Heliyon 10 (2024) e26908

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Improving a herbicide risk assessment model in paddy rice cultivation

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ARTICLE INFO

Keywords:
Pesticides
Indicator
Risk assessment
Sustainability
Groundwater
Surface water

ABSTRACT

Herbicides play a pivotal role in paddy rice cultivation by effectively controlling weeds, thus ensuring optimal resource utilisation and higher crop yields, making them indispensable for efficient rice production systems. However, herbicide applications could be related to potential environmental impacts such as water contamination and harm to non-target species, requiring special attention in their management to ensure the long-term sustainability of rice farming practices. The development and utilisation of robust risk assessment indicators for pesticides are essential tools in evaluating and mitigating potential environmental and human health hazards associated with pesticide use in agricultural practices. The Environmental Potential Risk Indicator for Pesticides (EPRIP) is not suitable for rice paddy cultivation due to its limitations in accurately assessing pesticide risk in this specific agricultural context. This is primarily attributed to the unique hydrological characteristics and ecosystem dynamics of paddy fields, which significantly differ from other agricultural systems. To address this issue and to enhance the accuracy of pesticide risk assessment in rice paddy fields, EPRIP has been improved and validated in two agricultural seasons. A synergistic approach involving field experiments and enhanced EPRIP model simulations was employed to assess the risk associated with the application of two herbicides in Italian paddy rice systems. The observed and model-predicted surface water (SW) concentrations exhibited a close alignment, though an overestimation was observed for groundwater (GW). In general, the estimated Risk Points (1 for SW and 4 for GW) were largely in accord with those derived from the field experiments (1 for SW and 3 for GW), suggesting that the refined EPRIP model holds promise for conducting reliable risk assessments following herbicide applications in such contexts.

1. Introduction

Worldwide, the pesticides applied to rice are recognised as responsible for high potential risks and adverse effects on the environment [1]. In flooded irrigation conditions, weeds represent a serious threat that can affect yields and grain quality due to

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https://doi.org/10.1016/j.heliyon.2024.e26908
Received 18 September 2023; Received in revised form 24 January 2024; Accepted 21 February 2024
Available online 27 February 2024
2405-8440/

competition for nutrients available for the plant. Chemical-based control with herbicides is considered the most effective option for farmers among the available possibilities for weed management and control in rice paddies [2,3]. Although the use of herbicides is essential for production, environmental contamination is inevitable [4].

The European Commission has developed an official guidance document [5,6] to evaluate environmental pollution caused by agricultural practices in the EU, through the Forum for the Coordination in the Use of Models (FOCUS). Traditional mathematical methods as the ones developed by FOCUS are not applicable to rice cultivation considering that rice is a particular environmental scenario with respect to pesticides fate [7,8]. To address this problem, a small group of experts (the MEDiterranean Rice or MED-Rice group) released a simple tier-1 spreadsheet model for Predicted Environmental Concentration (PEC) calculations and released guidelines for pesticide risk assessment in rice paddies [9] that can be used for calculating PECs in groundwater, paddy water and adjacent surface water bodies in the Mediterranean area (MED-Rice, 2003). The MED-Rice model is complemented by other existing models such as the Adsorption/Dilution Model (ADM) [10] and the US-EPA Rice Model (EPA-Rice) [11], both developed in the United States, the Aquatic Model developed in Japan (AMJ) [12] and Pesticide Risks in the tropics to Man, Environment and Trade (PRIMET) developed in the Netherlands [13]. After the release of the first tier-1 model, more realistic models for calculating pesticide concentrations at higher tier levels have been proposed, of which the RICEWQ 1.6.4v model showed the highest accuracy of the tested pesticides in paddy fields [1], followed by the most recent model, PestLCI upgraded in relation to life cycle assessment [14]. Despite the differences, all the above-mentioned models focused on the fate and transport of pesticides following deposition in paddy water, but none of those acts as an operational tool to assess crop protection strategies regarding environmental impact. To achieve this goal, risk assessment indicators to evaluate the fate of different chemicals in different environments aiding in minimising off-site impacts of pesticides and assist in decision-making and policy formulations have been developed [15]. User-friendly indicators are preferred over more complex systems that may provide more detailed output but are prohibitively difficult to use due to their data-richness. Among these EPRIP, Environmental Potential Risk Indicator for Pesticides (EPRIP) was developed [16]. EPRIP is representative of the Exposure Toxicity Ratio (ETR) indicators, a set of indicators in which ETR is calculated from quantifiable PEC and compared to legal or eco-toxicological endpoints through Risk Points (RPs) [16]. A 2017 French study compared the EPRIP indicator to other risk assessment indicators and concluded that, among all the indicators tested, EPRIP was better adapted to the study sites and showed better results despite being considered an elaborate model [17]. The application of the EPRIP indicator illustrates the varying environmental risks associated with different crops and pesticides. EPRIP considers the demands of multiple applications, assigns separate scores for distinct environmental compartments.

The EPRIP approach could serve as a valuable tool for experts and technicians, offering a quick screening method to assist farmers in evaluating the environmental impacts of alternative cropping and pest management strategies. However, EPRIP, in its actual state, does not apply to rice-flooded cultivation. Therefore, the main goals of this paper are 1) to update the EPRIP risk assessment indicator to adapt its formulation to rice cultivation in flooded conditions and 2) to assess the predictive quality in terms of risk assessment of the EPRIP indicator considering clomazone and MCPA herbicides.

2. Materials and methods

2.1. Experimental site crop and pest management

The study was conducted over two consecutive agricultural seasons (2019 and 2020) and involved the cultivation of the Centauro variety, short-grained rice at a seeding rate of 150 kg/ha. The traditional irrigation strategy, which includes water seeding and continuous flooding (WFL), was adopted for the crop. Plots were water seeded (May 16, 2019 and May 08, 2020) and the water management involved continuous flooding for most of the growing season, except for a 15-18-day period after sowing in which plots were drained to allow for root extension in a pint-point period and two mid-season drainage periods of 3–7 days (17–21/06/2019; 11–18/07/2019; 08–13/06/2020 and 29–2/07/2020) for fertilizer and herbicide applications.

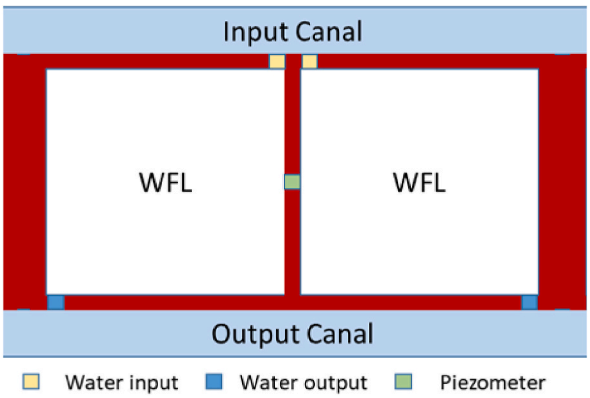

Fig. 1. Experimental site description with a traditional flooding irrigation method: water seeding and continuous flooding (WFL).

The study was conducted in one experimental rice plot in ENR - Rice Research Centre's experimental farm in Castello d'Agogna (Pavia, Italy). The two experimental rice subplots of about 20 m × 70 m each used for the present study are shown in Fig. 1 and had a median surface area of 0.14 ha and contained a silty-loam soil with pH 5.6 and an organic carbon content of 2.0%. Finally, agro-climatic data (air temperature, air humidity, rainfall, and wind velocity and direction) were collected at the agro-metrological station on site. In 2019 and 2020, the rainfall during the agricultural season was 185 mm and 357 mm, respectively, while the rainfall outside the agricultural season (OSR) was 449 mm and 350 mm, respectively. Rice subplots were set up according to standard agricultural practices, which included one application of the pre-emergence herbicides clomazone and MCPA on dry field. Table 1 provides information on the phenological stage at the time of application, dosage, eco-toxicological effects, and soil-water and soil degradation ($DT50_{water}$ and $DT50_{soil}$, respectively) for each applied AIs [18]. As an eco-toxicological parameter for surface water (SW), the minimum value between the NOEC for Algae, Daphnia and Fish was considered, while for groundwater (GW), the pesticide legal limit of 0.1 μg/L was adopted.

Soil OC% (2%) and pH (5.6) were in the range of those reported for the Italian scenario in the Med-Rice guidelines (OC% 0.8–10; pH 4–8) [9], which makes plausible the use of this tool for the EPRIP indicator.

2.2. Chemical and statistical analysis

To verify how well predicted herbicides Risk Points (RPs) relate to those occurring in the field, herbicide concentrations were determined in groundwater and drainage canals water. In addition, a possible presence of herbicides in water from the catchment entering the rice field plots was also evaluated at the beginning of each sample collection to correct the contribution from other fields upstream to the drainage canal. In both agricultural seasons, herbicides concentration was evaluated by collecting four replicate water samples nine times throughout the experimental period. The samples were collected from 28 days before application to 97 days after application of both herbicides. A total of 1 L samples were collected in 4250 mL Nalgene® bottles and sent to the laboratory frozen for chemical analysis.

Herbicides were separated with an RP-18 column (150 × 2.1 mm, Kinetex 5 μm Phenomenex) and quantified by high-performance liquid chromatography (HPLC) with a triple quadrupole mass detector. HLB cartridges (Supelco, Supel™-Select HLB SPE Tube) were considered as suitable SPE devices for pre-concentration, as reported by Tran et al. [19]. Following absorption of the herbicides on the cartridges, they were eluted with methanol (Sigma-Aldrich HPLC grade, ≥99%) and reduced to near dryness under a nitrogen stream. The samples were then reconstituted in a mixture of methanol and water (1:1) and an aliquot of 20 μL was injected into the HPLC system. The mobile phase consisted of methanol: water (30:70% v/v) and a gradient programme was applied from 30:70% v/v ($t = 14$ min) to 100:0% v/v ($t = 14$ min). The total analysis time was 24 min, including the equilibration time of the mobile phase prior to the next injection. Flow rate was 0.8 mL/min, and the injection volume was 20 μL. The chromatographic conditions were chosen in terms of peak shape, column efficiency, chromatographic analysis time, selectivity and resolution. Limits of quantification (LOQ) were 0.04 μg/L for both compounds analysed, with an analytical recovery of 96% ± 20% for MCPA and 97% ± 1% for clomazone (mean ± SD; $n = 4$). Among the nine analysed samples, maximum values recorded after the AI application were used for EPRIP validation. A statistical analysis was conducted to assess the differences in herbicide concentrations between the different samples in order to consider the maximum concentration obtained in the sampling period. The normality of the distribution was tested using the Shapiro-Wilk test, followed by an ANOVA test with the Tukey post hoc test for pairwise comparisons.

2.3. Improved risk assessment model

The Med-Rice model is based on the assumption of a partitioning of the AI between the water and sediment phase (Eq. (1)) and its degradation and sorption over time.

$$M_w \leftrightharpoons M_s \tag{1}$$

in this assessment, original Med-Rice equations were modified introducing the leakage rate constant (1/d) to take into account the amount of leached product over time.

2.3.1. PEC_{SW} and PEC_{Sed} calculation

For the calculation of PEC in surface water and canal sediment, degradation and sorption into the soil were taken into account considering appropriate input parameters and assuming instantaneous partitioning between water and sediment. In Fig. 2, a simple model scheme was presented, showing detailed mass balance of the applied AI.

At the time of application, an initial partitioning occurs, as reported in Eq. (2) and Eq. (3):

Table 1
Active Ingredients dosage, management, ecotoxicology, soil adsorption/mobility and degradation.

	Application Phenological stage	Dosage (g/ha)	NOEC SW (μg/L)	K_{oc} (mL/g)	$DT50_{water}$ (days)	$DT50_{soil}$ (days)
Clomazone	Bare soil	155	50	300	54	22.6
MCPA	2nd-3rd leaf	122	15,000	74	17	24

$$M_{pw,init} = Dose \bullet f_{dissolved} \bullet (1 - f_{int}) \tag{2}$$

$$M_{psed,init} = Dose \bullet f_{sorbed} \bullet (1 - f_{int}) \tag{3}$$

The initial mass Dose (g) is the application rate for 1 ha of paddy and is fractioned considering crop interception f_{int} (−) and mass fraction $f_{dissolved}$ (−) dissolved in paddy water phase and f_{sorbed} (−) sorbed into paddy sediment phase. Coefficients $f_{dissolved}$ and f_{sorbed} are strictly connected to the volume of water and sediment and can be expressed through Eqs. (4a) and (4b):

$$f_{dissolved} = \frac{depth_{water}}{depth_{water} + depth_{psed} \bullet BD \bullet K_d} \tag{4a}$$

$$f_{sorbed} = 1 - f_{dissolved} \tag{4b}$$

in case of dry application, the AI is directly applied on the paddy soil, then $f_{dissolved}$ is considered 0. Eq. (4b) is a direct consequence of the initial assumption made about the initial mass applied that is partitioned between paddy water and sediment. Parameters $depth_{water}$ and $depth_{psed}$ represent the paddy water and paddy sediment depth considered constant (0.1 and 0.05 m, respectively), BD is the soil bulk density (kg/dm^3) estimated as reported in Saxton and Rawls [20], and K_d is the sorption coefficient (dm^3/kg), calculated from soil organic carbon (OC%) and soil sorption coefficient normalised to organic carbon content (K_{oc}) with Eq. (5).

$$K_d = \frac{OC\% \bullet K_{OC}}{100} \tag{5}$$

when the AI is applied to dry paddy, $f_{dissolved}$ is zero as the initial mass in the paddy water (g). After the first application, the field remains dry until the following flooding. In this case, the mass of the product in the paddy sediment just before flooding is given by Eq. (6).

$$M_{psed,tdry} = M_{psed,init} \bullet e^{-t_{dry} \bullet ln(2) / DT50_{soil}} \tag{6}$$

where t_{dry} is the time between the application on dry paddy and flooding of the field (d), while $DT50_{soil}$ is the half-life in soil from aerobic lab studies (d). The initial masses (g) at the time the paddy is flooded of the AI in the paddy water ($M_{pw,flood\_init}$) and in the paddy sediment (g) ($M_{psed,\ flood\_init}$) are obtained by Eq. (7) and Eq. (8) as the respective fraction of the initial calculated mass in the relative phase:

$$M_{pw,flood\_init} = M_{psed,tdry} \bullet f_{dissolved} \tag{7}$$

$$M_{psed,flood\_init} = M_{psed,tdry} \bullet f_{sorbed} \tag{8}$$

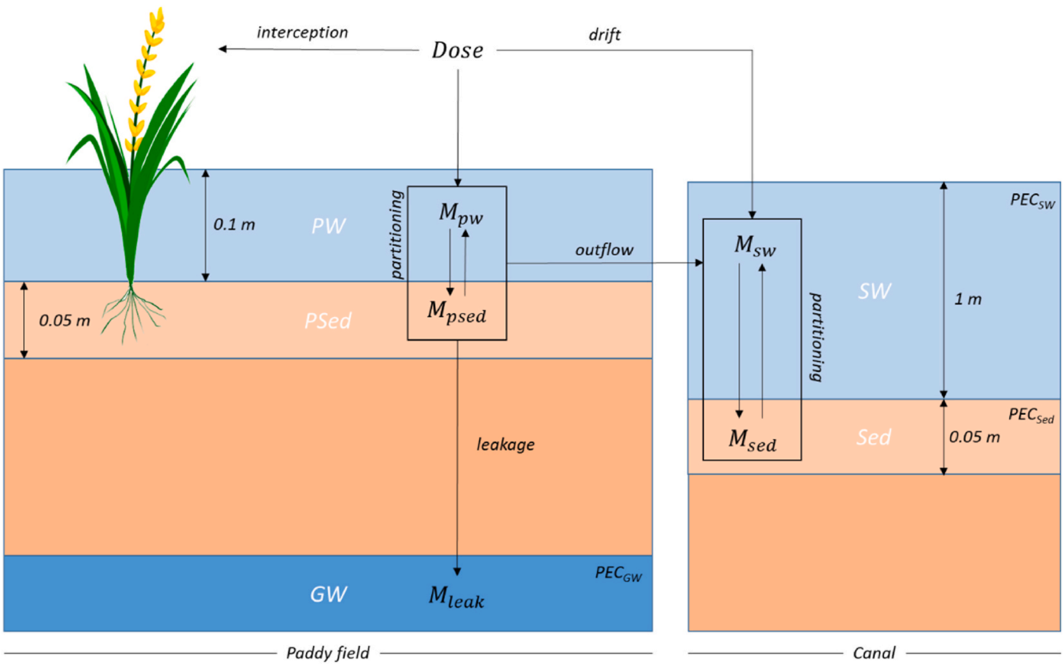

Fig. 2. Scenario description for surface water (SW), groundwater (GW) and sediment (Sed) for PEC calculations, considering Paddy Water (PW) and Paddy Sediment (PSed) partitioning, interception, outflow, drift and leakage of the mass (M).

After flooding, the paddy remains flooded until it is drained. Eqs. (9a)–(9b) give the mass of the product in paddy water and paddy sediment at the end of the water retention period considering degradation in water ($DT50_{water}$, d) and soil ($DT50_{soil}$, d) occurring during flooding.

$$M_{pw,tdrain} = M_{pw,flood\_init} \bullet e^{-t_{drain} \bullet \left(\frac{\ln(2)}{DT50_{water}} + k_{leak}\right)} \tag{9a}$$

$$M_{psed,tdrain} = M_{psed,flood\_init} \bullet e^{-t_{drain} \bullet \left(\frac{\ln(2)}{DT50_{soil}}\right)} \tag{9b}$$

where $M_{pw,tdrain}$ and $M_{psed,\ tdrain}$ are the masses of the product in paddy water and sediment at the end of the flooding period (g), t_{drain} is the time between the first application and drainage (d), and k_{leak} is the leakage rate constant (1/d) estimated with Eq. (10).

$$k_{leak} = \frac{Leakage}{100\ mm} \tag{10}$$

The infiltration rate (Leakage) is obtained from the scenario's water balance. The original equation in Med-Rice document does not include k_{leak} from Eq. (9a). With this modification, mass loss due to percolation through the soil has been considered, avoiding overestimation.

With a similar approach, partitioning due to the spray drift into surface water and sediment could be calculated with Eq. (11a) and Eq. (11b):

$$M_{sw,drift\_init} = f_{drift} \bullet Dose \bullet F_{dissolved} \tag{11a}$$

$$M_{sed,drift\_init} = f_{drift} \bullet Dose \bullet F_{sorbed} \tag{11b}$$

where $M_{sw,drift\_init}$ and $M_{sed,\ drift\_init}$ are the initial masses in water and sediment phases due to drift, respectively, in the receiving water body, while f_{drift} (−) is the fraction drift to the adjacent water body and is calculated as in Padovani et al. [21]. For mass partitioning into the canal, the coefficient $F_{dissolved}$ and F_{sorbed} are calculated with Eqs. (12a)–(12b) as shown for the paddy field with Eqs. (4a) and (4b):

$$F_{dissolved} = \frac{depth_{canal}}{depth_{canal} + depth_{sed} \bullet BD \bullet K_d} \tag{12a}$$

$$F_{sorbed} = 1 - F_{dissolved} \tag{12b}$$

After drainage, the masses obtained by the product drift into surface water and canal sediment considering degradation in water ($DT50_{water}$, d) and soil ($DT50_{soil}$, d) are given by Eqs. (13a)–(13b).

$$M_{sw,drift\_tdrain} = M_{sw,drift\_init} \bullet e^{-(t_{dry} + t_{drain}) \bullet \left(\frac{\ln(2)}{DT50_{water}}\right)} \tag{13a}$$

$$M_{sed,drift\_tdrain} = M_{sed,drift\_init} \bullet e^{-(t_{dry} + t_{drain}) \bullet \left(\frac{\ln(2)}{DT50_{soil}}\right)} \tag{13b}$$

Furthermore, the resulting total mass in the receiving surface water $M_{sw,tdrain}$ (g) is determined by Eq. (14). In particular, sediment and water partitioning due to drainage is calculated as a fraction of the mass of the receiving canal ($M_{pw,tdrain}$, g).

$$M_{sw,tdrain} = M_{sw,drift\_tdrain} + M_{pw,tdrain} \bullet F_{dissolved} \tag{14}$$

Finally, the resulting concentrations (μg/L) in the receiving surface water and the sediment of the canal at the end of the water retention period are determined by Eq. (15a) and Eq. (15b), where f_{dil} is the dilution factor of paddy water reaching adjacent surface water (assumed to be 10) and $depth_{canal}$ is the surface water depth (assumed 0.1 m):

$$PEC_{sw} = 0.1 \bullet \frac{M_{sw,tdrain}}{depth_{canal} \bullet (1 + f_{dil})} \tag{15a}$$

$$PEC_{sed} = 0.1 \bullet \frac{M_{sed,drift\_tdrain}}{depth_{sed} \bullet BD} + 0.1 \bullet \frac{M_{pw,tdrain} \bullet F_{sorbed}}{f_{dil} \bullet depth_{sed} \bullet BD} \tag{15b}$$

In Table 2 are summarised all input data required for PEC calculations.

2.3.2. PEC_{GW} calculation

Groundwater PEC calculation is based on the mass available for leaching (M_{leak}, g) that comes from the volume of paddy water percolating through the soil and is calculated considering the contribution of the first and following flooding. Using Eq. (7), which calculates the mass of the product in the paddy water at the time of flooding ($M_{pw,flood\_init}$), it is possible to estimate the time-weighted average mass (M_{TWA_1st}, g) of the product in paddy water during the period between the first flooding and first drainage of the field, as per Eq. (16):

$$M_{TWA\_1st} = M_{pw,flood\_init} \bullet \frac{1 - e^{-t_{drain} \bullet \left(\frac{\ln(2)}{DT50_{water}} + k_{leak}\right)}}{t_{drain} \bullet \left(\frac{\ln(2)}{DT50_{water}} + k_{leak}\right)} \tag{16}$$

As mentioned earlier for equation (9a), the original equation in the Med-Rice document did not incorporate k_{leak} from Eq. (16). The mass of the product in the paddy sediment at the end of the initial water retention period just before re-flooding ($M_{psed,\ re\text{-}flood}$, g) corresponds to the mass $M_{psed,\ tdrain}$ obtained from Eq. (9b), as shown in Eq. (17):

$$M_{psed,reflood} = M_{psed,tdrain} \tag{17}$$

Eq. (17) represents an overestimation since re-flooding of the field will not occur on the same day when the field is drained but some days later. Therefore, Eq. (17) is a worst-case assumption. When the field is re-flooded, the mass of the product in paddy sediment is re-suspended in paddy water. Thus, the mass of the product in paddy water at the time of re-flooding is calculated with Eq. (18):

$$M_{pw,reflood\_init} = M_{psed,reflood} \bullet f_{dissolved} \tag{18}$$

The time-weighted average mass in paddy water during the period between re-flooding of the field and final draining (M_{TWA_fdrain}) is given by Eq. (19):

$$M_{TWA\_pw} = M_{pw,reflood\_init} \bullet \frac{1 - e^{-t_{flood} \bullet \left(\frac{\ln(2)}{DT50_{water}} + k_{leak}\right)}}{t_{flood} \bullet \left(\frac{\ln(2)}{DT50_{water}} + k_{leak}\right)} \tag{19}$$

where t_{flood} is the time the paddy is flooded (d) [12].In order to simulate the modern irrigation scheme where no continuous overflow is allowed, the parameter *outflowrate* used in the original Med-Rice is not used in Eq. (19). If the parameter *outflowrate* is used, the time-weighted average mass (M_{TWA_pw}) will be lower than the mass calculated with Eq. (19); therefore the current approach is more

Table 2
Data input required by the model.

Parameter	Comment	Value
Dose	Measured (g/ha)	–
$f_{dissolved}$	Estimated (–)	Eq. 4a
f_{sorbed}	Estimated (–)	Eq. 4b
$F_{dissolved}$	Estimated (–)	Eq. 12a
F_{sorbed}	Estimated (–)	Eq. 12b
f_{int}	Estimated (–)	Ref. [21]
f_{drift}	Estimated (–)	Ref. [21]
Field area	Measured (m^2)	–
$depth_{water}$	Assumed constant (m)	0.1
$Depth_{sed}$	Assumed constant (m)	0.05
$Depth_{psed}$	Assumed constant (m)	0.05
Sand (Soil sand composition)	Measured (%)	–
Clay (Soil clay composition)	Measured (%)	–
Soil Skeleton	Measured (%)	–
OC_{soil} (soil organic carbon)	Measured (%)	–
BD_{soil} (soil bulk density)	Estimated (kg/dm^3)	Ref. [20]
K_{oc} (soil adsorption coefficient)	(dm^3/kg)	Ref. [18]
K_d (sorption coefficient)	Estimated (dm^3/kg)	Eq. 5
t_{dry}	Measured (d)	–
$DT50_{soil}$	(d)	Ref. [18]
Annual precipitation	Measured (mm)	–
Precipitation during agricultural season	Measured (mm)	–
Residual term water balance	Estimated (mm)	Eq. 22
Groundwater recharge coefficient	Estimated (–)	Ref. [22]
Leakage	Estimated (mm/d)	Eq. 23
k_{leak}	Calculated (1/d)	Eq. 10
t_{drain}	Measured (d)	–
$depth_{canal}$	Assumed constant (m)	1
$DT50_{water}$	(d)	Ref. [18]
f_{dil}	Assumed constant	10
t_{flood}	Measured (d)	–
$M_{leak>1000}$	Estimated (g)	Ref. [9]
NOEC Water (Water ecotoxicology)	(μg/L)	Ref. [18]

conservative.

Finally, the mass of the product available for leaching at the end of the flooding period is given by Eq. (20).

$$M_{leak} = M_{TWA\_1st} + M_{TWA\_pw} \quad (20)$$

Original Med-Rice equations 13–19 (section 5.3.2) to calculate retardation factors (R) due to sorption in the soil column and degradation in subsoil layers, the residence time of water in a horizon (t_{res}) and the mass of pesticide moving from the 0–300 mm horizon to the 300–600 mm horizon, from the 300–600 mm horizon to the 600–1000 mm horizon and the mass of pesticide moving below the 1000 mm horizon ($M_{leak>1000}$) are used without changes. Finally, the resulting groundwater concentration is calculated with Eq. (21):

$$PEC_{GW} = \frac{100 \bullet M_{leak>1000}}{365 \bullet Leakage} \quad (21)$$

For the purposes of PEC calculations, "groundwater" is defined as water in the saturated zone at 1 m below the soil surface.

2.4. Risk points from the EPRIP model

The PECs determined for each compartment were converted in ETR using the legal limit for pesticides into the groundwater and pesticide toxicity for non-target organisms in surface water considering the minimum value between the NOEC for Algae, Daphnia and Fish, as reported in the "Experimental site and pesticides management" section in Table 1. Thus, ETR were converted into Risk Points accordingly to Table 3, as adopted by Trevisan et al. [16].

Table 3 also shows the RPs judgement based on the scale adopted by Ref. [16]. Predicted ETR (PETR) and measured ETR (METR), together with predicted RP (PRP) and measured RP (MRP), have been obtained starting from PEC and from measured concentrations (MC) in samples.

2.5. Water management

Percolation to groundwater (P, mm) is calculated as the residual term of the water balance according to Eq. (22):

$$P = R + Q_{IN} - Q_{OUT} - ET_C - \Delta S \quad (22)$$

The water balance was computed daily for each irrigated plot considering a period ranging from pre-seeding flooding to harvesting. In Eq. (22), ΔS (mm) includes both the variation in ponding water (ΔL) and in soil moisture ($\Delta\theta$) within the rice root zone, R (mm) is the total rainfall (precipitation) over the agricultural season, Q_{IN} (mm) and Q_{OUT} (mm) are the irrigation inflow and outflow, respectively and finally, ET_C (mm) is the potential evapotranspiration from rice and the underlying soil and/or ponding water. Q_{IN}, Q_{OUT}, R and DS were measured through suitable measuring devices [23], while ET_C was estimated by applying the single coefficient FAO-56 method [24] based on the FAO-modified Penman-Monteith equation, in which the reference evapotranspiration ET_0 was multiplied by the rice crop coefficient K_C. This coefficient was assumed to be equal to the rice crop K_C when plots were dry (i.e. not flooded), while the maximum between rice crop K_C and K_W (evaporation co-efficient for open water) (i.e. 1.05, K_C for free water bodies [24]; was assumed in case of flooded fields. The time-varying value of the rice crop coefficient (K_C) was determined based on a previous study conducted near the pilot study area. The growth stages of rice (ini, mid, end) were determined by observing crop phenology in the field and measuring LAI data series [24]. The study established the following KC values for dry-seeded rice: $K_{C\text{-ini}} = 0.35$, $K_{C\text{-mid}} = 1.1$, $K_{C\text{-end}} = 0.6$ [25,26].

Leakage (mm/d) was calculated according to Eq. (23):

$$Leakage = \frac{P + OSR \bullet \mathrm{RC}}{365} \quad (23)$$

where OSR represents the rainfall out of the agricultural season and RC the recharge coefficient [22].

Table 3
Normalisation of ETR values into Risk Points (RPs).

Range of ETR	RISK POINT	JUDGEMENT
<0.01	1	negligible
0.01–0.1	2	low
0.1–1.0	3	present
1.0–10.0	4	high
>10.0	5	very high

3. Results and discussion

3.1. Water management parameters

Table 4 reports the simulated percolations (P) obtained using Eq. (22) during the agricultural seasons of 2019 and 2020, along with the leakage values obtained using Eq. (23).

The slightly highest P obtained during 2020 is due to a higher precipitation (357 mm in 2020 vs 185 mm in 2019). This difference is also reflected in the Leakage values, which are in the range of values (6–11 mm/d) reported in the Italian scenarios in Med-Rice guidelines [9].

3.2. Chemical analysis

Clomazone and MCPA maximum concentrations achieved after application in both agricultural seasons and both compartments (GW and SW) are reported in Table 5, together with the number of days passed from application (Δ).

Generally, the lower the K_{oc}, the sooner the compound is expected to reach water bodies (see Eqs. (12a)–(14)). MCPA is slightly more mobile than clomazone, which should reach the peak value sooner after treatment than for clomazone. However, mobility is not the only factor to be considered. A combination of water management, water-soil degradation and mobility must be taken into account in order to explain the results (Eq. (14)). Indeed, clomazone is slightly more persistent than MCPA ($DT50_{water}$ of 54 vs 17 days), contributing to a higher concentration in SW. Moreover, drainage during clomazone treatment occurred sooner than for MCPA (t_{drain} for clomazone 3 days in 2019 and 5 days in 2020, t_{drain} for MCPA 23 days in 2019 and 18 days for 2020) contributing to clomazone earlier peak.

3.3. Predicted and experimental RPs for applied AIs

The accuracy of the improved herbicide risk assessment model PRP was assessed by comparing estimated results with measured ones, as reported in Table 6. The predicted concentrations for both clomazone and MCPA in SW and GW were comparable during the two agricultural seasons (MCPA PEC_{SW}: 0.04 μg/L in 2019 vs 0.06 μg/L in 2020; clomazone PEC_{SW}: 0.13 μg/L in 2019 vs 0.11 μg/L in 2020; MCPA PEC_{GW}: 0.86 μg/L in 2019 vs 0.95 μg/L in 2020; clomazone PEC_{GW}: 0.70 μg/L in 2019 vs 0.66 μg/L in 2020). The slight difference in PECs for clomazone in the two agricultural seasons is attributed to a longer t_{drain} in 2020 (5 days) compared to 2019 (3 days). This could be interpreted as allowing more time for the AI to degrade in paddy water and paddy sediment. Considering MCPA PECs, the slight differences in the two agricultural seasons are mainly due to a higher leakage in 2020. The difference in measured concentrations for clomazone and MCPA in the two agricultural seasons could be explained by a higher precipitation that increased the concentration of both herbicides due to significant paddy field runoff into the canal. As a consequence, less AI is available for leaching into groundwater, explaining the lower GW value obtained for MCs compared to PECs.

The difference for both predicted and measured concentrations between MCPA and clomazone, despite similar dosage application, is mainly due to MCPA's higher degradation rate and mobility. This leads to a lower MCPA concentration that reaches the canal and a higher concentration that reaches the groundwater. The deviations between the overall values of the predicted and measured concentrations ranged from 0.04 μg/L to 0.95 μg/kg. The deviations can be caused by several factors and are higher for GW estimations. PRP and MRP in the SW compartment were 1 (negligible risk) for both MCPA and Clomazone in both agricultural seasons, while PRP values in the GW compartment for both Clomazone and MCPA in both agricultural seasons were 4 (high risk), and MRP 3 PRP values (4) with predicted values higher than the measured ones.

This difference could be explained by considering that PEC was estimated under the worst-case scenario. A potential explanation of the overestimation of GW PRP could be found in the overestimation made in Eq. (17): it was assumed that the mass in the sediment remains constant from drainage to re-flooding, but it is actually lower since re-flooding generally occurs a few days after the drainage. Another possible explanation that leads the model to overestimate groundwater herbicide's fate is the natural groundwater flux that could effectively move herbicides away from the corresponding groundwater catchment. Moreover, DT50 values used as model input are obtained by field or laboratory values from a database and may not be applicable to pesticide behaviour under flow conditions in the field [4].

Stadlinger et al. reported a method for assessing pesticides in surface water with a similar approach adopted for EPRIP [27]. The method involves calculating exposure toxicity ratios (ETRs) from predicted environmental concentrations (PECs) estimated using the PRIMET model [13] and EC50 toxicity concentration. While their results suggest an overestimation of pesticides in surface water due to a worst-case scenario assumption, our results for surface water are correctly predicted, with overestimated results only in groundwater. This difference could be explained considering that PRIMET was not intended, like Med-Rice, for flooded conditions in

Table 4
Plots data for each agricultural season.

	P[a] (mm)	Leakage (mm/d)
2019	1934	6.30
2020	2167	6.70

[a] P: percolation.

Table 5
AIs application and SW sample collection dates with analysed maximum concentration.

	MCPA		Clomazone	
Season	2019	2020	2019	2020
Δ_{SW} (days)	15	11	11	9
SW Max Conc. (μg/L)	0.045	0.081	0.18	0.37
Δ_{GW} (days)	12	12	8	12
GW Max Conc. (μg/L)	0.04	<0.04	0.08	<0.04

Table 6
Predicted and measured MCPA and clomazone concentrations, exposure toxicity ratios and risk points in each compartment for 2019 and 2020.

	PEC (μg/L)	MC (μg/L)	PETR	METR	PRP	MRP
CLO_SW_2019	0.13	0.18	2.60E-03	3.60E-03	1	1
CLO_SW_2020	0.11	0.37	2.20E-03	7.40E-03	1	1
MCPA_SW_2019	0.04	0.045	2.67E-06	3.00E-06	1	1
MCPA_SW_2020	0.06	0.081	4.00E-06	5.40E-06	1	1
CLO_GW_2019	0.70	0.08	7.00E+00	8.00E-01	4	3
CLO_GW_2020	0.61	0.02	6.10E+00	2.00E-01	4	3
MCPA_GW_2019	0.86	0.04	8.60E+00	4.00E-01	4	3
MCPA_GW_2020	0.95	0.02	9.50E+00	2.00E-02	4	3

PEC: predicted environmental concentration; MC: measured concentration; PETR: predicted exposure toxicity ratio; METR: measured exposure toxicity ratio; PRP: predicted risk point; MRP: measured risk point. The MC column represents the maximum statistically significant value of all collected samples at $p < 0.05$ for each herbicide, agricultural season, and compartment.

rice paddies. Other studies found in the literature for pesticides assessment in rice paddy include a higher tier approach, like the one proposed by Karbouzas & Capri [8], using combined RICEWQ 1.6.2v and RIVWQ 2.02 models in Greece for herbicides assessment in surface and groundwater. Their approach for the environmental evaluation was based on the calculation of toxicity exposure ratios (TER) as EC50 or LC50 toxicity concentration divided by estimated PEC through the already mentioned mathematical models. Their simulation was performed considering two different soil scenarios, suggesting a higher threat for groundwater than for surface water in the case of sandy soils in comparison with clay soils, and this result is in line with our findings considering the highest sandy content and RPs values obtained.

4. Conclusions

The study combined field experiments and improved EPRIP model simulations to investigate the risk associated with the application of two herbicides in paddy rice systems in Italy. The measured and predicted surface water concentrations were consistent, while an overestimation was obtained for groundwater. The estimated RPs were generally consistent with those obtained from the field experiments, indicating that the improved EPRIP model can be used for risk assessment after herbicide applications. The study provides a fast and low-cost method to estimate water concentration after herbicide application in paddy rice systems and predict the RP, extending the application of EPRIP to other crops. The measured and predicted concentrations showed a negligible threat to aquatic life for both herbicides in surface water. While the PRPs for groundwater were higher than the MRPs for groundwater (4 and 3, respectively), it is important to underline that experimental groundwater concentrations were always under the legal endpoint imposed by European Directive 2006/118/EC of 0.1 μg/L for both herbicides. Despite the existence of higher-tier mathematical models to calculate PECs in paddy fields, the improved EPRIP tool adopted in this study was a good compromise for a Tier-1 environmental assessment in the agricultural management of paddy rice fields in the Mediterranean area. Furthermore, although this study was conducted in the Mediterranean area, EPRIP could be implemented globally with appropriate parameterization and adjustments, using different PEC calculators. The developed methodology is currently in the form of a Microsoft Excel sheet and enables the evaluation of RPs and EPRIP indicator for one field per run. However, in the future, it could be highly beneficial to develop a standalone desktop/mobile application or an online HTML/JavaScript dashboard that could assist rice farmers in making agricultural decisions.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

D. Voccia: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **L. Lamastra:** Writing – review & editing, Validation, Methodology, Investigation, Data curation, Conceptualization. **G. Fragkoulis:** Validation, Methodology, Data curation, Conceptualization. **A. Facchi:** Writing – review & editing, Funding acquisition, Data curation. **O. Gharsallah:** Writing – review & editing, Data curation. **F. Ferrari:** Formal analysis. **A. Tediosi:** Writing – review &

editing, Data curation. **M. Trevisan:** Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This research is part of the project 'MEDWATERICE: Towards a sustainable water use in Mediterranean rice-based agro-ecosystems', financed in the context of the PRIMA Programme (PRIMA Section 2–2018; Topic: 1.1.3: Irrigation technologies and practices). Italian researchers are co-funded by the Italian Ministry of Instruction, University and Research (MUR), which we wish to thank. A particular thank goes to Mr. Husain Sadeqi for the art contribution in Fig. 2 and to Marco Romani and Elisa Cadei from Ente Nazionale Risi for their support.

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