; Miao et al. 2003b) or calculated through pedo-transfer functions.

Koc and half-life of tricyclazole in paddy water and sediment were derived from field experiments where crop practice, water management and weather conditions were similar to our scenario. K_d, the water/sediment partition coefficient (10^{-3} m^3 kg^{-1}), is calculated by the formula:

$$K_d = K_{OC} * O.C./100 \quad (11)$$

where $O.C.$ is the percentage of the organic carbon in the soil sample.

The wilting point (l) and the bulk density (10^3 kg m^{-3}) of paddy field and bed sediment, were derived from Baumer-ASW/EPIC of SOILPAR software using observed soil physical and chemical data of the study area (Donatelli et al. 1996; Fig. 4).

Table 1 Summary of main input parameters/variables used in RICEWQ

Data	Parameter	Units	Comments	Values
Weather	Rainfall	10^{-2} m	Daily	
	Potential evapo-transpiration	10^{-2} m	Daily and monthly, calculated with Penman-Monteith equation	
Crop practice	Emergence and harvest dates		From field experiment	May 20/Sept 3, 1999–2000
	Maximum area (crop coverage)	m^2	At maximum crop leaf area	0.98
	Deposition of pesticide residues at harvest		−1=left alone; −2= foliar residues removed from ecosystem; 0–100= tillage	−1
	Surface area of paddy	10^4 m^2	From field experiment	4
	Number of pesticide applications per year		From field experiment	1
	Pesticide applied date		From field experiment	July 25, 1999–2000
	Pesticide applied rate		From field experiment	0.60
	Application efficiency		From field experiment and estimated	0.97
Hydrology	Paddy water depth of initial and terminal irrigation	10^{-2} m	From field experiment	9.0/10.0 (June) 18.0/20.0 (July) 28.0/30.0 (August)
	Depth of paddy outlet	10^{-2} m	To control paddy water depth at which overflow occurs	10.0 (June) 20.0 (July) 30.0 (August)
	Maximum irrigation	10^{-2} m day^{-1}	From field experiment	2.00
	Maximum drainage	10^{-2} m day^{-1}	From field experiment	2.59
	Seepage rate	10^{-2} m day^{-1}	Literature (Ferrero 2001)	0.23
	Depth of active sediment layer	10^{-2} m	From field experiment	5.0
	Wilting point	1	Calculated with Baumer-ASW/EPIC methods	62 Soil-type values, see Fig. 2
	Bulk density	10^3 kg m^{-3}	Calculated with Baumer-ASW/EPIC methods	62 Soil-type values, see Fig. 2
	Suspended sediment concentration	10^{-6} kg L^{-1}	Empirically estimated	45.00
	Mixing depth to allow direct partitioning to bed	10^{-2} m	Empirically estimated	0.10
Pesticide	Numbers of transformation paths for simulating metabolites		Literature (Tomlin 1994)	1
	Water/ sediment partition	L kg^{-1}	Calculated by Koc and soil organic carbon (%)	62 Soil-type values, see Fig. 2
	Degradation rate in water, sediment and plant foliage	L day^{-1}	Calculated from DT50 (half-lives)	0.0231/0.0693/0.0693
	Pesticide solubility in water	l 10^{-6} kg L^{-1}	Literature (Tomlin 1994)	1,600
	Settling velocity	m day^{-1}	Empirically estimated	0.0
	Mixing velocity (diffusion)	m day^{-1}	Empirically estimated	0.0
	Number corresponding to parent chemical			1
	Number corresponding to metabolite chemicals			0

The following formula was utilized to estimate the porosity of the stream bed sediment (total pore space %):

$$T_t = \left[1 - \frac{BD}{D_p}\right] * 100 \tag{12}$$

where BD is the bulk density (10^3 kg m^{-3}) and D_p is the density of bed particles (10^3 kg m^{-3}). For most subsoil or bed sediments, the particle density (D_p) can be assumed to be $2.65{\times}10^3$ kg m^{-3} (Hall et al. 1977).

RIVWQ version 2.02 also includes the Muskingum routing option for flood routing through a reach. A linear model for Muskingum routing flow in a stream could be written as:

$$S = K[XI + (1 - X)Q] \tag{13}$$

where S is water storage of one node at a certain time (m^3), Q is stream water flow (m^3 s^{-1}), I is water inflow (m^3 s^{-1}) from the previous node of the stream, K and X are Muskingham coefficients (s) and fraction, respectively. Generally, the value of the Muskingum X coefficient ranges from 0 for reservoir-type storage to 0.5 for a full wedge, dependent on the shape of the modeled wedge storage. In this work, it was assumed to be 0.2. The Muskingham K coefficient is the time of travel of the flood wave through a stream reach. Muskingum K was estimated by dividing the length of the stream segment by an assumed stream velocity. In our instance, Muskingum K was set to the quotient of the maximum link length of 10 km divided by 0.35 m s^{-1} of the observed stream flow velocity. The cross-section of the stream is assumed to be rectangular and the discharge exponent coefficient in the stage-flow rating curve has been shown to be 0.4 for velocity and 0.6 for width (Williams et al. 1999b). The dead storage of the stream was set to 0.01 m at the head junction and 0.18 m at the maximum output point, with increments of 0.01 m, so that the scenario featured with dead storage of the stream revealed the impact of lake-side and rough stream-bed situations. The sediment sorption capability for pesticide was set with K_d values of 72.00 for 0.5- and 1-m-wide streams and 56.86 for the 5-m-wide stream. The sediment scouring routine was switched off since this research concentrated

Table 2 Summary of main input parameters/variables used in RIVWQ

Data	Parameter	Units	Comments	Values
Runoff inflow	Daily stream inflow	$m^3\ day^{-1}$	Paddy runoff output by RICEWQ	Runoff from paddy field of 20 ha /40 ha/200 ha
	Daily mass loading history	10^{-6} kg day^{-1}	Chemical mass runoff output by RICEWQ	Runoff from paddy field 20/40/200 ha
	Date to begin simulation		From field experimental	05/20/1999–2000
	Date to end simulation		From field experiment	09/30/1999–2000
Stream properties	Length of link (stream) downstream of junction I	10^3 m	From field experimental	0.5/2.0/10.0
	Incremental drainage area of junction	$10^6\ m^2$	From field experiment	0.2/0.4/2.0
	Dispersion coefficient of stream downstream of junction I	$m^2\ s^{-1}$	Literature (Williams et al. 1999b)	5.0
	Bottom width of stream downstream of junction		Estimated	0.5/1.0/5.0
	Stream geometry: 1=rectangular stream w/flow rating curve, 2=variable stream based on flow rating curve, 3=rectangular stream w/Manning equation		Literature (Williams et al. 1999b)	1
	B exponent coefficient in stage-flow rating curve		Literature (Williams et al. 1999b)	0.40
	D exponent coefficient in stage-flow rating curve		Literature (Williams et al. 1999b)	0.60
	Muskingum K coefficient		Literature (Williams et al. 1999b)	28,571
Hydrology	Muskingum X coefficient		Literature (Williams et al. 1999b)	0.2
	Depth of active sediment layer	m	Estimated	0.05
	Porosity of bed sediment		Derived from the measurement	0.490 (for 0.5- and 1-m-wide stream) 0.443 (for 5-m wide-stream)
	Bulk density of bed sediment	10^3 kg m^{-3}	From the observed	1.35 (for 0.5- and 1-m-wide stream) 1.48 (for 5-m-wide stream)
	Water/sediment partition	$10^{-3}\ m^3\ kg^{-1}$	Calculated by Koc and O.C.%	72.00 (for 0.5- and 1-m-wide stream) 56.86 (for 5-m-wide stream)
	Dead storage (depth)	m	Estimated	0.01—0.180, incremental is 0.01
	Constant or base flow	$10^{-3}\ m^2\ s^{-1}$of drainage area	From the measurement	0.88/0.0
	Suspended sediment concentration	10^{-6} kg L^{-1}	Estimated	45.00
Chemical properties	Number of chemicals simulated (parent and metabolite)		Literature (Tomlin 1994)	1
	Initial chemical concentration of constituents in stream sediment	10^{-9} kg L^{-1}	From the measurement	0.0
	Initial chemical concentration of constituents in stream water	10^{-9} kg L^{-1}	From the measurement	0.0
	Degradation rate in water, sediment and plant foliage	L day^{-1}	Calculated from DT50 (half-lives)	See Table1
	Pesticide solubility in water	10^{-6} kg L^{-1}	Literature (Tomlin 1994)	See Table 1
	Mixing depth to allow direct partitioning to bed	10^{-2} m		0.10

on PEC in surface water. Two equal paddy runoff inflows were used as inputs for the stream, one at the head junction and one 4×10^3 m downstream. The first carried chemical runoff and the second was clean, so it could be thought of as a paddy area without tricyclazole treatment. Three stream scales were defined to assess the impact of some key parameters including size of channel and paddy surface area (Table 3).

Paddy rice emerged on 20 May and was harvested on 3 September in both years. The simulation interval covered the entire growing season of the paddy from 20 May to 30 September, several days longer than the crop growing season. RICEWQ requires daily precipitation (10^{-2} m) and daily evaporation (10^{-2} m) during the simulation period. Evapo-transpiration is assumed to be equal to pan-evaporation (Williams et al. 1999a). The potential evapo-transpiration was calculated with the Penman-Monteith approach using the software RadEst version 3.00, which uses daily rainfall, maximum and minimum temperatures and relative humidity to estimate radiation and hence evapo-transpiration (Donatelli et al., 2000).

RICEWQ and RIVWQ models were loosely coupled. The systems are separate and linked by the exchange of information through input/output file exchanges (Pullar and Springer 2000). The daily-based paddy runoff generated by RICEWQ was regarded as the water and chemical inputs to RIVWQ to the head junction (node 1) (Fig. 2). Meanwhile, another clean water runoff (without pesticide) was input as water dilution from the point at the distance of 4 km from the head junction (Fig. 2).

Table 3 The key parameters applied in the PECsw calculation using RICEWQ coupled with RIVWQ

Variables[a]	Level 1	Level 2	Level 3[b]
Surface area of paddy field (10^4 m$^{2)}$	20	40	200
Size of channel (m)	0.5	1.0	5.0
The channel length from output points to channel head junction (10^3 m)	0.5	2.0	10

[a] Total of nine scenarios are generated and every scenario has three output points. With a 2-year dataset there will be 54 output results
[b] Realistic scenario: 200×10^4 m^2 paddy field and 5.0-m-wide stream

Evaluation of the model efficiency

Model performance was then assessed objectively by comparing the degree of agreement of the model with measurements (chemical concentration in paddy field and surrounding water) in the two-year data sets, and the following formula was applied to define the general model performance (Warren-Hicks et al. 2002):

$$PE = \frac{\sum_{i=1}^{n} X_i\{X_i = 1 \text{ if } P_i \geq M_j, \text{else } X_i = 0\}}{n} * 100 \qquad (14)$$

where PE is percentage exceedence, n=number of site-to-site rice paddies, M_j {j=1 to the number of field observations} is an individual field measurement, {i=1 to the number of site-to-site rice paddy iterations} is an individual model prediction, and $X_i$kkis an indicator variable.

The expected value of PE is 50%, indicating that half the model predictions are above the measurement, and half are below the measurement. Model accuracy is evaluated by examining the percentage of model predictions below and above the measured value. When the measured field value is shown to be in the general center of the predicted distribution, the model can be considered to be reasonably predictive. When the measured values occur in the lower or upper portions of the predicted distribution, the model can be considered less accurate (within the bounds of uncertainty) but acceptable given the variability in the model parameters. If the entire predicted distribution is above or below the measured value, the model can probably but not absolutely be considered too inaccurate for those given circumstances.

Results and discussions

The prediction of tricyclazole concentration in paddy water

The average results of the monitoring study are reported in the Table 4. Tricyclazole was detected in the surface water of the paddies just after the treatment then quickly disappearing in the following days. The irrigation system used-water inlet to the paddy field was also contaminated which might have been from the upstream field that had also been applied with tricyclazole. At the larger scale the dilution factor and the tricyclazole mitigation of paddy runoff due to the ecosystem characteristic reduced the residues below the detection limit. During the winter time the pesticide was always below the detection limit. Comparing these results with the simulation carried out in the exercise 1, the simulated edge-of-field tricyclazole concentration in paddy water runoff was 2.85×10^{-9} kg L^{-1} at 2 days after the treatment (DAT) and 1.5×10^{-13} kg L^{-1} (<LOD) at DAT 30, which are close to the observed values of 3.55×10^{-9} kg L^{-1} at DAT 2 and <LOD at DAT 93.

Table 4 The average experimental results of the monitoring study area at DATs 2 and 93 (10^{-9}kg l^{-1})

Sampling sites[a]	Summer	Autumn
G (inlet of paddy field)	1.05	0.00
H (outlet of paddy field)	4.60	0.00
A	0.00	0.05
B	0.00	0.00
C	0.00	0.00
D	0.55	0.00
E	0.65	0.00
F	1.10	0.00
I	1.30	0.00
L	0.15	0.00
The 95th percentile of all samples	1.89	0.00
The 85th percentile of all samples	0.09	0.00
Mean of all samples (excluding samples of sites G and H)	0.47	0.00

[a] Sites H and G were monitored for paddy field level, sites A, B, C, D, E, F, I and L were observed for basin level. The results are the 2-year mean concentration of all samples at each site

When the edge-of-field simulation was carried out including the soil variability (exercise 2) (Fig. 4) all the concentration distributions were in accordance with a log-normal or skewed log-normal distribution (Fig. 5), the cause is probably partially a result of the distribution of soil property values. The means of the 1st-concentration, C-concentration and T-concentration were 2.2×10^{-9}, 3.3×10^{-9}, and 0.8×10^{-9} kg L^{-1}, respectively (Table 5). However, the predicted pesticide concentrations in paddy runoff are sensitive to site-specific soil properties: the coefficients of variation (CV%) of the 1st-concentration, C-concentration and T-concentration were 48, 67 and 76%. The simulated values of 1st-concentration, C-concentration and T-concentration ranged from 0.09–5.0×10^{-9}, 0.09–12.8×10^{-9}, and 0.02–3.3×10^{-9} kg L^{-1} L, respectively. The 95th and 85th percentiles of 1st-concentration were 3.94 and 3.25×10^{-9} kg L^{-1}, which conform to the observed concentrations of 3.55×10^{-9} kg L^{-1} at DAT 2 at paddy level (the difference between the observed concentrations of sites H and G at DAT 2) (Table 4), but overestimated in comparison with the corresponding observed concentrations of 1.89 and 0.09×10^{-9} kg L^{-1} at DAT 2 at basin level, respectively (Table 4). However, at DAT 45, the predicted tricyclazole concentrations were lower than LOD, which agrees with the measurements of 0.0×10^{-9} kg L^{-1} at any DAT after harvesting.

The average observed concentration of all samples of the basin was of 0.47×10^{-9} kg L^{-1}, while most of the

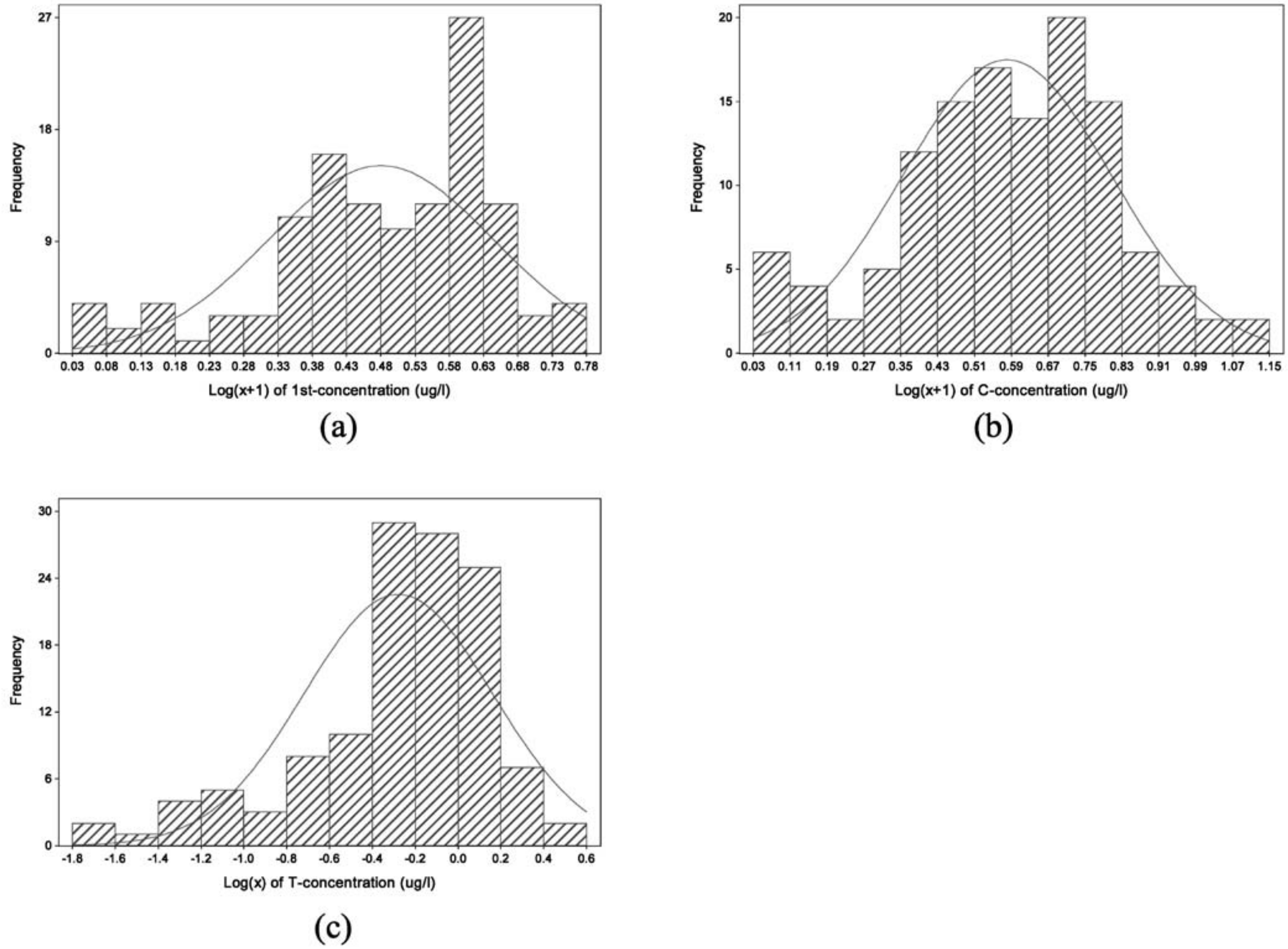

Fig. 5 The probabilistic distribution of the log-algorithmic transformation of site-to-site predicted **a** 1st-concentration, **b** C-concentration and **c** T-concentration with RICEWQ

Table 5 The predicted tricyclazole concentration in paddy water runoff with RICEWQ (10^{-9} kg L^{-1})

Indicators[a]	Mean	Min.	Max.	Standard deviation	CV%	85th Percentile	95th Percentile
1st-concentration	2.23	0.09	4.95	1.06	47.52	3.25 (0.09[c])	3.94 (3.55[b], 1.89[c])
C-concentration	3.34	0.09	12.78	2.23	66.57	4.96	7.47
T-concentration	0.76	0.20	3.30	0.58	76.36	1.21	1.84
Concentration at DATs 45	0.00143	0.00	0.35	0.00914	639.70	6.16E−05	0.00165

[a] Values in the table refer to the 2-year prediction at 62 site-specific paddy fields by RICEWQ (124 values)
[b] The observed value at paddy level
[c] The 85th and 95th percentile of measured values at basin level

predicted values in the paddy fields for all 62 soil types are higher than this value (PE=92.7%), which illustrates that the model of RICEWQ overestimates the chemical concentration at this scale. This lack of agreement occurred because the RICEWQ model is a water and pesticide mass balance model for paddy field not a flowing water model for basin level, so at this scale, very conservative results are expected.

The prediction of tricyclazole concentration in stream water

To predict chemical concentrations in a basin system, a river model such as RIVWQ is needed to take into account chemical decay, adsorption, infiltration, dilution, etc., in stream flow and bed sediment, such as was carried out in the exercise 3.

Figure 6 indicates the predicted tricyclazole concentration in stream flow with 200 ha of paddy surface area

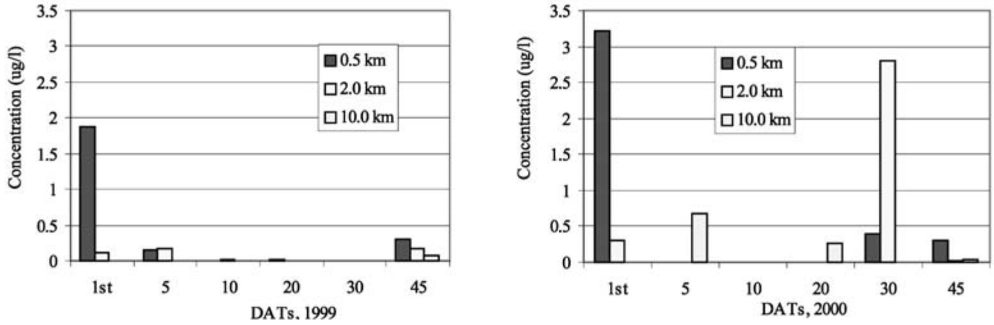

Fig. 6 The PECsw predicted with realistic scenario datasets (5-m stream size and 200-ha paddy area)

and a 5 m wide stream without considering the base flow (the constant water flow before paddy runoff inflow into the stream). On the day when runoff occurred, the 1st-concentration of tricyclazole at 0.5×10^3 m was 1.87 and 3.22×10^{-9} kg L^{-1} in 1999 and 2000, respectively. At the point of 2.0×10^3 m from the chemical input point, 1st-concentrations were 0.11 and 0.30×10^{-9} kg L^{-1} in 1999 and 2000, which are lower than the concentrations at 0.5×10^3 m. These values are more or less similar to the observed mean concentration, 0.47×10^{-9} kg L^{-1}, respectively (Tables 4, Fig. 6). At 10×10^3 m the predicted chemical concentration is lower than the LOD (LOD=0.1×10^{-9} kg L^{-1}) with an exception of 0.27×10^{-9} kg L^{-1} at DAT 20 in 1999. Additionally, at 10×10^3 m, the peak concentration appeared one or two days later than the peak at 0.5 km$\times10^3$ m and 2.0×10^3 m.

Figure 7 shows the distribution of the 2-year predicted 1st-concentration and time-weighted mean concentration over 28 DATs for all three levels of channel size, paddy surface area, and distances from the paddy field, respectively (54 simulations). The 1st-concentration and mean concentration both fit to a log-normal distribution.Table 6 shows that the CV% of the 1st-concentration and the mean concentration over 28 DATs was high (200% and 202% respectively). At 0.5×10^3 m, for instance, the 1st-concentration ranges from 0.16×10^{-9} to 21.8×10^{-9} kg L^{-1} in the 2-year simulation, and the mean concentration over 28 DATs ranges from 0.05–9.55×10^{-9} kg L^{-1}. At 10.0 km, the 1st-concentration ranges from 4.3×10^{-14} 10^{-9} kg L^{-1} (<LOD) to 1.8×10^{-8} 10^{-9} kg L^{-1} (<LOD) in the 2-year simulation, and the mean concentration over 28 DATs ranges from 5.2×10^{-16} (<LOD) to 4.13×10^{-9} kg L^{-1}. These results seem to illustrate that the channel size, paddy surface area, and distance from the paddy may strongly influence the PECsw.

A forward stepwise regression approach was applied to analyze the influence of channel size, chemical-treated area, base flow velocity and dilution on the calculation of PECsw in the adjacent surface water (Table 7; Snedecor and Cochran 1989; Keller et al. 2002). The result demonstrated that whichever measure of PECsw is used, the PECsw is negatively correlated to the channel size and distance from the pollution point at the 95% confidence level, and is positively correlated to the pesticide-treated area at the 99% confidence level. Annual weather also has a strong effect on mean concentration over 28 DATs and the time series concentration. In other words, the model is very sensitive to these parameters that need to be well measured or estimated for a correct PECsw calculation.

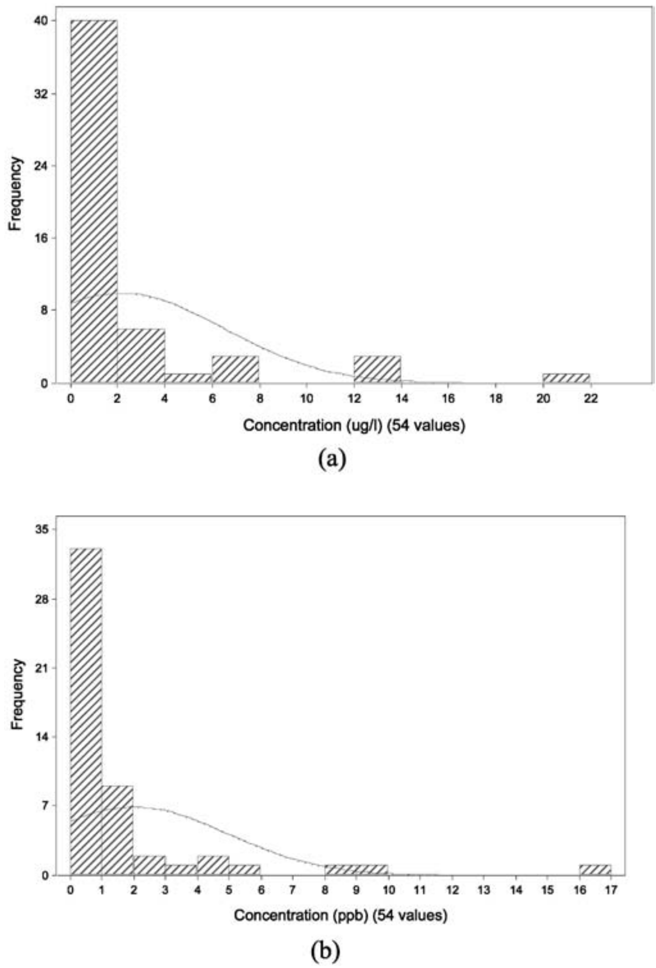

Fig. 7 The probabilistic distribution of the predicted **a** 1st-concentration (54 values) and **b** mean-concentration (54 values) in stream water

A comparison of Figs. 6 and 8 shows the effects of base flow and water dilution on PECsw in surface water. The base flow and dilution greatly reduced the PECsw in the stream, regardless of the stream sizes. When the observed base flow velocity of 0.35 m s^{-1} was used, the PECs at 0.5×10^3, 2.0×10^3 and 10×10^3 m were not

Table 6 The predicted tricyclazole PEC in surrounding surface water bodies of all scenarios (10^{-9}kg l^{-1}; see Table 3)

Indicators	Mean	Standard deviation	CV%	50th Percentile	85th Percentile	95th Percentile
1st-concentration	2.18	4.34	199.5	0.14	3.97 (0.09[a])	12.86 (1.89[a])
Mean concentration over 28 DATs	1.43	2.89	201.6	0.34	2.13	6.31

[a] The observed value at DATs 2 at basin level with 5-m-wide stream and 200 ha of paddy area

Table 7 Results of the forward stepwise regression coefficients of the main parameter set for the RICEWQ/RIVWQ simulations

Dependent variables (10^{-9} kg L^{-1})	Independent variables				
	Constant	Channel size (m)	Distances (km 10^3 m)	Paddy area (10^4 m^2)	Years variable[a]
1st-concentration	3.212(P<0.0011)[b]	−0.668(P<0.0040)	−0.409(P<0.0004)	0.024(P<0.0001)	–
Mean-concentration over DATs 28	5.866(P=0.0000)	−0.502(P<0.0020)	−0.219(P<0.0060)	0.016(P<0.0001)	−2.639(P<0.0001)
Time series concentration[c]	2.094(P<0.0007)	−0.207(P<0.0149)	−0.097(P<0.0169)	0.007(P<0.0005)	−0.787(P<0.0201)

[a] In the stepwise regression, the year variables of 1999 and 2000 are set to 1 and 2 respectively
[b] Values in brackets are F-test probability
[c] The chemical concentration (μg/l) of 1st-concentration at DATs 5, 10, 20, 30, 45

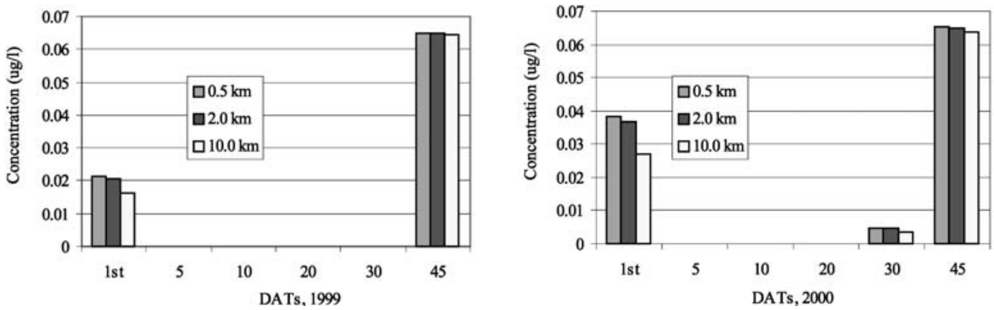

Fig. 8 The PECsw in the surface water bodies surrounding the paddy fields with base water flow

significantly different from each other because the pesticide is diluted faster than it can degrade or be adsorbed in the stream. These results confirm the monitoring study that chemical toxicity in water runoff may be greatly reduced upon dilution with pre-existing marsh water and mixing of the water column increased the rate of toxicity diminution significantly below the ecotoxicological end-points (Capri et al. 1999). That is the case with the test compound, tricyclazole, used in this study, and may be extended to many non-leaching pesticides used in the paddy fields. However, although the worst case scenario can guarantee a conservative exposure assessment of the pesticide tested, an additional two to three scenarios should be developed for covering the variability due to the different pedo-climatic and agronomic conditions.

Conclusions

In this paper, a pesticide fate model, RICEWQ alone and coupled with the RIVWQ model was used to assess the surface water contamination from a pesticide. Simulations were carried out to predict the environmental concentrations of pesticides in the paddy field, and adjacent surface water bodies (PECsw) and to compare both with the test compound tricyclazole. The results confirm that RICEWQ is a good model for the prediction of edge-of-field concentrations suitable for the risk assessment process such as in the registration procedure. Applying the RICEWQ model at a larger scale such as a basin is a conservative approach because it doesn't consider the effect of the adjacent water bodies such as an irrigation channel in enhancing the overall pesticide dissipation. However, this approach may be useful for delineating PECsw and developing estimates of vulnerability along the streams. When a more deterministic approach is needed, linking the RICEWQ model with RIVWQ is the most suitable approach because both processes are considered such as the fate at edge-of-field and the mitigation of PECsw at the basin scale. These tools when improved and when applied at basin level can be well used by a decision-maker for risk mitigation analysis. An improvement of the RIVWQ model is expected to include other aspects that mitigate the pesticide impact in the surface water bodies such as aquatic plants and suspended matter sorption and an improvement of the representation of volatilization and photolysis.

The model approaches presented in this paper may represent a useful scientific starting point for discussing and implementing the lower and the higher tier of the exposure procedure of this Directive.

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