

Pesticide exposure assessment in rice paddies in Europe: a comparative study of existing mathematical models

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Abstract: A comparative test was undertaken in order to identify the potential of existing mathematical models, including the rice water quality (RICEWQ) 1.6.4v model, the pesticide concentration in paddy field (PCPF-1) model and the surface water and groundwater (SWAGW) model, for calculating pesticide dissipation and exposure in rice paddies in Europe. Previous versions of RICEWQ and PCPF-1 models had been validated under European and Japanese conditions respectively, unlike the SWAGW model which was only recently developed as a tier-2 modelling tool. Two datasets, derived from field dissipation studies undertaken in northern Italy with the herbicides cinosulfuron and pretilachlor, were used for the modelling exercise. All models were parameterized according to field experimentations, as far as possible, considering their individual deficiencies. Models were not calibrated against field data in order to remove bias in the comparison of the results. RICEWQ 1.6.4v provided the highest agreement between measured and predicted pesticide concentrations in both paddy water and paddy soil, with modelling efficiency (EF) values ranging from 0.78 to 0.93. PCPF-1 simulated well the dissipation of herbicides in paddy water, but significantly underestimated the concentrations of pretilachlor, a chemical with high affinity for soil sorption, in paddy soil. SWAGW simulated relatively well the dissipation of both herbicides in paddy water, and especially pretilachlor, but failed to predict closely the pesticide dissipation in paddy soil. Both RICEWQ and SWAGW provided low groundwater (GW) predicted environmental concentrations (PECs), suggesting a low risk of GW contamination for the two herbicides. Overall, this modelling exercise suggested that RICEWQ 1.6.4v is currently the most reliable model for higher-tier exposure assessment in rice paddies in Europe. PCPF-1 and SWAGW showed promising results, but further adjustments are required before these models can be considered as strong candidates for inclusion in the higher-tier pesticide regulatory scheme.

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Keywords: rice paddies; RICEWQ 1.6.4v; SWAGW; PCPF-1; pesticide exposure modelling

1 INTRODUCTION

In recent years, mathematical modelling has proved to be a useful tool for pesticide regulatory purposes in Europe. Although detailed guidelines for the proper use of mathematical models are now available in Europe,^{1,2} these are not applicable to rice cultivation. In order to address this problem, the Standing Committee for Plant Health suggested the formation of a small group of experts, which was called Mediterranean Rice (Med-Rice).³ The Med-Rice group produced general guidelines for how risk assessment should be performed in rice paddies and developed a simple tier-1 spreadsheet which could be used for calculating predicted environmental concentrations (PECs) in groundwater (GW) and adjacent surface water (SW) bodies.³ Two standard European scenarios, corresponding to two different but representative situations, were

developed, including a sandy soil with a high infiltration rate, representing a situation vulnerable to GW contamination, and a clay soil with poor infiltration, representing a situation vulnerable to SW contamination.³

Within the remit of the Med-Rice group, the development of a more realistic model for calculating SW and GW PECs at tier-2 level was proposed. In order to address this issue, a more complex mechanistic model – the surface water and groundwater (SWAGW) model – was developed by Cervelli.⁴ The SWAGW model incorporates certain improvements in PEC calculations, including a more realistic partitioning of pesticide between paddy water and soil.⁵ A preliminary validation of the SWAGW model showed promising results.⁶ However, further evaluation is necessary in order for it to be readily implemented in the standard tiered risk assessment scheme.

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According to the tiered approach used for risk assessment in rice paddies (Fig. 1), when a potential risk is identified at the lower tiers (tiers 1 and 2), a more sophisticated mathematical model should be used in order to assess more realistically the potential exposure. However, only a few models are currently available for this purpose. The pesticide paddy field (PADDY) model and the pesticide concentration in paddy field (PCPF-1) model were both developed in Japan for simulating the environmental fate of pesticides in rice paddy systems.^{7,8} In comparison with PADDY, PCPF-1 has incorporated a routine to account for the daily fluctuation in paddy water depth and also for pesticide losses due to photolysis.⁸ PCPF-1 has been validated with field datasets obtained under Japanese conditions.^{9–11} However, its potential for use under European rice cultivation conditions has yet to be explored.

The rice water quality (RICEWQ) 1.6.1v model was initially developed in the USA for providing pesticide exposure assessment in rice paddies.¹² Both PCPF-1 and RICEWQ 1.6.1v could calculate chemical dissipation within the paddy and SW releases, but could not simulate pesticide leaching.¹³ To address this problem, a new rice water quality model – RICEWQ 1.6.2v – was developed by coupling the standard RICEWQ 1.6.1v and the vadose zone flow and transport model (VADOFT). The latter is a vadose zone transport submodel contained within the pesticide root zone model (PRZM), and it is used to simulate the fate of pesticides in the soil layers beneath the root zone.¹⁴ Validation of the RICEWQ 1.6.2v model under European conditions showed that it could be an effective tool for higher-tier exposure assessments in rice paddies.^{15–17} However, further improvements to its water management routines were required since

it did not allow irrigation and drainage to occur concurrently. Therefore, RICEWQ 1.6.2v could not closely simulate the continuous flow-through systems of irrigation/drainage which are common in rice-cultivating areas in Europe.^{15,16} Consequently, an improved model – RICEWQ 1.6.4v – was developed which allows irrigation and drainage to occur concurrently and also distinguishes the different degradation processes (hydrolysis, photolysis, microbial degradation) involved in the dissipation of pesticide in paddy water and soil. Validation of the new RICEWQ 1.6.4v model under European rice-cultivating conditions will be necessary in order for it to be implemented in the regulatory process.

The aims of the present study were (1) to validate improved or newly developed modelling tools such as RICEWQ 1.6.4v and SWAGW against field data, (2) to evaluate the potential of the PCPF-1 model for predicting pesticide dissipation and exposure under European rice-cultivating conditions and (3) to compare and contrast the efficiency of the models tested and to identify their deficiencies and limitations.

2 MATERIALS AND METHODS

2.1 Description of the SWAGW model

A computer program called SWAGW was developed in order to calculate PECs and time weighted averages (TWAs) of pesticides in paddy soil, paddy water, SW and GW systems associated with rice paddies.⁴ The basic assumptions and scenarios developed in tier 1 by the Med-Rice group formed the basis for the development of this tier-2 model. SWAGW could be used for calculating pesticide exposure according to the two standard scenarios developed in tier 1. However, SWAGW could also be used outside the

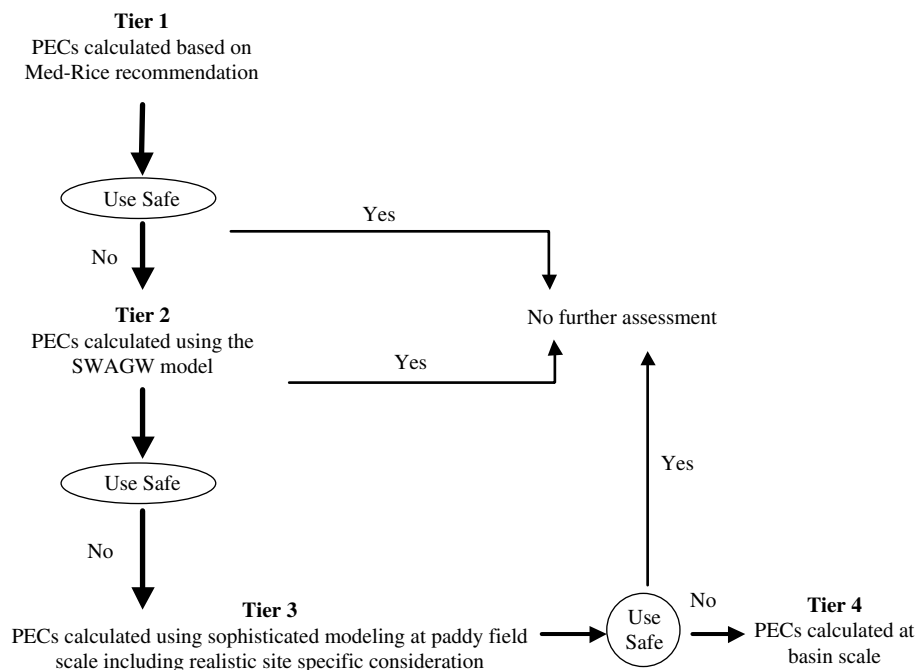


Figure 1. Standard tiered exposure assessment scheme applied for pesticides used in rice paddies.³⁵

framework of the two standard Med-Rice scenarios. Therefore, certain parameters, including the period of rice cultivation and paddy closure, the percolation rate, the depth of soil horizon beneath the rice paddy, the fraction of pesticide lost by drift and other hydraulic parameters such as the diffusion coefficient, constants a and b , and dispersivity, are allowed to be given values other than the scenario default ones.

As a first improvement of the assumptions for paddy water predictions, a more realistic adsorption is proposed to be modelled in tier 2.⁵ The amount of substance adsorbed on paddy soil is in constant equilibrium with its amount in paddy water, while in tier-1 the sorption occurs instantaneously and no interaction takes place thereafter. For GW, SWAGW assumes a miscible displacement behaviour of pesticide, a constant moisture content corresponding to saturation, and a constant addition of pesticide corresponding to its TWA in paddy water, both during paddy closure and paddy opening.⁵

In the relevant EU member states, rice cultivation is mainly divided into two distinct time periods of water submersion:

- a first period which follows pesticide application where the paddy field is maintained submerged by a static body of water and no irrigation or drainage is applied (closed rice environment);
- a successive second period, where irrigation and drainage occur concurrently, maintaining a constant water depth in the paddy field (open rice environment).

According to this practice, the SWAGW model simulates pesticide dissipation in rice paddies by dividing the simulation period into two different time-dependent systems: a closed paddy system [0–5 days after treatment (DAT)] and an open paddy system (5 DAT onwards).

2.1.1 Closed system

The conservation of mass in the paddy environment during the period of paddy closure is given by the following equation:

$$A_{Total} - A_{LL} = A_L + A_S + B_L \quad (1)$$

where A_{Total} (μg) is the total pesticide mass added in the paddy system, A_{LL} (μg) is the pesticide mass leached through soil, A_L (μg) is the pesticide mass dissolved in the paddy water, A_S (μg) is the pesticide mass adsorbed onto the paddy soil and B_L (μg) is the amount of residue formed. From these, A_S is given by the following equation:

$$A_S = K_2 (1 - e^{-\alpha t}) A_L \quad (2)$$

where K_2 is the adsorption ratio of pesticide in the soil. By substituting the different components of (1) and (2), the differential equation takes the form

$$\frac{dA_L}{dt} = -\frac{k_{2w} + k_{inf} + \alpha K_2 e^{-\alpha t}}{1 + K_2 (1 - e^{-\alpha t})} A_L \quad (3)$$

where k_{2w} is the daily degradation rate of pesticide in the paddy water, k_{inf} is a pseudo-first-order degradation constant taking into account the daily pesticide leaching, and α is a constant taking into account the time dependence of ratio K_2 . When $t \rightarrow \infty$, equation (2) is equal to $A_S = K_2 A_L$. At the initial time condition, $t = 0$, $A_L = A_0$, where A_0 (μg) is the initial amount of pesticide, and equation (3) takes the form

$$A_L = A_0 e^{\alpha t} [-K_2 + e^{\alpha t} (1 + K_2)]^{-\left(1 + \frac{k_{2w} + k_{inf}}{\alpha (1 + K_2)}\right)} \quad (4)$$

The TWAs in the time interval $0 \leq t \leq T_1$, where T_1 (d) is the end of the paddy closing period, are computed according to the equation

$$\begin{aligned} \text{TWA}_{A_L} = & \frac{A_0}{t(k_{2w} + k_{inf})} [-K_2 + e^{\alpha t} \\ & \times (1 + K_2)]^{-\left(1 + \frac{k_{2w} + k_{inf}}{\alpha (1 + K_2)}\right)} \\ & \times \left[K_2 - e^{-\alpha t} (1 + K_2) - (K_2 - e^{\alpha t} \right. \\ & \left. \times (1 + K_2))^{+\left(1 + \frac{k_{2w} + k_{inf}}{\alpha (1 + K_2)}\right)} \right] \quad (5) \end{aligned}$$

2.1.2 Open system

The conservation of mass in the paddy environment during the period of paddy opening is calculated by the following formula:

$$A_{Total} - A_{LL} - \overline{A}_L = A_L + A_S + B_L \quad (6)$$

where \overline{A}_L (μg) is the pesticide mass flowing out of the paddy owing to controlled drainage and calculated by the following formula:

$$\frac{d\overline{A}_L}{dt} = k_{out} A_L \quad (7)$$

where k_{out} is a pseudo-first-order degradation constant taking into account the daily water discharge from the paddy. By substituting the different components of Eqn (6), the differential equation takes the form

$$\frac{dA_L}{dt} = -\frac{k_{2w} + k_{inf} + k_{out} + \alpha K_2 e^{-\alpha t}}{1 + K_2 (1 - e^{-\alpha t})} A_L \quad (8)$$

The solution of Eqn (8), for the initial condition

$$t = T_1 \longrightarrow A_L = A_0^\circ \quad (9)$$

where A_0° (μg) is the pesticide mass at the end of the closing time T_1 , is therefore

$$\begin{aligned} A_L = & A_0^\circ e^{\alpha t} [-K_2 + e^{\alpha t} \\ & \times (1 + K_2)]^{-\left(1 + \frac{k_{2w} + k_{inf} + k_{out}}{\alpha (1 + K_2)}\right)} \quad (10) \end{aligned}$$

The TWAs are calculated from Eqn (11) for the time interval $T_1 \leq t \leq T_2$, where T_2 is the harvest time:

$$\text{TWA}_{A_L} = \frac{A_0}{(t - T_1)(k_{2w} + k_{\text{inf}} + k_{\text{out}})} \times \left[(-K_2 + e^{\alpha T_1} (1 + K_2)) \frac{k_{2w} + k_{\text{inf}} + k_{\text{out}}}{\alpha(1 + K_2)} - (-K_2 + e^{\alpha t} (1 + K_2)) \frac{k_{2w} + k_{\text{inf}} + k_{\text{out}}}{\alpha(1 + K_2)} \right] \quad (11)$$

2.1.3 Pesticide leaching to groundwater

The equations used to calculate PECs at different times and depths are derived from the general equation for the conservation of mass:

$$\frac{\partial c}{\partial t} = \text{Disp} \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - kc \quad (12)$$

where c is the concentration (μgL^{-1}), Disp is the dispersion coefficient of the pesticide in soil water ($\text{cm}^2 \text{d}^{-1}$), x is the soil depth (cm), v is the velocity of water flow (cm d^{-1}) and k is the degradation rate constant (d^{-1}). Equation (12) can be solved analytically owing to the constant values of Disp and v . In accordance with tier-1 assumptions, the depth of the soil horizon beneath rice paddies was set to 1 m and was divided into three horizons of 30, 30 and 40 cm.³ The properties of the different horizons differ in their ability to adsorb and degrade pesticides, and both adsorption and degradation of pesticides decrease by default factors of 0.5 and 0.3 in the second and third horizons respectively. A more detailed description of the SWAGW model can be found elsewhere.^{4,5}

2.2 Description of the PCPF-1 model

PCPF-1 is a lumped-parameter model that simulates the fate and transport of pesticides in the two compartments of paddy fields: paddy water and paddy soil.⁸ The paddy water compartment is assumed to be a completely mixed reactor having variable water depths. The paddy soil is also assumed to be a completely mixed compartment but with a constant depth of usually 1.0 cm where pesticide dissipation and transport processes occur under oxidative flooded condition. Both compartments are assumed to be homogeneous and to have uniform and unsteady chemical concentrations.

The water balance in the rice field is determined by the following components: irrigation, precipitation, overflow/controlled drainage, evapotranspiration, lateral seepage and vertical percolation. PCPF-1 provides daily concentrations of pesticide in the paddy water, considering that the dominant processes controlling pesticide dissipation in paddy water are: pesticide dissolution from granular formulation; pesticide desorption from paddy soil to water; volatilization; microbial

and photochemical degradation; and dilution or concentration of the pesticide dissolved in the paddy water by precipitation, irrigation or evapotranspiration. In the paddy soil layer, PCPF-1 also provides daily pesticide concentrations in the paddy soil, considering that adsorption/desorption, microbial degradation and leaching of pesticides to the subsurface soil beneath the surface soil layer are the major processes controlling pesticide dissipation in paddy soil. Pesticide mass balance equations in paddy water and surface paddy soil compartments were iteratively solved using the fourth-order Runge–Kutta method. The PCPF-1 model program was coded using Visual Basic[®] for applications in Microsoft Excel[®]. The input data consist of 23 measured parameters, together with the daily water balance of the paddy water and local meteorological data. The Macro program calculates and automatically creates output data and figures in a Microsoft Excel[®] file. A more detailed description of the PCPF-1 model is provided elsewhere.^{8,9,11}

2.3 Description of the RICEWQ 1.6.4v model

The RICEWQ 1.6.4v model is an improved version of the standard RICEWQ 1.6.1v and the more recent RICEWQ 1.6.2v. In comparison with the older versions, RICEWQ 1.6.4v incorporates an improved irrigation/drainage routine and considers losses of pesticide through drift. In addition, RICEWQ 1.6.4v distinguishes between the different degradation processes controlling dissipation of pesticide in paddy water and soil. Thus, the user is allowed to input separate rate constants for microbial, photochemical and hydrolytic degradation of pesticides in paddy water, unlike in the older versions where a lumped degradation rate constant of pesticide in paddy water was used. Similarly, degradation of pesticides in paddy soil can be separated into microbial and abiotic degradation, in contrast to the previous RICEWQ versions where a lumped degradation rate constant was used. RICEWQ 1.6.4v, using daily time steps, simultaneously tracks the mass balance of the chemical in the rice foliage, paddy water and paddy soil.

RICEWQ 1.6.4v considers all the major processes controlling the environmental fate of a pesticide applied in rice paddies, including chemical and microbial decay in water, paddy soil and foliage, pesticide loss through leaching, overflow or controlled drainage and volatilization. Chemical partitioning between paddy water and soil occurs through direct partitioning, diffusion, settling of chemical adsorbed on suspended paddy soil and resuspension of adsorbed paddy soil.

RICEWQ 1.6.4v was linked to the VADOFT model in order to provide GW PECs. RICEWQ 1.6.4v and VADOFT were integrated by transferring water and pesticide flux predicted as seepage by RICEWQ as prescribed boundary loadings into VADOFT. The VADOFT performs one-dimensional modelling of water flow and transport of dissolved contaminants in variably or fully saturated soil/aquifer systems. The

code employs the Galerkin finite element technique to approximate the governing equations for flow and transport. VADOFT can be operated as a stand-alone code or operated in conjunction with another surface model such as RICEWQ. In the latter case, boundary conditions at the interfaces of the modelled domains are established via model linkage procedures. VADOFT solves the Richards' equation, the governing equation for infiltration of water in the vadose zone. It can handle various transport processes, including hydrodynamic dispersion, advection, linear equilibrium sorption and first-order decay.¹⁴ The top 5 cm of the soil profile is represented by the active soil layer in RICEWQ. The remainder of the soil profile is represented as multiple compartments in VADOFT. The bottom of the active soil layer is the interface between the two subsystems represented by the two models. RICEWQ 1.6.4v is driven by daily weather data and operates at a subdaily time step to obtain the daily decay, runoff and leaching amount by integration. When irrigation and precipitation exceeds the depth of the paddy outlet, overflow occurs. When soil moisture in the paddy exceeds field capacity, percolation to VADOFT commences. As the paddy dries, soil moisture can decrease to wilting point through evapotranspiration. A detailed description of the model is given in the user's manuals for RICEWQ,¹² and elsewhere.^{15,16}

2.4 Datasets used for validation test

The two datasets used for the validation test of the models were derived by field studies conducted in the same rice-cultivating area in northern Italy. This area is the most northern rice growing area in Italy and is part of the Po Valley. Owing to its crop uniformity and the nature of agricultural management practices used, the study area was considered as representative of rice-growing systems in northern Italy. The surface soil layer (0–20 cm) of the test paddy was sandy loam, according to the USDA classification (sand 55.5%, clay 8.4%, silt 36.1%), with a pH of 5.5 and a 1.3% organic carbon content. In both experiments, rice was cultivated under submerged conditions and a continuous flow-through system of irrigation and drainage was applied in order to maintain a water depth in the test paddy of between 9 and 11 cm.

2.4.1 Cinosulfuron

The environmental fate of the herbicide cinosulfuron was evaluated in a field study undertaken in 1997 and 1998. Cinosulfuron 200 g kg⁻¹ WG (Setoff; Syngenta AG, Basel, Switzerland) was applied to the test paddy at a rate of 70 g active ingredient (AI) per hectare. The herbicide was applied to fields flooded with 16 cm water on 24 April 1997 and 19 April 1998. After the treatment, water circulation was halted for 14 days in 1997 and 22 days in 1998. Further interruptions of water circulation occurred from 22 to 30 DAT and from 52 to 47 DAT in 1997 and from 30 to 37 DAT and from 52 to 65 DAT in 1998. After

its application, the concentration of cinosulfuron was monitored in paddy water and paddy soil. Triplicate water samples were collected from the east, central and west parts of the studied paddy field immediately after the treatment, 2 DAT and every 7 days for 60 days. Triplicate paddy soil samples were also collected in the same manner, before and immediately after the treatment and 21, 42 and 64 DAT. A further soil sampling, 15 days after treatment, was made in 1998. Residues of cinosulfuron in water and sediment samples were analysed in an HPLC system with a diode array detector set at 220 nm. A more detailed description of the study is reported by Ferrero *et al.*¹⁸

2.4.2 Pretilachlor

The environmental fate of the herbicide pretilachlor was evaluated in a field study undertaken in 2001 and 2002. Pretilachlor 500 g L⁻¹ EC (Rifit; Syngenta AG, Basel, Switzerland) was applied to the test paddy at a rate of 1125 g AI ha⁻¹. Irrigation of the test paddy commenced 6 days before pretilachlor treatment. Herbicide was applied on 5 April in both years. At the time of herbicide application the water level in the test paddy was 12 and 9 cm in 2001 and 2002 respectively. After treatment, water circulation was halted for 23 and 18 days in 2001 and 2002 respectively. After its application, the concentration of pretilachlor was monitored in paddy water and paddy soil. Triplicate water samples were taken from the east, central and west parts of the paddy field before and immediately after treatment and 2, 8, 15, 21, 29, 36, 44, 57 and 74 DAT in 2001 and 1, 5, 7, 14, 21, 31, 45, 56, 73 and 84 DAT in 2002. Triplicate paddy soil samples were collected in a similar manner before and immediately after treatment and 2, 6, 9, 29, 36, 44, 57, 85 and 110 DAT in 2001 and 1, 5, 14, 31, 45, 56, 73 and 84 DAT in 2002. Residues of pretilachlor were analysed in a gas chromatograph equipped with an electron capture detector. A more detailed description of the study is reported by Vidotto *et al.*¹⁹

2.5 Model parameterization

Models were parameterized according to experimental measurements as much as possible. Owing to different calculation routines, SWAGW and PCPF-1 models could not consider all the different agronomic and water management practices that had been applied in the field studies. Generally, crop practice and water management parameters were obtained from field experiments. Pesticide decay rates in soil were calculated from DT₅₀ values reported in the literature for cinosulfuron²⁰ and pretilachlor,²¹ assuming first-order decay. Pesticide decay rates in paddy water were derived from the field experiment for cinosulfuron and pretilachlor.^{18,19} The default DT₅₀ values of 10 days in crop foliage, as set by the FOCUS GW group, were used for the calculation of pesticide decay rates in rice foliage.¹ The water/soil partition coefficients of pretilachlor²² and cinosulfuron²³ were derived from the literature. Volatilization routines

Table 1. Values used for the parameterization of the SWAGW model

Parameter	Cinosulfuron	Pretilachlor
Application rate (g ha ⁻¹)	70	1125
Degradation rate in paddy water (d ⁻¹)	0.0355	0.1023/0.1473
Degradation rate in paddy soil (d ⁻¹)	0.0346	0.06923
Adsorption coefficient K_{oc} (ml g ⁻¹)	115	542.3
Constant α (dimensionless)	0.085	0.013
Period of paddy closure after pesticide application (d)	14/22	23/18
Drift losses (% of applied amount)		2.77
Diffusion coefficient (cm ² d ⁻¹)		0.32
Constant a (dimensionless)		0.0075
Constant b (dimensionless)		10
Dispersivity (cm)		5
Percolation rate (cm d ⁻¹)	0.23	0.07/0.27
Organic carbon content (%)		1.3
Saturation volumetric water content (cm ³ cm ⁻³)		0.43

of the models were switched off since neither of the herbicides studied is considered volatile. In addition, the use of field-derived decay rates for both herbicides in paddy water includes volatilization losses. It should be mentioned that all participants in the modelling exercise agreed that blind model runs would be applied and any model calibration against the measured data would be avoided in order to remove any bias in comparing and contrasting the results obtained by the three models tested. A summary of the parameters used for the parameterization of the three models is presented in Tables 1 to 3.

2.5.1 SWAGW model

The SWAGW model was parameterized outside the framework of the two tier-1 scenarios developed by the Med-Rice group.³ This allowed its parameterization according to field experimentation, and the values used are shown in Table 1. It should be noted that SWAGW does not allow the application of more than one period of paddy closure. Therefore, the additional paddy closure periods that were undertaken after application of the test herbicides in the field studies were not considered in the parameterization of the model. Another limitation in the parameterization of SWAGW was that the model does not allow variation of the hydrological and soil textural parameters along the soil profile. Therefore, no variation in saturated volumetric water content, saturated hydraulic conductivity and soil texture with soil depth was considered in the GW predictions of the SWAGW model. Finally, SWAGW does not require the use of local meteorological data, unlike RICEWQ and PCPF-1 models which require daily precipitation (cm) and evapotranspiration (cm). The SWAGW

model assumes a fixed paddy water depth of 10 cm which is not allowed to fluctuate during the simulation period since precipitation or evapotranspiration are not considered.

2.5.2 PCPF-1 model

The PCPF-1 model has been used for simulating the dissipation of pesticides in paddy systems, assuming that pesticides are always applied as granules, which is a common practice in paddy fields in Japan. This original version of the PCPF-1 model effectively simulated pesticide dissipation in paddy fields cultivated under Japanese conditions.^{9–11} However, preliminary simulations of the current European datasets with the original PCPF-1 model showed that the model failed to predict the dissipation pattern of the two pesticides in paddy soil when they were directly sprayed onto paddy water. The PCPF-1 model could not predict the initial rapid build-up of pesticide residue in paddy soil during the first 5 days after application. Therefore, the algorithm of the PCPF-1 model was slightly modified more realistically to represent the fate of pesticides in paddy fields when they are sprayed onto paddy water.

Originally, the PCPF-1 algorithm allocated the total applied pesticide mass in both paddy water and paddy soil at a rate of pesticide dissolution based on the soil/water partition coefficient of the pesticide. Since pesticide granules settle and dissolve on the paddy soil surface, a significantly higher concentration of pesticide will partition onto the paddy soil compartment via percolation and diffusion. On the other hand, in cases where pesticides are sprayed directly onto drained or flooded paddies, which is the common practice in European rice cultivation, sprayed pesticide is initially dissolved into paddy water and then partitions into paddy soil via dissolution and diffusion/advection processes. Therefore, during and shortly after pesticide application, much smaller amounts of pesticide are expected to partition into paddy soil when the pesticide is applied via spraying as compared with granular application. Therefore, the original PCPF-1 algorithm was modified so as more realistically to represent the process involved in pesticide fate after spraying application. The pesticide dissolution was assumed to proceed only in the paddy water compartment. For the soil compartment, it was assumed that the transfer of pesticide from paddy water to paddy soil was achieved mainly by the vertical percolation of paddy water.

The parameters used for the parameterization of the PCPF-1 model are presented in Table 2. The period of simulation was 119 days for cinosulfuron in both years and 109 and 45 days respectively for the 2001 and 2002 simulations of pretilachlor. The simulation period of the year 2002 was only 45 days because the paddy water depth became 0 cm at 45 DAT and PCPF-1 was unable to simulate pesticide fate in completely drained paddy fields. In the absence of specific data on pesticide desorption, volatilization

Table 2. Values used for the parameterization of the PCPF-1 model

Parameter	Cinosulfuron	Pretilachlor
Maximum simulation period (d)	119	109/45
Time interval (d)		1
Application rate (g m ⁻²)	0.0070	0.1125
Paddy field area (m ²)		21 600
Pesticide water solubility (mg L ⁻¹)	4000	50
First-order desorption rate constant (phase 1) (d ⁻¹)		0
Mass transfer coefficient of pesticide volatilization (m d ⁻¹)		0
First-order photolysis rate constant (m ² kJ UVB ⁻¹)		0
Biochemical degradation rate constant in paddy water (d ⁻¹)	0.0355	0.1023/0.1473
Pesticide concentration in irrigation water (mg L ⁻¹)		0
First-order desorption rate constant (phase 2) (d ⁻¹)		0
Phase intercept concentration for desorption (mg L ⁻¹)		1
Factor for light attenuation by the crop (d ⁻¹)		0.0103
Depth of paddy soil (cm)		5
Bulk density (g mL ⁻¹)		1.5
Saturated volumetric water content (cm ³ cm ⁻³)		0.43
Biochemical degradation rate constant in paddy soil (phase1) (d ⁻¹)	0.0346	0.06923
Adsorption coefficient (L kg ⁻¹)	1.495	7.05
Biochemical degradation rate constant in paddy soil (phase 2) (d ⁻¹)	0.0346	0.06923
Phase intercept concentration for biochemical degradation (mg L ⁻¹)	0.1	0.1

and photolysis, the corresponding parameter values were set at 0. In addition, the degradation of both pesticides in paddy water and soil was assumed to follow single first-order kinetics, and thus the second-phase degradation rates were set to be the same as the first phase. The factor for daily light attenuation by the crop was obtained from previous studies.¹¹ For uniformity and comparison reasons, the depth of the paddy soil compartment was set at 5 cm. PCPF-1 calculates the depth of paddy water through its daily water balance routine, and thus it cannot simulate the environmental fate of pesticides in rice paddies in cases where paddy fields are drained.

2.5.3 RICEWQ 1.6.4v model

The RICEWQ 1.6.4v model was mainly parameterized using field observations (Table 3). In the absence of measured data for certain parameters, parameterization was done according to expert judgement. In the absence of specific DT₅₀ values for pesticide photolysis and chemical hydrolysis in paddy water, these parameters were set at 0 and a lumped DT₅₀ value was utilized for calculating the degradation rate of pesticide in paddy water. Similarly, in the absence of specific DT₅₀ values for microbial and abiotic degradation of the studied pesticides in paddy soil, the abiotic degradation was set at 0 and a lumped DT₅₀ value for paddy soil was utilized for calculating the degradation rate of pesticide in paddy soil. Earlier validation studies with the previous version of RICEWQ model (RICEWQ 1.6.2v) included minimal model calibration, and mixing depth for direct partitioning to paddy soil (VBIND) was the only parameter that was calibrated against the field data.^{15,16} Parameterization of VBIND (cm) of the RICEWQ 1.6.4v model in the present study was based on these previous calibration studies without any calibration applied in the current

exercise.^{15,16} This was done in order to remove any bias towards the RICEWQ model. Previous sensitivity analysis of the RICEWQ model has demonstrated the sensitivity of the leaching predictions of the model to the VBIND parameter.²⁴

Soil hydrological properties were calculated using point pedotransfers. Field capacity (cm³ cm⁻³), wilting point (cm³ cm⁻³) and bulk density (t m⁻³) were calculated with the soil parameters estimate software SOILPAR (Research Institute of Industrial Crops, Bologna, Italy) using Baumer-ASW/EPIC point pedotransfers, which require soil texture, pH and organic carbon content as minimal inputs in order to calculate field capacity, wilting point and bulk density.²⁵ The initial soil moisture content (cm³ cm⁻³) was set to field capacity. Irrigation and drainage rates were obtained from field observations. Percolation rates for both studies were calculated from the water balance, considering the total volume of water inflowing (cm) and outflowing (cm) from the paddy field, precipitation (cm) and evapotranspiration (cm) during the study period. In rice, evapotranspiration is assumed to be equal to pan evaporation, which is a valid assumption for an aquatic environment.²⁶ Therefore, the potential evapotranspiration was calculated with the Penman-Monteith approach using the global solar radiation estimate software RadEst 3.00 (Research Institute of Industrial Crops, Bologna, Italy).²⁷ This software uses daily precipitation, daily maximum and minimum temperatures and relative humidity and solar radiation to calculate the potential evapotranspiration.²⁷

The VADOFT submodel was parameterized according to field measurements and literature values, as shown in Table 4. For reasons of comparison with the SWAGW model, the soil profile beneath the test paddy was considered to be 1 m deep and was divided into three soil horizons of 30, 30 and 40 cm. According

Table 3. Values used for the parameterization of the RICEWQ 1.6.4v model

Parameter	Cinosulfuron	Pretilachlor
Emergence date	12/4/1997 & 6/4/1998	10/5/2001 & 6/5/2001
Harvest date	9/9/1997 & 1998	24/7/2001 & 7/8/2002
Maximum crop coverage at maturation time		0.90
Depth of paddy outlet (cm)	17.0	13.0
Irrigation rate (cm d ⁻¹)	6.0	4.5
Drainage rate (cm d ⁻¹)	2.0	3.0
Percolation rate (cm d ⁻¹)	0.23	0.07/0.27
Depth of active soil layer (cm)		5.0
Wilting point (cm ³ cm ⁻³)		0.05
Bulk density (g cm ⁻³)		1.50
Concentration of suspended paddy soil (mg L ⁻¹)		45.0
Mixing depth for direct partitioning to paddy soil (VBIND) (cm)	0.1	0.04
Settling velocity (m d ⁻¹)		0.0
Mixing velocity (m d ⁻¹)		0.0
Drift losses (% of applied rate)		2.77
Adsorption coefficient (ml g ⁻¹)	1.495	7.05
Decay rates in paddy water (d ⁻¹)	0.0355	0.1023/0.1473
Decay rates in paddy soil (d ⁻¹)	0.3466	0.06923
Decay rate in foliage (d ⁻¹)		0.06923
Water solubility (mg L ⁻¹)	4000	50

to the field measurements, the first two soil horizons were uniform as far as soil texture (sandy loam) and hydrology were concerned, unlike the third horizon (60–100 cm) which was a gravel-based loamy horizon with different hydrological characteristics. In accordance with Med-Rice recommendations, a reduction in pesticide degradation with soil depth was applied.³ However, pesticide adsorption and thus the retardation coefficient for each soil layer was adjusted according to the measured organic carbon content of the separate soil horizons. The size of the model layers [nodal space Δz (cm)] and the time step value (Δt) (s) were set according to the Peclet number and Courant number criteria:

$$\frac{\Delta z}{\alpha_L} \leq 4 \tag{13}$$

where α_L is the longitudinal dispersion (cm). The Darcy velocity (cm d⁻¹) and the retardation coefficient

for the two soil horizons were calculated with the following equations:

$$q = K_m \frac{H_i}{\sum L_i} \tag{14}$$

$$R = 1 + \frac{K_d \rho}{\theta_s} \tag{15}$$

where q (cm d⁻¹) is the Darcy velocity, K_m (cm d⁻¹) is the mean saturated hydraulic conductivity, H (cm) is the hydraulic head, L (cm) is the length of each soil zone, R is the retardation coefficient (dimensionless), K_d (cm³ g⁻¹) is the adsorption coefficient, ρ is the soil bulk density (g cm⁻³) and θ_s (cm³ cm⁻³) is the saturated water content. Input parameters for the VADOFT model, including saturated hydraulic conductivity (cm d⁻¹), saturated water content (θ_s , cm³ cm⁻³), residual water content (θ_r , cm³ cm⁻³) and van Genuchten model parameters α , β and γ ,

Table 4. Physicochemical and hydraulic parameters of VADOFT for both datasets

Parameter	First horizon (0–30 cm)	Second horizon (30–60 cm)	Third horizon (60–100 cm)
Saturated hydraulic conductivity, K (cm d ⁻¹)	106.1	106.1	712.8
Saturated water content, θ_s (cm ³ cm ⁻³)	0.41	0.41	0.43
Residual water content, θ_r (cm ³ cm ⁻³)	0.065	0.065	0.045
Effective porosity, φ (dimensionless)	0.345	0.345	0.385
Residual water phase saturation, S_{wr} (dimensionless)	0.159	0.159	0.104
Leading coefficient of saturation versus capillary head, α (cm ⁻¹)	0.075	0.075	0.145
Power index of saturation versus capillary head relationship, β (cm ⁻¹)	1.89	1.89	2.68
Power index of saturation versus capillary head relationship, γ (cm ⁻¹)	0.47	0.47	0.62
Longitudinal dispersion, α_L (cm)	2.5	2.5	5.0
Retardation coefficient, R (dimensionless)	9.14 ^a /26.8 ^b	9.14/26.8	2.74/8.04
Darcy velocity, V (cm d ⁻¹)	465.7	465.7	465.7

^a Retardation coefficient value for cinosulfuron.

^b Retardation coefficient value for pretilachlor.

were derived using the PRZM 3.0 user's manual for the different porous materials of the soil horizon.¹⁴ Other parameters such as effective porosity (ϕ , dimensionless) and residual water phase saturation (S_{wr} , dimensionless) were calculated with the following formulae:

$$\phi = \theta_s - \theta_r \tag{16}$$

$$S_{wr} = \frac{\theta_r}{\theta_s} \tag{17}$$

2.6 Statistical analysis

Model performance was objectively assessed by comparing the graphical agreement between predicted and observed concentrations of both pesticides in paddy water and paddy soil. In addition, the goodness of fit was assessed using appropriate statistical indices including root mean square error (RMSE) and modelling efficiency (EF):

$$RMSE = \frac{100}{\bar{O}} \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}} \tag{18}$$

$$EF = \frac{\sum (O_i - \bar{O})^2 - \sum (P_i - O_i)^2}{\sum (O_i - \bar{O})^2} \tag{19}$$

where P_i and O_i are the predicted and observed values respectively, \bar{O} is the average of the observed values and n is the number of observations. In general, the lower the RMSE, the higher is the agreement

between measured and predicted data.²⁸ In contrast, the optimal value for EF is 1, and thus the closer to 1 the values of EF, the greater is the correspondence between measured and predicted data.²⁸

3 RESULTS

3.1 Model predictions in paddy water

The agreement between measured and predicted concentrations of cinosulfuron and pretilachlor in paddy water is shown in Fig. 2. Generally, all three models predicted with acceptable accuracy the dissipation of cinosulfuron in paddy water in both 1997 (Fig. 2(a)) and 1998 (Fig. 2(b)). The good agreement between observed and predicted concentrations of cinosulfuron in paddy water is reflected in the low RMSE and high EF values of the RICEWQ and PCPF-1 models (Table 5). The values of the statistical indices for SWAGW suggested lower but still acceptable agreement between predicted and measured concentrations. For example, the RMSE values for cinosulfuron in 1997 were 52.6, 86.8 and 104.2 for RICEWQ, PCPF-1 and SWAGW respectively (Table 5). All three models predicted with high accuracy the dissipation of pretilachlor in paddy water, as shown in Figs 2(c) and (d). This good agreement is reflected in the low RMSE and high EF values for all models in both years studied. For example, the RMSE values for SWAGW in 2001 and 2002 were 62.8 and 24.8 respectively, compared with 42.3 and 36.5 for RICEWQ and 11.5 and 33.9 for PCPF-1 (Table 5). Therefore, the highest agreement

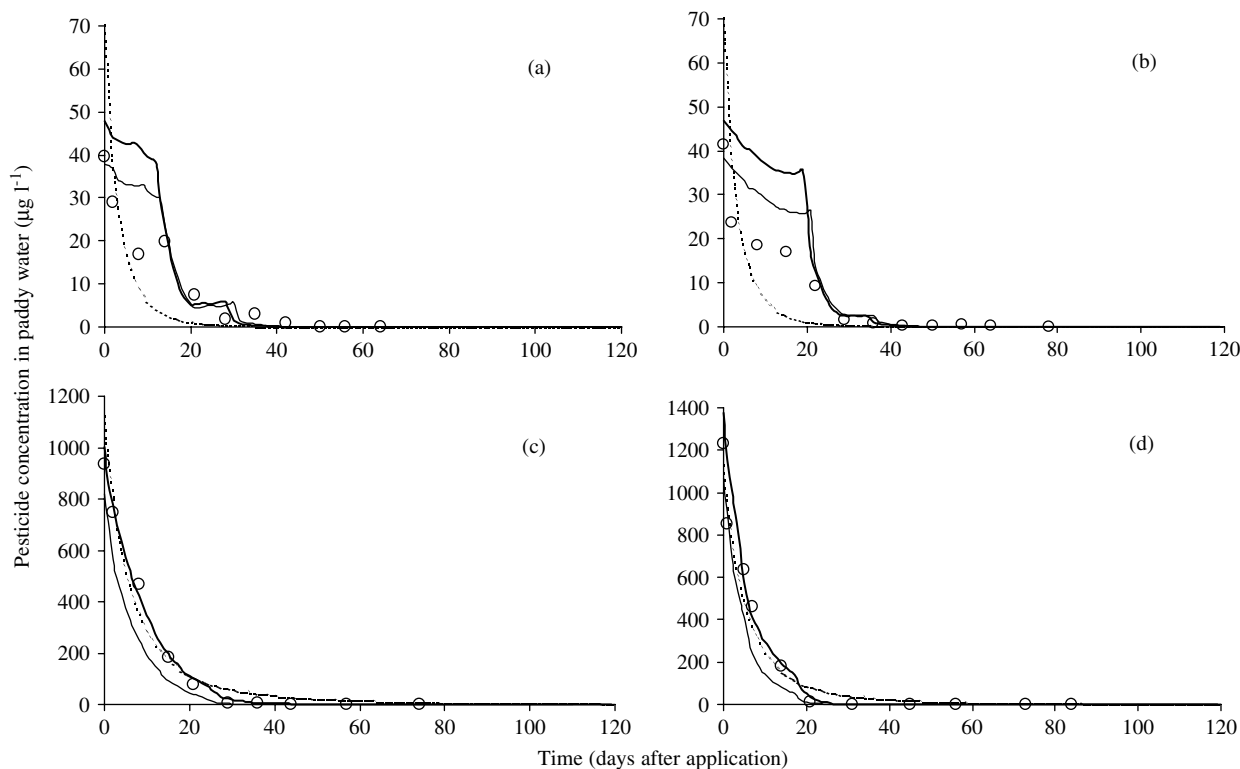


Figure 2. Measured (O) and predicted dissipation in paddy water of cinosulfuron in (a) 1997 and (b) 1998, and of pretilachlor in (c) 2001 and (d) 2002. Pesticide dissipation as simulated by (---) SWAGW, (—) RICEWQ and (—) PCPF-1.

between measured and predicted concentrations of pretilachlor in paddy water was achieved by PCPF-1 in 2001 and by SWAGW in 2002 (Table 5).

3.2 Model predictions in paddy soil

The agreement between measured and predicted concentrations of cinosulfuron and pretilachlor in paddy soil are shown in Fig. 3. RICEWQ and PCPF-1 showed a similar dissipation pattern and simulated with good accuracy the concentrations of cinosulfuron in paddy soil in both 1997 (Fig. 3(a)) and 1998 (Fig. 3(b)). In contrast, the SWAGW model predicted a more rapid partitioning and dissipation of cinosulfuron in paddy soil, leading to an overall underestimation of its concentration in paddy soil. The results of the statistical indices verify the higher agreement between predicted and observed concentrations achieved by the RICEWQ and PCPF-1 models (Table 6). Therefore, the RMSE values for RICEWQ and PCPF-1 were 29.5 and 32.1 in 2001 respectively,

Table 5. Statistical analysis of the observed and predicted concentrations of cinosulfuron and pretilachlor in paddy water

Models	Statistical indices	Cinosulfuron		Pretilachlor	
		1997	1998	2001	2002
RICEWQ	RMSE	52.6	63.0	42.3	36.5
	EF	0.810	0.780	0.905	0.926
SWAGW	RMSE	104.2	106.8	62.8	24.8
	EF	0.253	0.274	0.791	0.966
PCPF-1	RMSE	86.8	106.2	11.5	33.9
	EF	0.482	0.376	0.993	0.936

Table 6. Statistical analysis of the observed and predicted concentrations of cinosulfuron and pretilachlor in paddy soil

Models	Statistical indices	Cinosulfuron		Pretilachlor	
		1997	1998	2001	2002
RICEWQ	RMSE	29.5	42.7	87.0	51.3
	EF	0.891	0.256	0.508	0.801
SWAGW	RMSE	115.2	102.3	144.9	86.2
	EF	0.112	0.175	0.273	0.518
PCPF-1	RMSE	32.1	44.4	122.7	100.4
	EF	0.868	0.194	0.021	0.237

compared with the corresponding value of 115.2 for SWAGW (Table 6).

Somewhat different results were evident with pretilachlor simulations. The highest agreement between predicted and observed concentrations of pretilachlor in paddy soil was obtained by the RICEWQ model (Figs 3(c) and (d)). Although SWAGW and PCPF-1 models predicted the general dissipation pattern of pretilachlor in paddy soil, they either over- or underestimated the concentrations of pretilachlor in paddy soil (Figs 3(c) and (d)). This is illustrated by the higher EF values obtained for the RICEWQ model (0.508 and 0.801) compared with the lower corresponding EF values for the SWAGW model (0.255 and 0.518) and PCPF-1 model (0.021 and 0.237) (Table 6). Generally, a higher agreement between observed and predicted concentrations of pretilachlor in paddy soil was evident for all models in the year 2002, as shown by the lower RMSE values of

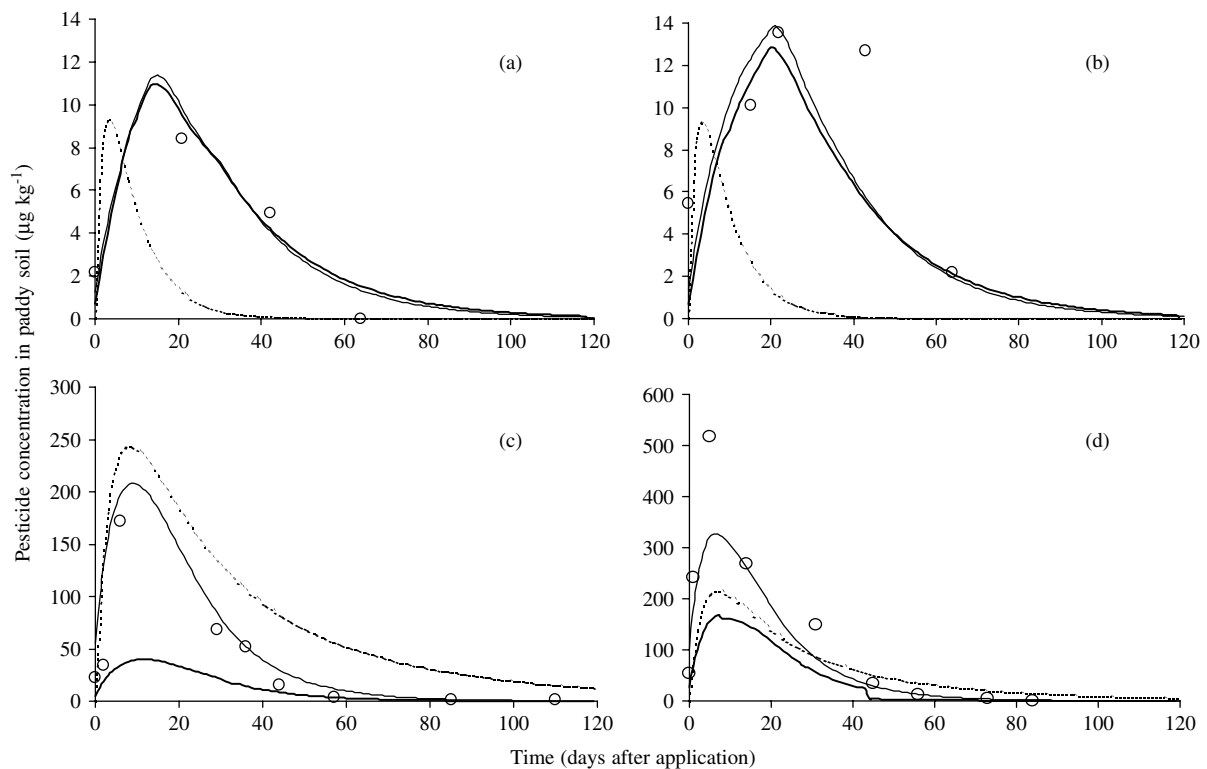


Figure 3. Measured (O) and predicted dissipation in paddy soil of cinosulfuron in (a) 1997 and (b) 1998, and of pretilachlor in (c) 2001 and (d) 2002. Pesticide dissipation as simulated by (---) SWAGW, (—) RICEWQ and (—) PCPF-1.

Table 7. Predicted environmental concentrations ($\mu\text{g L}^{-1}$) of cinosulfuron and pretilachlor in groundwater (1 m depth) provided by the tested models RICEWQ and SWAGW

	Cinosulfuron		Pretilachlor	
	1997	1998	2001	2002
RICEWQ	3.9×10^{-13}	4.0×10^{-13}	2.2×10^{-22}	4.2×10^{-21}
SWAGW	6×10^{-11}	4.1×10^{-11}	1.8×10^{-140}	4.8×10^{-36}

51.3, 86.2 and 100.4 for the RICEWQ, SWAGW and PCPF-1 models respectively.

3.3 Model predictions in groundwater

The GW PECs of cinosulfuron and pretilachlor as predicted by both RICEWQ and SWAGW at 1 m depth were calculated as the average of the daily concentrations of the pesticides for the whole simulation period in each year. No results are presented for PCPF-1, since this model could not simulate the fate of herbicide beneath the top paddy soil layer. The GW PECs for cinosulfuron and pretilachlor are shown in Table 7. Both the SWAGW model (6×10^{-11} and $4.1 \times 10^{-11} \mu\text{g L}^{-1}$) and the RICEWQ model (3.9×10^{-13} and $4 \times 10^{-13} \mu\text{g L}^{-1}$) predicted low PECs for cinosulfuron in both years, suggesting no pesticide transfer to GW. Similarly, the GW PECs for pretilachlor provided by the SWAGW model (1.8×10^{-140} and $4.8 \times 10^{-26} \mu\text{g L}^{-1}$) and the RICEWQ model (2.2×10^{-22} and $4.2 \times 10^{-21} \mu\text{g L}^{-1}$) were very low, suggesting no pesticide transfer in the GW.

4 DISCUSSION

Higher tier exposure assessment in rice paddies in Europe is still not adequately developed. Therefore, a validation test was organized to compare and contrast some of the available mathematical models. Generally, the RICEWQ 1.6.4v model simulated with the highest accuracy the dissipation of the tested pesticides in paddy fields. The modified PCPF-1 model predicted with good accuracy the dissipation of both herbicides in paddy water and also the concentration of cinosulfuron in paddy soil but significantly underestimated the concentration of pretilachlor in paddy soil. The SWAGW model simulated with acceptable accuracy the dissipation of pesticides, and especially pretilachlor, in paddy water but failed adequately to predict the concentrations of either pesticide in paddy soil.

The SWAGW model appeared consistently to overpredict the concentration of herbicides in paddy water at time 0 by showing that almost all of the applied dose of cinosulfuron is recovered in paddy water at time 0, whereas RICEWQ and PCPF-1 predicted a lower recovery of cinosulfuron at time 0 for both years, providing a greater agreement with the concentrations measured immediately after application. This could be attributed to the more advanced water management routines included in the

RICEWQ 1.6.4v and PCPF-1 models. In particular, the improved water management routine of RICEWQ 1.6.4v accurately simulated paddy water depth at the time of cinosulfuron application (16 cm), unlike SWAGW which assumes that the depth of paddy water is maintained constant (10 cm) throughout the cultivating season. Previous studies with RICEWQ and PCPF-1 have shown that both models could simulate with high accuracy the water balance in rice paddies.^{10,15,16} In addition, RICEWQ 1.6.4v and PCPF-1 assume an immediate partitioning of pesticide between paddy water and paddy soil and a constant equilibrium thereafter.¹² In contrast, SWAGW assumes that the whole pesticide amount applied is initially diluted into paddy water and partitioning occurs from day 1, depending on the pesticide adsorption coefficient.⁴

Both the RICEWQ and PCPF-1 models predicted a gradual dissipation and even a slow increase in cinosulfuron concentration in paddy water at the later stages of the paddy closure period. This dissipation pattern of cinosulfuron predicted by the two models is consistent with experimental observations where the very rapid dissipation of cinosulfuron within the first 2 days after its application was followed by a period between 2 and 15 DAT where little or no dissipation of cinosulfuron was observed (Figs 2(a) and (b)). This slow dissipation of cinosulfuron during paddy closure could be attributed to the high evaporation of paddy water during the period of paddy closure, resulting in a gradual concentration of cinosulfuron in the remaining paddy water. During the 22 day period of paddy closure after application of cinosulfuron in 1998, the sum of water loss by evaporation was 5.2 cm compared with only 0.5 cm of water input in the same period through precipitation. Unlike the other two models, SWAGW did not closely predict the dissipation pattern of cinosulfuron in paddy water. This result could be attributed to some inherent limitations of the SWAGW model, which assumes a constant paddy water depth throughout the cultivating season and does not consider the contribution of meteorological data in its calculations.⁵ A different dissipation pattern was evident for pretilachlor where a consistently rapid dissipation in paddy water was observed and predicted by all models. This could be explained by the higher precipitation (3.5 and 5.5 cm) and the lower evaporation losses (0.93 and 0.84 cm) of water occurring during the period of paddy closure after application of pretilachlor in both 2001 and 2002 respectively.

Neither PCPF-1 nor SWAGW predicted well the concentrations of pretilachlor in paddy soil. Both models constantly underestimated the concentrations of pretilachlor in paddy soil, with the exception of SWAGW which overpredicted the concentrations of pretilachlor in paddy soil in the year 2001 (Figs 3(c) and (d)). The new modified algorithm of the PCPF-1 model assumes that pesticide partitioning in paddy soil is directly associated with the percolation rate of paddy water to paddy soil. This results in major discrepancies with measured data when the dissipation of a pesticide with high adsorption affinity, such as pretilachlor, is simulated. No such discrepancy was evident with cinosulfuron simulations by PCPF-1, and this could be explained by the lower adsorption affinity of cinosulfuron compared with pretilachlor. In addition, in 2001 the PCPF-1 model predicted much lower concentrations of pretilachlor in paddy soil compared with its corresponding concentrations predicted by the model in 2002 (Figs 3(c) and (d)). This difference is reflected in the lower percolation rate calculated in 2001 (0.07 cm d^{-1}) compared with that in 2002 (0.27 cm d^{-1}). All the models tested failed to predict the high concentration of pretilachlor measured 4 DAT in paddy soil in 2002. This discrepancy could be attributed to the utilization of literature K_d values in the absence of K_d values specific for the paddy soil studied. Previous studies have indicated that the selection of non-specific degradation and adsorption parameters contributes significantly to the uncertainty of model predictions.^{29,30}

Generally, both the RICEWQ and SWAGW models predicted that the application of cinosulfuron and pretilachlor in paddy fields posed low risk of GW contamination. PCPF-1 in its current form cannot simulate the fate of pesticides beneath the top 5 cm paddy soil layer. However, only recently an interface between the PCPF-1 model and SWMS 2D, which is the open Fortran code of the Hydrus 2D model, allowed the simulation of pesticide fate and transport in the soil profile beneath rice paddies.³¹ The lack of measured data in the GW aquifers beneath rice paddies did not allow a direct comparison between predicted and observed concentrations of pesticides in GW. However, previous monitoring studies undertaken in rice-cultivated areas of Europe have not so far reported the presence of detectable concentrations of cinosulfuron or pretilachlor in GW wells.^{32–34}

The present validation exercise revealed that the RICEWQ model is currently the most adequate model for simulating the environmental fate of pesticides in rice paddies in Europe. PCPF-1 has the potential to be used under European conditions, but further calibration and adjustments of certain parameters are needed in order to predict more effectively pesticide exposure in rice paddies in Europe. Finally, the SWAGW model in its current form can be useful as a lower-tier screening tool for exposure assessment in rice paddies, but it failed to efficiently simulate the fate of pesticide in paddy fields when site-specific

considerations were included. Further improvements and optimization of SWAGW are needed in order for it to be considered in the future as a higher-tier pesticide exposure model. The comparative study presented in this paper has enabled the participants to identify the deficiencies involved in certain routines of the models tested and has provided the initiative for further testing and improvement of these uncertainties in order to predict pesticide exposure in rice paddies more realistically.

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