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Measurement and modelling of water flows and pesticide leaching under low input cropping systems

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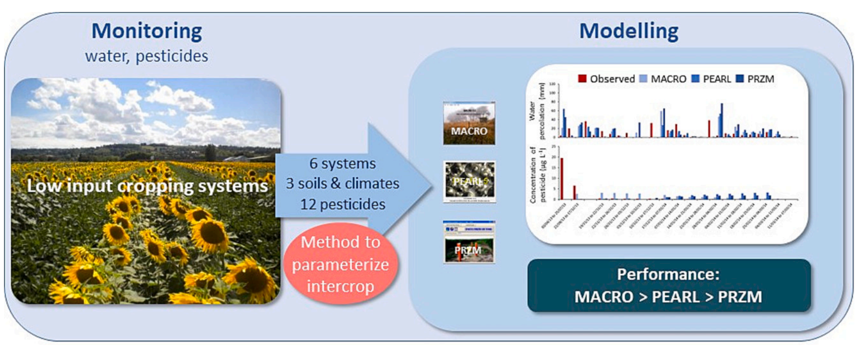
HIGHLIGHTS

- Water flows and pesticide leaching were measured in six low input cropping systems.
- MACRO, PEARL and PRZM performance in modelling observations was assessed without calibration.
- An original parameterization was developed to consider intercrops in the models.
- MACRO performs better than PEARL and PRZM, but performances were mostly poor.
- Groundwater contamination may be underestimated in several situations.

GRAPHICAL ABSTRACT



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ABSTRACT

One current challenge in sustainable agriculture is to redesign cropping systems to reduce the use and impacts of pesticides, and by doing so protect the environment, in particular groundwater, and human health. As a large range of systems could be explored and a wide number of pesticides used, field experiments cannot be carried out to study the sustainability of each of them. Thus, the objectives of this work were (1) to measure water flows and pesticide leaching in six contrasted low input cropping systems based on sunflower-wheat rotation, oilseed rape-wheat-barley rotation, and maize monoculture, experimented for three years in three different soil and climatic conditions, and (2) to assess and to compare the ability of three pesticide fate models (MACRO, PEARL, PRZM) to simulate the observed water flows and pesticide concentrations. The systems were designed using various crop

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rotations, including cover crops and intercrops. The models were parameterized with generic parameter estimation routines as done for regulatory risk assessment, and a method was developed to parameterize intercrops, not represented in the models: the use of average crop factors, maximum LAI, crop height and rooting depth of the crops constituting the intercrop allowed acceptable simulations of cumulative water flows, but not their dynamic. Twelve pesticides of 70 applied were quantified in lysimeter samples (*e.g.* bentazone, glyphosate, S-metolachlor), and their concentrations exceeded 0.1 μg L^{-1} in several occasions. The performance of the models to reproduce pesticide concentrations was generally poor illustrating the great challenge and the progress needed to simulate accurately pesticide transfers into the soil. The best fits to measured data were attained using "worst-case" pesticide sorption and degradation parameters. Overall, MACRO performed better than PEARL and PRZM. The method developed to parameterize intercrops could be used for risk assessment of groundwater contamination by pesticides in low input cropping systems, but the use of the three models without any calibration is likely to underestimate pesticide leaching in several situations.

1. Introduction

The intensification of agriculture, with the associated decrease in crop diversity and high pesticide use, has led to environmental pollution, loss of biodiversity, loss of ecosystem services, human health concerns, and pest resistance (Guinet et al., 2023; Pesce et al., 2024). Thus, one current challenge for a more sustainable agriculture is to redesign cropping systems to reduce the use and impacts of pesticides, thereby contributing to preserve the environment and protect human health (Lechenet et al., 2017; Guinet et al., 2023).

To foster the sustainability of agricultural systems, the European Directive 2009/128/EC (2009) encourages the development of integrated pest management (IPM), *i.e.*, combinations of non-chemical solutions for the management of pests, weeds, and diseases, with pesticides used at a last resort. Increasing plant diversity in agriculture is suggested as a pathway towards more resilient and sustainable production systems (Duru et al., 2015). At the farm scale, diversification can occur by diversifying successive crops in rotations, while at the field scale plant diversity can be increased through within-field mixtures of at least two crop species (intercropping) (Gaudio et al., 2019). Other technical solutions include cover crops, mulching, cultivar mixtures, false seedbed, pest-resistant plant varieties, inter-row plant cover, chemical weeding limited to the row (band spraying), change of sowing date and density, *etc.* (Lamichhane et al., 2015; Lechenet et al., 2017).

As a large range of innovative cropping systems can be explored, field experiments cannot be carried out to study the sustainability of each of them, and for a wide range of soil, climatic, and cropping system conditions. Therefore, *in silico* tools are useful for *ex ante* assessment of potential cropping systems. Moreover, field data on the fate of pesticides and their impacts on the environment are pretty scarce, especially for more diversified cropping systems. Consequently, pesticide fate models are relevant tools providing estimations of pesticide flows and concentrations at the base of the soil profile or in the drainage system. The most used models at the European level, as well as in many countries, are the four models selected for pesticides risk assessment before approval: MACRO (Water flow and solute transport in macroporous soil, Larsbo and Jarvis, 2003), PEARL (Pesticide Emission model At the Regional and Local scales, Leistra et al., 2001), PELMO (Pesticide Leaching Model, Klein, 2000), and PRZM (Pesticide Root Zone Model, Carsel et al., 2005) (FOCUS, 2000). As these models have their own strengths and weaknesses, it is recommended to use at least two of them for regulatory risk assessment (EFSA, 2004).

The predictive quality of these models has been extensively studied, which is a crucial step before assessing or simulating new situations without observed data. The models proved to be able to simulate the observed field dissipation of pesticides, but the quality of simulations depends on the climate, the soil, and the crop and pesticide properties (Brown et al., 2004; Jackson et al., 2005; Scorza Junior et al., 2007; Mamy et al., 2008; Rosenbom et al., 2009; Undabeytia et al., 2009; Fait et al., 2010; Leistra and Boesten, 2010; Marín-Benito et al., 2014; Lammoglia et al., 2017; Dufilho and Falco, 2020; Marín-Benito et al., 2020). However, these studies do not consider the whole cropping systems, as most of them focus on only one year or one cropping season, and they do not compare several cropping systems. Thus, the predictive performances of the models at this scale, on a pluri-annual basis, remains to be evaluated. Moreover, the models have to be adapted to simulate intercropping since it has not been considered in pesticide fate models so far (Klein, 2000; Leistra et al., 2001; Larsbo and Jarvis, 2003; Carsel et al., 2005; Gaudio et al., 2019).

The objectives of this work were (1) to measure water flows and pesticide concentrations in leachates in six low input cropping systems experimented for three years in three different soil and climatic conditions, and (2) to assess and to compare the ability of MACRO, PEARL and PRZM models (the structure of PELMO is comparable to that of PRZM, so it was not considered) to simulate the observed water flows and pesticide concentrations (metabolites were not investigated). The six cropping systems were designed to enhance sustainability as compared to contrasted standard systems based on durum wheat–sunflower rotation, oilseed rape–winter wheat–winter barley rotation, and maize monoculture. The models were used with routine parameterization and no calibration.

2. Materials and methods

2.1. Field experiments

Modelling was based on six low input cropping systems tested in three French experimental sites: Auzeville (Occitanie), Bretenière (Bourgogne-Franche-Comté) and Lamothe (Occitanie). They have been selected to cover a wide diversity of (1) crops (alfalfa, barley, faba bean, maize, oilseed rape, peas, soybean, sorghum, sunflower, triticale, wheat, *etc.*), (2) cropping practices (cover crops, intercropping, diversified crop rotation, mechanical weeding, *etc.*), and (3) pesticide use (Table 1). All three sites were equipped with sampling lysimeters to collect percolated water, and to monitor water flows and pesticides leaching.

2.1.1. Cropping systems

2.1.1.1. Durum wheat–sunflower based cropping systems. The experimental site of Auzeville (INRAE experimental unit, 43°31′38″N, 1°30′22″E) was set up in 2010 with the objective of assessing innovative low input cropping systems designed as alternatives to the traditional durum wheat–sunflower rotation under rainfed conditions in southwest France (Peyrard et al., 2016). Three cropping systems with a decreasing gradient in N fertilizer and pesticide use, combined with the use of cover crops during fallow period, were compared (Bonnet et al., 2021). In this study we used two of these cropping systems: the "Low input with cover crops" (LI) and the "Very low input with intercrops and cover crops" (VLI) systems (Table 1).

The LI system was designed to reduce nitrate leaching as well as pesticide use (reduction of 50 % of the treatment frequency index (TFI, Ministère de l'Agriculture, de la Souveraineté Alimentaire et de la Forêt, 2023) compared to the conventional system). Following the principles of IPM, the crop rotation was extended to three years including sorghum in

Table 1
Description of the low input cropping systems based on durum wheat–sunflower rotation (Auzeville), oilseed rape–winter wheat–winter barley rotation (Breteniére), and maize monoculture (Lamothe) with the corresponding treatment frequency index (TFI). Cover crops are written in *italic*. IWM: Integrated Weed Management.

Experimental site (studied period)	Cropping system	Crop sequence	TFI
Auzeville (2010–2015)	Conventional	Durum wheat–sunflower–durum wheat–sunflower–durum wheat–sunflower	5.1
	Low input with cover crops (LI)	*Egyptian clover*–durum wheat–*phacelia* + *purple vetch*–sorghum–sunflower + *alfalfa* + *Egyptian clover* + *red clover*–durum wheat–*mustard* + *purple vetch*–sorghum	3.4
	Very low input with intercrops and cover crops (VLI)	*Winter oat* + *phacelia*–sunflower + soybean–triticale + faba bean–*mustard* + *purple vetch*–durum wheat + peas–*winter oat* + *vetch*–sunflower + soybean–durum wheat + peas	3.1
Breteniére (2010–2014)	Conventional	Oilseed rape–winter wheat–winter barley–oilseed rape–winter wheat	7.9
	IWM reduced tillage (IWM_{RT})	Winter wheat–*spring oat* + *vetch* + *phacelia*–spring barley–winter oat–soybean–winter wheat	5.8
	IWM with mechanical weeding (IWM_{MW})	Winter wheat–maize–winter wheat–spring barley–triticale + peas	4.6
Lamothe (2010–2014)	Conventional	Maize–maize–maize–maize–maize	5.2
	Low input maize monoculture (M_{LIM})	*Hybrid ray grass* + *crimson clover*–maize + hybrid ray grass + crimson clover–*hybrid ray grass* + *crimson clover*–maize + hybrid ray grass + crimson clover–*hybrid ray grass* + *crimson clover*–maize + hybrid ray grass + crimson clover–*hybrid ray grass* + *crimson clover* + maize + crimson clover–*crimson clover*	2.8
	Integrated maize rotation (M_{IMR})	*Faba bean*–maize–winter oat–soybean–winter wheat–*mustard* + *purple vetch*–maize	1.9

addition to durum wheat and sunflower. The cover crops were alfalfa, Egyptian clover, red clover, phacelia, purple vetch or mustard, often in mixture (Table 1). The reduction in pesticide use was achieved through mechanical weeding and on-row band spraying. Fungicides were allowed only when necessary, according to decision rules based on harm threshold of pests and diseases causing significant damages (Bonnet et al., 2021). From 2010 to 2015, 20 applications of pesticides were done (Tables 2, S1 and S2), corresponding to an average annual TFI of 3.4 (compared to an average annual TFI of 5.1 for the corresponding conventional system) (Table 1). Only 28 mm of water was added for irrigation once (2 June 2015) to ensure cover crop emergence.

The objectives of the VLI system were to reduce N-fertilizer use and TFI by 75 % compared to the conventional system. To reach such objectives, legumes were introduced into the rotation comprising sunflower + soybean, triticale + faba bean and durum wheat + peas intercrops, and mechanical weeding and resistant wheat varieties were used (Table 1) (Peyrard et al., 2016; Bonnet et al., 2021). A total of 12 applications of pesticides was done (Tables 2, S1 and S2), corresponding to an average annual TFI of 3.1 (TFI = 5.1 for the conventional system) (Table 1). There was no irrigation.

2.1.1.2. Oilseed rape–winter wheat–winter barley based cropping systems. In the Breteniére site (INRAE experimental unit, 47°241′N, 5°115′E), the experiment was set up in the beginning of the 2000s with the objective to study the economic, social, and environmental impacts of one conventional system and four associated innovative low input cropping systems. These systems are based on integrated weed management (IWM) principles, aiming at gradually reducing the reliance on herbicides compared to the conventional cropping system which is based on an oilseed rape–winter wheat–winter barley rotation (Chikowo et al., 2009). In this work, a crop management period was studied from 2010 (year of lysimeters installation) to 2014 for two systems: the “IWM reduced tillage” (IWM_{RT}) and the “IWM with mechanical weeding” (IWM_{MW}) systems (Table 1). The plots are tile-drained.

The IWM_{RT} system was primarily designed to reduce labour requirement by excluding time consuming operations such as mouldboard ploughing, rotary harrowing and mechanical weeding. Shallow tillage was implemented during the first years of the experiment, but this system transitioned to full no-till in 2010 to better conform to principles of conservation agriculture while still adhering to IWM principles (Adeux et al., 2019). All IWM techniques applicable in the no-till context were used including diversified crop rotation, late cereal sowings, and competitive cultivars (Table 1). From 2003 to 2014, 71 applications of pesticides were done (Tables 2, S1 and S2), and the average annual TFI was 5.8 (compared to an average annual TFI of 7.9 for the corresponding conventional system) (Table 1). There was no irrigation.

The IWM_{MW} system used all the available prophylactic measures to reduce the potential weed infestations. In this system, scarce herbicide applications were combined with mechanical weeding, using flex-tine harrow in cereals, flex-tine harrow followed by hoe in oilseed rape, and hoe in crops with wide row spacing such as sugar beet, sunflower or faba bean. One intercrop (triticale + peas) was introduced in the rotation (Table 1). Sixty-five pesticide treatments were done on this system from 2003 to 2014 (Tables 2, S1 and S2). The average annual TFI was 4.6 (TFI = 7.9 for the conventional system) (Table 1). No irrigation was applied.

2.1.1.3. Maize-based cropping systems. The Lamothe experimental site (INP-EI Purpan experimental farm, 43°506′N, 1°237′E) was set up in 2010 with the objective of developing and evaluating the agronomic, environmental, and socio-economic performances of different maize-based cropping systems. One conventional irrigated maize monoculture and three low input maize-based cropping systems were designed and experimented with (Giuliano et al., 2021). This study considers two low input cropping systems from 2010 to 2014: the “Low input maize monoculture” (M_{LIM}) and the “Integrated maize rotation” (M_{IMR}) systems (Table 1).

The M_{LIM} system was designed to reduce the use of N fertilizer by 25 %, herbicides by 50 % (thanks to mechanical weeding and on-row band spraying), and irrigation by 25 % (using an early variety of maize to reduce water needs and post-harvest drying costs) compared to the conventional system. Soil and water protection was reinforced by introducing mixtures of cover crops and by associating maize to hybrid ray grass and Crimson clover (Table 1) (Giuliano et al., 2021). From 2010 to 2014, 16 applications of pesticides were done (Tables 2, S1 and S2) corresponding to an average annual TFI of 2.8 (compared to an average annual TFI of 5.2 for the conventional system) (Table 1), and plot was irrigated with a total of 490 mm of water.

The M_{IMR} system was based on a three-year rotation of maize–soybean–winter wheat and was designed to reduce, at the rotation level, the inputs of herbicides, irrigation, and N fertilizer by 50 % compared to the conventional system. At the maize crop level, M_{IMR} had the same input reduction objectives and management strategy as M_{LIM}, decreasing herbicide use by 50 % and irrigation water by 25 % to reduce pesticide leaching by 70 % (Giuliano et al., 2021). A total of 15 applications of pesticides was done (Tables 2, S1 and S2), with an average annual TFI of 1.9 (TFI = 5.2 for the conventional system) (Table 1), and the total irrigation corresponded to 265 mm of water.

2.1.2. Soils

The physico-chemical properties of the three soils were measured throughout the entire profiles and are summarized in Table 3. The Auzeville soil is a deep calcareous clayey soil, the Breteniére soil is a superficial calcareous clayey soil, and the Lamothe soil is a deep clay loam soil (Table 3).

Table 2
Dates of application and corresponding doses of pesticides observed in leachates in the low input cropping systems of Auzeville, Bretenière and Lamothe experimental sites. IWM: Integrated Weed Management.

Experimental site	Cropping system	Pesticide	Date of application	Dose (g ha^{-1})	Crop	Interception (%)[a]
Auzeville	Low input with cover crops (LI)	Imidacloprid	12 December 2013	124.95	Winter wheat	0
		S-metolachlor	7 May 2013	537.6	Sunflower + alfalfa + Egyptian clover + red clover	0
Bretenière	IWM reduced tillage (IWM$_{RT}$)	2,4-D	29 October 2013	240	Winter wheat	0
		Azoxystrobin	29 May 2012	200	Spring barley	70
		Bentazone	1 July 2013	696	Soybean	35
		Boscalid	23 April 2010	125	Oilseed rape	50
			5 May 2011	187.6	Winter wheat	70
		Glyphosate	8 October 2010	720	Winter wheat	20[a]
			14 October 2010	180	Winter wheat	15[a]
			27 July 2011	518.4	Spring oat + vetch + phacelia	10[a]
			16 March 2012	540	Spring barley	10[a]
			14 May 2013	1800	Before soybean	15[a]
			29 October 2013	612	Before winter wheat	30[a]
	IWM with mechanical weeding (IWM$_{MW}$)	Azoxystrobin	13 June 2013	200	Spring barley	70
		Cyproconazole	13 June 2013	80	Spring barley	70
		Florasulam	13 May 2013	7.5	Spring barley	50
Lamothe	Low input maize monoculture (M$_{LIM}$)	Glyphosate	15 April 2013	1440	Maize + ray grass hybrid + C majuscule	10[a]
		Mesotrione	16 May 2012	150	Maize + ray grass hybrid + C majuscule	25
			11 June 2012	150	Maize + ray grass hybrid + C majuscule	50
			14 June 2013	52.5	Maize + ray grass hybrid + C majuscule	50
			15 April 2014	45.6	Maize + ray grass hybrid + C majuscule	0
		Nicosulfuron	11 June 2012	60	Maize + ray grass hybrid + C majuscule	25
			14 June 2013	21	Maize + ray grass hybrid + C majuscule	25
		S-metolachlor	24 April 2013	470.4	Maize + ray grass hybrid + C majuscule	0
			22 April 2014	456	Maize + ray grass hybrid + C majuscule	0
		Thiamethoxam	18 April 2011	69.3	Maize + ray grass hybrid + C majuscule	0
			6 April 2012	69.3	Maize + ray grass hybrid + C majuscule	0
			24 April 2013	69.3	Maize + ray grass hybrid + C majuscule	0
			15 April 2014	69.3	Maize + ray grass hybrid + C majuscule	0
	Integrated maize rotation (M$_{IMR}$)	Mesotrione	14 April 2014	45.6	Maize	0
		S-metolachlor	26 April 2012	430.1	Soybean	0
			14 April 2014	456	Maize	0

[a] From FOCUS (2000) except for glyphosate (the interception was based on visual observations).

2.1.3. *Climate*

Climatic data (solar radiation, air temperature, relative humidity, wind speed and precipitation) for the Lamothe experimental site were monitored using a meteorological station located on the site. For Bretenière and Auzeville, climatic data were obtained from the INRAE Climatik (2023) database: Bretenière meteorological station for Bretenière, and Auzeville-Tolosane for Auzeville. Each station is located on the corresponding experimental site.

From 2010 to 2015, the average annual temperature in Auzeville was 13.8 °C and the average total annual precipitation was 663 mm (Fig. S1). In Bretenière, from 2010 to 2014, the average annual temperature was 11.4 °C and the average annual precipitation was 771 mm (Fig. S1). In

Table 3
Main soil properties of Auzeville, Bretenière, and Lamothe experimental sites. IWM: Integrated Weed Management.

Experimental site	Cropping system	Depth (cm)	Clay (<2 µm) (%)	Silt (2–50 µm) (%)	Sand (50–2000 µm) (%)	Organic carbon (%)	Bulk density (g cm^{-3})	pH (water)
Auzeville	Low input with cover crops (LI)	0–30	25.1	36.1	37.0	0.99	1.37	8.3
		30–60	30.6	40.6	23.3	0.82	1.38	8.4
		60–90	26.9	30.4	37.4	0.50	1.51	8.6
		90–110	24.7	36.1	26.0	0.42	1.51	8.7
	Very low input with intercrops and cover crops (VLI)	0–30	31.0	35.1	31.0	1.05	1.59	7.8
		30–60	33.5	39.0	22.5	0.90	1.51	8.1
		60–90	18.4	34.9	11.9	0.19	1.52	8.8
		90–110	14.2	32.5	11.9	0.13	1.59	9.0
Bretenière	IWM reduced tillage (IWM$_{RT}$)	0–23	43.52	51.92	4.56	2.25	1.46	6.65
		23–48	44.61	50.96	4.43	1.77	1.46	6.83
		48–81	46.62	49.13	4.25	0.67	1.46	7.48
	IWM with mechanical weeding (IWM$_{MW}$)	0–13	41.52	53.34	5.14	1.57	1.51	7.02
		13–29	41.32	53.53	5.16	1.52	1.43	7.02
		29–75	47.42	47.71	4.88	0.68	1.37	7.52
Lamothe	Low input maize monoculture (M$_{LIM}$)	0–10	40.8	46.9	12.3	1.44	1.57	7.1
		10–30	37.5	46.5	16.0	1.12	1.57	7.3
		30–60	47.2	42.5	10.3	0.82	1.57	7.8
		60–90	50.1	40.1	9.8	0.49	1.65	8.3
	Integrated maize rotation (M$_{IMR}$)	0–10	40.9	41.1	18.0	1.41	1.48	7.3
		10–30	39.9	40.0	20.1	1.18	1.48	7.4
		30–60	45.4	36.3	18.3	0.87	1.67	7.8
		60–90	45.0	26.8	28.2	0.49	1.74	8.2

Lamothe, they were 13.5 °C and 627 mm, respectively, from 2010 to 2014 (Fig. S1).

2.2. Measurements of water flows and pesticide concentrations in leachates

Water flows and pesticide concentrations in leachates were monitored using tension plate lysimeters (SIC300, UMS GmbH, München, Germany) in Auzeville and Lamothe, and using fiberglass wick lysimeters (1/2″ fiberglass wick, Pepperell Braiding Company, MA, USA) in Bretenière, all located in the middle of the experimental plots. The tension plate lysimeters had a fixed tension of −100 hPa and were installed at 1 m depth in Lamothe and Auzeville, while wick lysimeters had a tension of −70 hPa and were installed at 0.5 m depth above drainage tiles in Bretenière. Leachates were collected every week using vacuum pumps, and stored at −20 °C until pesticide analyses. When the amounts of water were low (dry periods) and not sufficient for analysis, they were cumulated.

Pesticide analyses were done by the Laboratoire Départemental d'Analyses de la Drôme (Valence, France) accredited by COFRAC (French Committee of Accreditation). For all pesticides, the limit of quantification (LOQ) and the limit of detection (LOD) were 0.02 and 0.007 μg L^{-1}, respectively.

Pesticide concentrations were assessed in view of the regulatory threshold of 0.1 μg L^{-1} for groundwater (Council Directive 80/778/EC, 1980). This regulatory does not apply to the vadose zone above water table, where concentrations were measured, and where concentrations are expected to be higher than in groundwater, since pesticides transferred to the water table are diluted in a larger water volume. However, leaching of water with pesticide concentration exceeding the regulatory threshold is likely to increase both the concentration in groundwater and the risk to exceed the regulatory threshold in groundwater. Therefore, considering this threshold of 0.1 μg L^{-1} ensures the groundwater will not be negatively impacted.

2.3. Models

MACRO (Larsbo and Jarvis, 2003), PEARL (Leistra et al., 2001), and PRZM (Carsel et al., 2005) are one-dimensional models designed to simulate the movements of chemicals in unsaturated soil systems. The three models use different approaches to describe water and solute transport, pesticide fate and crop development.

2.3.1. Water and solute transport

MACRO is a dual-permeability model, which includes a description of preferential flow processes by dividing the pore system into micropores and macropores. The boundary between the two domains is defined by a soil water pressure head close to saturation, and its associated water content and hydraulic conductivity. Water flow in micropores is calculated by the Richards equation while it is gravity driven in the macropore domain. Solute transport in micropores is described by the advection-dispersion equation while it is assumed to be solely convective in macropores. Exchange between the two domains is calculated according to approximate, physically based expressions using an effective aggregate half-width. In this work, we used a development version of the MACRO model allowing the simulation of crop rotations (aiming at replacing the official release MACRO 5.2 in the future). PEARL 4.4.4 implements the Richards equation and the advection-dispersion equation to simulate the water flow and solute transport, respectively. In PRZM 3.21, the description of soil hydrology is based on a “tipping-bucket” approach (capacity model) where water will only percolate to the deeper soil layer if field capacity is exceeded. Solute transport is described by convection and numerical dispersion. PEARL and MACRO, but not PRZM, are able to take into account the upward movement of water and solute.

2.3.2. Pesticide fate

The three models simulate instantaneous adsorption of pesticides using linear or Freundlich formalisms. The degradation of pesticides follows first-order degradation kinetics, although PRZM also enables the use of a bi-phasic equation. MACRO, PEARL and PRZM consider the effect of soil moisture content and soil temperature on the pesticide degradation rate. MACRO simulates degradation and sorption processes in both micro and macropore domains. PEARL and PRZM can simulate the pesticide volatilization while MACRO does not include a comprehensive description of this process. PRZM is the only one of the three models which simulates soil erosion and surface runoff using the Modified Universal Soil Loss Equation (MUSLE) and a modified Soil Conservation Service curve number technique, respectively. However, these two subroutines were switched off in this study because the field slopes were below 1 % (negligible soil erosion), and because no surface runoff was observed in the fields (this was regularly monitored).

2.3.3. Crop development

In MACRO, the representation of crop development is simply based on crops' emergence and harvest dates, maximum leaf area index (LAI), maximum root depth, and maximum crop height. Root depth and crop height are assumed to increase linearly until the crop reaches its maximum development. The increase of the LAI is divided in two phases, a slow linear growth phase (for describing autumn crop overwintering) and a fast non-linear growth phase until the LAI reaches its full extent. When the maximal development is reached, root depth, crop height and total LAI are kept constant until harvest, but the green LAI decreases (non-linearly) until the harvest date. MACRO assumes that the root density varies logarithmically with depth and allows the user to set a value for the fraction of root density in the uppermost 25 % of the root depth. In PEARL, the growth of the crop is expressed as a function of the development stages, defined by the user, ranging from emergence date to harvest date. Each stage, where the crop development is linear, is defined by a LAI, a crop factor, a root depth, and a crop height. The root density profile can be freely defined. In PRZM, the development of the crop is also simply based on crops' emergence, maturation and harvest dates, maximum root depth, maximum crop height, and maximum areal coverage of the canopy. The crop grows linearly until crop maturity and then stays constant until harvest. PRZM assumes a triangular root distribution from the soil surface to the maximum rooting depth, with the maximum root density being near the surface which cannot be modified by the user.

2.4. Parameterization

This work aimed at testing MACRO, PEARL and PRZM following the FOCUS methodology (FOCUS, 2000) used for European regulatory risk assessment of pesticides, *i.e.*, using the University of Hertfordshire/IUPAC pesticide property database which compiles data from European regulatory reports (hereafter “PPDB”, Lewis et al., 2016), and generic model-parameterization routines. Thus, no calibration was done.

2.4.1. Crops

The site-specific sowing and harvest dates of the various crops and cover crops are summarized in Table S3. The plant uptake factors were set to 0.5 as recommended by FOCUS (2000).

2.4.1.1. Sole crops. One of the key inputs for crop in MACRO, PEARL and PRZM is the crop factor. This parameter is inputted as ZALP in MACRO, kc in PEARL, and PFAC in PRZM (Leistra et al., 2001; Larsbo and Jarvis, 2003; Carsel et al., 2005). MACRO and PEARL allow defining a specific crop factor for each crop of the cropping system while, in PRZM, only one value can be defined for the entire system. We chose to use FOCUS (2000) which provides several crop factor values according to the type of crops. For PEARL, the seasonal crop factors (kc_season) were used as kc inputs for each individual crop (Table S3). In PRZM, PFAC was calculated based on the average of the annual crop factors (kc_year) of all crops involved in the cropping system (Table S3). For MACRO, the ZALP values were used (Table S3). When parameter values for a crop or a cover crop which was cultivated in the experimental sites were not listed in FOCUS (2000), we used values for a crop with similar traits: for example, for Egyptian clover and sorghum we used parameter values for peas and maize, respectively (Table S3).

Then, PEARL and MACRO had to be parameterized with the LAI (maximum, harvest) of crops, but only few measurements were available (Table S3). Consequently, the maximum LAI values were taken from FOCUS (2000): for Auzeville and Lamothe, the maximum LAI were obtained from FOCUS Piacenza, and for Breteniѐre, they were obtained from FOCUS Châteaudun, as the climate of these two scenarios are close to those of the three experimental sites. The LAI at harvest were taken from Jarvis et al. (2007) as no value was available in FOCUS (2000).

Regarding the height of the crops and the maximum rooting depths, values were taken from FOCUS (2000).

2.4.1.2. Intercrops. In the three models, only one crop can be defined at a given time (Leistra et al., 2001; Larsbo and Jarvis, 2003; Carsel et al., 2005), therefore a new method was developed to parameterize the intercrops, such as the sunflower + soybean cash crop mixture, and the oat + vetch + phacelia or maize + hydrid ray grass + Crimson clover cover crop mixtures (Table S3). To the best of our knowledge, only a few values of crop factors for intercrops are available in the literature, and these do not correspond to our case studies (*e.g.* de Araújo et al., 2017; Bastos de Souza et al., 2015). Therefore, several options were explored to estimate crop factors for intercrops: (1) the equation proposed by Miao et al. (2016); (2) the maximum of the crop factor values (ZALP for MACRO, kc_season for PEARL, kc_year for PRZM; FOCUS, 2000) of the crops constituting the intercrop; and (3) the mean of the crop factor values (ZALP, kc_season or kc_year; FOCUS, 2000) of the crops constituting the intercrop.

Then, for the maximum LAI, which were taken from FOCUS (2000), (1) the sum of the maximum LAI values of the crops or (2) the maximum of the maximum LAI values among all crops, were tested. The LAI at harvest (Jarvis et al., 2007) were tested similarly.

Finally, the maximum height and maximum rooting depth of the crops constituting the intercrops were retained, as several studies demonstrated that there was no significant difference in root depth penetration and in height between sole crops and intercrops (Li et al., 2006; Corre-Hellou et al., 2009; Ma et al., 2019). In addition, considering the water balance, the maximum rooting depth among all crops was considered as appropriate as it determines the maximum depth of water and pesticides uptake.

Since the objective was to propose a generic method for parameterizing intercrops, the various options of parameterization were tested iteratively: once an option was deemed acceptable for one system and one model regarding the statistical indices (see Section 2.4) and the observed and simulated cumulative volumes of percolated water, it was then tested for another system and model. If an option did not yield satisfactory results, it was discarded, and another one was tested and so on. Thus, not all options were tested for all systems.

2.4.2. Soils

The soil physico-chemical properties were parameterized with the measured values (see Section 2.1.2) (Table 3). Neither measurement of soil hydraulic properties nor calibration were used to parameterize the models. For MACRO, soil hydraulic properties (TPORV, XMPOR, WILT, RESID, CTEN, N, KSATMIN, KSM, ASCALE, ALPHA) were obtained from the MACRO 5.0/5.1 build-in pedotransfer function. For PEARL, van Genuchten's soil-water retention parameters (θr, θs, Ksat, α, n) were derived from soil texture and bulk density using Rosetta pedotransfer functions of RETC (RETention Curve) (van Genuchten et al., 1991) (Table S4). The corresponding water retention curves obtained with RETC were then used to calculate the soil water content at field capacity (pF = 2) and at wilting point (pF = 4.2) as required for PRZM (Table S4).

For MACRO and PEARL, the soil profiles at the three experimental sites were divided into five layers of various thickness with free drainage conditions at the bottom of the soil profile, as the groundwater level remained below these depths throughout the simulation period (Table S4). For PRZM, to get the water flows and pesticide concentrations in the leachates at the lysimeter depths, soil profiles of 1 m were split into four horizons for Auzeville and Lamothe, and the soil profile of 0.5 m was split into four horizons for Breteniѐre (Table S4). The thickness of compartments in each horizon was set to 1 cm.

2.4.3. Pesticides

The 70 different pesticides (30 herbicides, 28 fungicides, 10 insecticides, 2 molluscicides) applied on the six cropping systems, indication if they were investigated or not in leachates, their main physicochemical properties and the corresponding doses and dates of application, are summarized in Tables 2, S1 and S2.

The pesticide molecular weights, water solubilities, vapour pressures, degradation half-live (DT50), and Freundlich adsorption coefficients (Kf, nf) were obtained from the PPDB (Lewis et al., 2016) (Tables S2 and S5). For each observed pesticide, the minimum, mean, typical, and maximum values of DT50 (either field or laboratory), and the minimum, mean, and maximum values of Kf and nf were tested as inputs to determine the combination leading to the best model performances (Table S5). The DT50 values for deep soil layers (>30 cm) were estimated from the PPDB values according to FOCUS (2000) (*i.e.*, degradation rate k (= ln(2)/DT50) in 0–30 cm depth, k × 0.5 in 30–60 cm, k × 0.3 in 60–100 cm, k = 0 below 100 cm). The sorption coefficient values for deep soil layers were also estimated from PPDB values, assuming this coefficient was proportional to organic carbon content (Marín-Benito et al., 2014). The nf was assumed constant all along the soil profile.

2.4.4. Simulations

To compare the volumes of percolated water observed in the lysimeters with the model outputs, the method of Marín-Benito et al. (2014) was used: for MACRO and PEARL, the simulated daily water percolation was considered only if the simulated soil pressure head was higher than −100 hPa in Auzeville and Lamothe, and higher than −70 hPa in Breteniѐre, respectively (see Section 2.2). This approximation cannot be used for the PRZM capacity model which was parameterized with field capacity at pF = 2 (−100 hPa).

Each simulation started with a minimum warmup period of one year to reduce the effect of the initial conditions on the results.

The simulations lasted from 1 January 2010 to 31 December 2014 for Breteniѐre and Lamothe. They lasted from 1 January 2010 to 31 December 2015 and to 31 December 2014 for LI and VLI in Auzeville, respectively.

2.5. Model performance

The performance of MACRO, PEARL and PRZM in simulating the dynamic of water flows (mm) and of the pesticide concentrations in leachates ($\mu g\ L^{-1}$), represented by the weekly (or more, depending on the available measures) cumulative water volume and pesticide mass samples, was evaluated by calculating four statistical indices:

(i) the sample correlation coefficient *r*, which is a measure of the degree of association between simulation and measurement, and indicates whether the shape of the plotted simulation is similar to the measured data or not:

$$r = \frac{\sum_{i=1}^{n}(O_i - \overline{O}) \times (P_i - \overline{P})}{\left[\sum_{i=1}^{n}(O_i - \overline{O})^2\right]^{1/2}\left[\sum_{i=1}^{n}(P_i - \overline{P})^2\right]^{1/2}} \quad (1)$$

where O_i and P_i are the observed and predicted values, respectively, $\overline{O}$ and $\overline{P}$ are the mean observed and predicted values, respectively, and n is the number of sampling dates. If $r = +1$ (-1), then there is perfect positive (negative) correlation between simulated and measured values, if $r = 0$, then there is no correlation between simulations and measurements.

(ii) the modelling efficiency EF indicates if the simulated values correspond closely to measured values:

$$EF = \frac{\sum_{i=1}^{n}(O_i - \overline{O})^2 - \sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}(O_i - \overline{O})^2} \quad (2)$$

$EF = 1$ indicates a perfect correspondence.

(iii) the relative root mean square error $RRMSE$ provides a percentage term for the total difference between the predicted and the observed values:

$$RRMSE = \frac{100}{\overline{O}}\sqrt{\sum_{i=1}^{n}\frac{(P_i - O_i)^2}{n}} \quad (3)$$

The lower limit for $RRMSE$ is 0, in which case there is no difference between measured and simulated values.

(iv) the coefficient of residual mass CRM gives an indication of the consistent errors in the distribution of all simulated values across all measurements with no consideration of the order of the measurements:

$$CRM = \frac{\sum_{i=1}^{n}O_i - \sum_{i=1}^{n}P_i}{\sum_{i=1}^{n}O_i} \quad (4)$$

A negative (positive) value indicates that the majority of predicted values are greater (less) than the measured values. A CRM value of 0 denotes no bias in the distribution of predicted values with respect to measured values.

3. Results and discussion

3.1. Field measurements

Most of the pesticides applied in the various cropping systems were investigated (58 of 70) (Tables 4 and S1). Twelve different pesticides were found in the lysimeters (two in LI, zero in VLI, five in IWM_{RT}, three in IWM_{MW}, five in M_{LIM}, two in M_{IMR}), concentrations of the other pesticides were below LOQ (Tables 2, 4, S1 and S2).

The lack of quantification of the investigated pesticides is consistent with their mobility, persistence, and/or doses and years of application (Tables S1 and S2). Indeed, pesticides with high mobility (Koc < 150 L kg^{-1}, McCall et al., 1980), such as bromoxynil octanoate or cymoxanil, also generally have low persistence (DT50 < 25 d) (Table S2). As their degradation is rapid, the amounts that could potentially be leached quickly become negligible, unless rainfall events or irrigation occur soon after the application of the pesticide. In this case the pesticide may reach the subsoil where degradation is much slower. The mobility of the other pesticides ranges from moderate to null (immobile compounds) (McCall et al., 1980) (Table S2), which can explain why they were not found in water (*e.g.* alpha-cypermethrin, flurochloridone, thiram). In addition, some pesticides were applied at very low doses (few g ha^{-1}) such as cymoxanil, deltamethrin or fludioxonil (Table S2), and/or several years (>5 years) before the experiments, such as myclobutanil or napropamide (Table S2), which supports the lack of quantification.

Table 4
Number of different pesticides which were applied, investigated and observed (>LOQ) in the low input cropping systems of Auzeville, Bretenière, and Lamothe experimental sites. IWM: Integrated Weed Management, F: fungicide, H: herbicide, I: insecticide.

Experimental site	Cropping system	Number of different applied pesticides[a]	Number of investigated pesticides[a]	Observed pesticides
Auzeville	Low input with cover crops (LI)	16	16	Imidacloprid (I) S-metolachlor (H)
	Very low input with intercrops and cover crops (VLI)	7	7	–
Bretenière	IWM reduced tillage (IWM_{RT})	44	39	2,4-D (H) Azoxystrobin (F) Bentazone (H) Boscalid (F) Glyphosate (H)
	IWM with mechanical weeding (IWM_{MW})	45	40	Azoxystrobin (F) Cyproconazole (F) Florasulam (H)
Lamothe	Low input maize monoculture (M_{LIM})	6	6	Glyphosate (H) Mesotrione (H) Nicosulfuron (H) S-metolachlor (H) Thiamethoxam (I)
	Integrated maize rotation (M_{IMR})	12	11	Mesotrione (H) S-metolachlor (H)

[a] See Tables 2, S1 and S2 for more details.

Among the 12 different observed pesticides, seven are herbicides (2,4-D, bentazone, florasulam, glyphosate, mesotrione, nicosulfuron, S-metolachlor), three are fungicides (azoxystrobin, boscalid, cyproconazole), and two are insecticides (imidacloprid, thiamethoxam) (Tables 2 and 4). This result is in agreement with monitoring conducted at the French national level by public authorities, where >50 % of observed pesticides in groundwater are herbicides (notre-environnement, 2023). The pesticides quantified are also among the most frequently observed in groundwater in France: glyphosate, S-metolachlor, boscalid, and imidacloprid (Tables 2 and 4; notre-environnement, 2023). Indeed, of 12 quantified molecules, six (2,4-D, bentazone, florasulam, mesotrione, nicosulfuron, thiamethoxam) have high to very high mobility, *i.e.*, Koc < 150 L kg^{-1} (McCall et al., 1980); four (azoxystrobin, cyproconazole, imidacloprid, S-metolachlor) have moderate mobility (150 L kg^{-1} < Koc < 500 L kg^{-1}); one (boscalid) has low to very low mobility (500 L kg^{-1} < Koc < 5000 L kg^{-1}). One pesticide, glyphosate, is considered immobile in solution (Koc > 5000 L kg^{-1}) but it can be transported associated to colloids (Carretta et al., 2022) (Table S5). Pesticides with moderate to very low mobility have high persistence (DT50 > 90 days, Regulation (EC) No 1107/2009, 2009) (Table S5) which could explain they were found in water.

For Auzeville, no pesticide was observed (above the LOQ) in the VLI system while two of the 16 applied and investigated pesticides were found in water in LI, which is consistent with higher amounts applied (Tables 2, 4 and S2). In LI, the maximum average concentration of S-metolachlor (0.31 μg L^{-1}) was observed one month after application (Fig. S2b) and was higher than the regulatory threshold for groundwater of 0.1 μg L^{-1} (Council Directive 80/778/EC, 1980). On the contrary, the concentrations of imidacloprid remained lower than 0.1 μg L^{-1} (Fig. S2a).

For the cropping systems tested in Bretenière, five pesticides were quantified (of 39 applied and investigated) in IWM_{RT}, and three (of 40 applied and investigated) in IWM_{MW} (Tables 2, 4 and S2). The concentrations of bentazone in IWM_{RT} were high and most of the time higher than 0.1 μg L^{-1} (Fig. S2e). The maximum observed concentration was 19.6 μg L^{-1}, it was due to one rainfall event of 18 mm occurring the day after the application (Figs. S1 and S2e). The concentration of glyphosate reached the high concentration of 2.3 μg L^{-1} in May 2013 (Fig. S2g), probably due to transport through preferential flows after a rainfall event of 21 mm in the hours following application, and co-transport (Figs. S1 and S2g) (Carretta et al., 2022). The concentrations of 2,4-D and boscalid in IWM_{RT} (Fig. S2c and f), and of cyproconazole in IWM_{MW} (Fig. S2i), were lower than 0.1 μg L^{-1}, while those of azoxystrobin were lower than 0.1 μg L^{-1} in IWM_{RT} but slightly higher in IWM_{MW} (0.11 μg L^{-1}) (Fig. S2d and h). Indeed, in IWM_{RT}, the measurements of azoxystrobin concentrations in water were done one year after the application while they were done some days after in IWM_{MW} (Fig. S2d and h, Table 2). Finally, the concentrations of florasulam in IWM_{MW} reached 0.10 μg L^{-1} several days after its application, probably because of 74 mm of rain in the next ten days (Figs. S1 and S2j). It has to be underlined that, in Bretenière, pesticide concentrations were measured at 0.5 m depth, not at 1 m depth. However, the gravity water flows will reach the groundwater 0.5 m below.

In Lamothe, five pesticides (of 6 applied and investigated) were quantified in M_{LIM}, but only two (of 11 applied and investigated) in M_{IMR} (Tables 2, 4, and S2). For all pesticides, the concentrations were higher than 0.1 μg L^{-1} (Fig. S2k–q). Mesotrione peak (*i.e.*, maximum) concentrations were observed on average 1.5 month after application (Fig. S2l and p, Table 2). The high concentrations of S-metolachlor in M_{LIM} (0.73 and 5.46 μg L^{-1}) and M_{IMR} (2.4 and 0.78 μg L^{-1}) were consecutive to several episodes of >20 mm of rain (Figs. S1 and S2n and q). For nicosulfuron, the peak concentration (1.15 μg L^{-1}) observed in 2012 is due to a total of 14 mm of rain from the day of application (11 June 2012) until 13 June. In 2013, the maximum concentration (0.25 μg L^{-1}) was observed more than two months after application, while a high concentration (5.43 μg L^{-1}) was observed in June 2014, more than one year after the last application (Fig. S2m, Table 2). Giuliano et al. (2021) demonstrated that the drainage volume was the main factor explaining the maximum concentrations recorded each year for mesotrione, S-metolachlor, and nicosulfuron in Lamothe. The highest concentration of glyphosate (0.25 μg L^{-1}) in M_{LIM} in 2013 correspond to a total amount of 184 mm of rain during the measurement period (Figs. S1 and S2k). The peak concentration of 0.41 μg L^{-1} in June 2014, more than one year after the application, may be due to slower degradation of the herbicide than usually estimated, co-transport, release of bound glyphosate and/or large drainage volume (Holten et al., 2019; Giuliano et al., 2021; Carretta et al., 2022). Finally, for thiamethoxam, high concentrations (from 0.28 to 0.34 μg L^{-1}) were observed in M_{LIM} each year, two to three months after its application (Fig. S2o, Table 2).

Overall, the analysis of the pesticide concentration measurements in the studied sites and cropping systems showed that most of the pesticides which were quantified in leachates were herbicides (having high mobility and/or high persistence), and that their concentrations were often higher than the regulatory threshold for groundwater of 0.1 μg L^{-1}. For the durum wheat-sunflower system, the best management with no pesticide quantified in water was the VLI system (Table 4). For the oilseed rape–winter wheat–winter barley based cropping systems, the IWM_{MW} allowed the most significant reduction of applied and quantified pesticides, while for maize systems, the best system was the M_{IMR} (Table 4).

3.2. Modelling

3.2.1. Modelling of water flows

3.2.1.1. Testing the developed method to parameterize intercrops. The results of the simulated cumulative volumes of percolated water showed that the best crop factor value to input for intercrops was the mean of all the crop factors of the associated crops (Tables 5 and S6). For the LAI of intercrops (PEARL and MACRO), the most acceptable results were obtained with the selection of the maximum value of the LAIs of all crops constituting the association of crops. This is consistent with previous findings demonstrating that the LAI of each crop in an intercrop is lower than that it would be as a sole crop due to interspecific competition (Gao et al., 2014; Ren et al., 2016). Other authors showed that the LAI of an intercrop was higher than the LAI of the crop having the higher LAI (Rahman et al., 2017; Yang et al., 2018) but such parameterization did not lead to acceptable simulation of the total percolated water amounts: the addition of the LAIs led to very high simulated evapotranspiration leading to strong underestimation of the observed volumes of percolated water (data not shown). As indicated in Section 2, for crop height and rooting depth, the highest values among the crops of intercrop were selected.

As a summary, for intercrops, the best parameterization for crop parameters was the mean of crop factors, the maximum LAI, the maximum crop height and the maximum rooting depth of the crops present at the same time. This parameterization led to acceptable simulated cumulative volumes of percolated water, as detailed below in Section 3.2.1.2 (Tables 5 and 6). However, one avenue of improvement could be to use simulated plant growth and evapotranspiration data for intercropping systems, using crop models such as STICS, as inputs for pesticide fate models (Vezy et al., 2023).

3.2.1.2. Model performances to simulate water flows. Without calibration, MACRO allowed acceptable simulations of the total volumes of percolated water, followed by PEARL, and then PRZM (Table 6). MACRO reproduced well the cumulative percolated water in LI, IWM_{RT} and M_{LIM}. It slightly overestimated the amounts of water in IWM_{MW} (15 %), overestimated them in VLI (46 %), while it underestimated the amounts of percolated water in M_{IMR} (23 %) (Table 6). PEARL was able to simulate satisfactorily the amounts of water in M_{LIM}. The model underestimated percolated water in LI (44 %), VLI (36 %) and IWM_{MW} (22 %), it slightly overestimated those of IWM_{RT} (6 %), and strongly overestimated those of M_{IMR} (88 %) (Table 6). PRZM was the least efficient model: it overestimated the amounts of water in Auzeville, from 13 % in LI to 44 % in VLI, as well as in Bretenière, from 28 % for IWM_{RT} to 78 % for IWM_{MW}, and underestimated those in Lamothe, from 20 % for M_{LIM} to 18 % for M_{IMR} (Table 6). In general, PRZM predicted higher percolation of water than MACRO and PEARL, except in Lamothe (Table 6). As stated by Marín-Benito et al. (2014), this can be due to the approximation carried out on the percolation predicted by MACRO and PEARL to mimic fixed tension lysimeter condition (−100 hPa or −70 hPa) (see Section 2.4.4), as this type of bottom boundary condition is not explicitly simulated by the models. While in PEARL and MACRO vertical water flow occurs throughout the entire water potential range, it occurs in PRZM only if the saturation condition of the soil is above field capacity (−100 hPa). This is also consistent with the findings of Garratt et al. (2003) who simulated a higher percolation of water with capacity models than with models based on Richard's equation, and assumed it was due to the absence of upward movement of water in the capacity models.

Although the models satisfactorily simulated the cumulative

Table 5
Modelling efficiency (EF), correlation coefficient (r), coefficient of residual mass (CRM) and relative root mean square error (RRMSE, %) of MACRO, PEARL and PRZM for the volumes of percolated water (mm) in the low input cropping systems of Auzeville, Bretenière and Lamothe experimental sites. IWM: Integrated Weed Management.

Experimental site	Cropping system	MACRO				PEARL				PRZM			
		EF	r	CRM	RRMSE	EF	r	CRM	RRMSE	EF	r	CRM	RRMSE
Auzeville	Low input with cover crops (LI)	0.20	0.75	−0.012	94	−7.09	0.235	0.435	93	−7.48	0.256	−0.126	95
	Very low input with intercrops and cover crops (VLI)	−2.90	0.430	−0.460	173	0.116	0.558	0.358	83	−0.52	0.489	−0.445	108
Bretenière	IWM reduced tillage (IWM_{RT})	−1.34	0.026	−0.006	189	−1.61	0.042	−0.059	199	−3.00	−0.037	−0.283	248
	IWM with mechanical weeding (IWM_{MW})	−2.45	0.336	−0.154	199	−1.43	0.352	0.216	167	−4.84	0.325	−0.781	259
Lamothe	Low input maize monoculture (M_{LIM})	−0.92	0.164	−0.021	149	−1.27	0.117	−0.034	162	−1.11	0.161	0.197	156
	Integrated maize rotation (M_{IMR})	−1.95	0.099	0.229	138	−6.39	−0.042	−0.882	218	−3.90	−0.045	0.177	178

Table 6
Soil water balance observed and simulated with MACRO, PEARL and PRZM in the low input cropping systems of Auzeville, Bretenière and Lamothe experimental sites. In the same site, the amounts of precipitations are different from one system to another because they correspond to the dates of the observed amounts of percolated water which were measured with the lysimeters. IWM: Integrated Weed Management.

Experimental site	System	Date	Precipitation (mm)	Irrigation (mm)	Observed cumulative volumes of percolated water (mm)	Simulated cumulative volumes of percolated water (mm)			Simulated actual evapotranspiration (mm)		
						MACRO	PEARL	PRZM	MACRO	PEARL	PRZM
Auzeville	Low input with cover crops (LI)	7 February 2013 to 17 July 2015	1548	28	279	282	157	314	1391	1292	1362
	Very low input with intercrops and cover crops (VLI)	7 February 2013 to 10 July 2014	672	0	97	142	62	140	584	500	552
Bretenière	IWM reduced tillage (IWM_{RT})	9 November 2012 to 13 May 2014	1007	0	399	401	422	511	632	572	569
	IWM with mechanical weeding (IWM_{MW})	9 November 2012 to 13 May 2014	1245	0	358	413	281	637	673	586	661
Lamothe	Low input maize monoculture (M_{LIM})	6 April 2012 to 11 August 2014	1165	490	230	225	238	185	1260	1386	1353
	Integrated maize rotation (M_{IMR})	22 May 2012 to 11 August 2014	1006	265	232	179	437	191	988	835	1045

volumes of water, the dynamic of water percolation was poorly reproduced as indicated by the low values of the statistical indices (Table 5). Only a few studies have previously assessed the performance of the three models regarding water percolation. The statistical indices obtained in this work were consistent with those reported by Lammoglia et al. (2017) for MACRO, and better than those obtained by Marín-Benito et al. (2014) for the three models (Table 5). MACRO, PEARL and PRZM allowed better representation of the dynamic of water percolation in Auzeville cropping systems than in Bretenière and in Lamothe cropping systems highlighting that the performance of the models depended on the site (Table 5, Fig. 1). This variability in model performance across different soil and climatic conditions has also been observed by several authors (*e.g.* Moeys et al., 2012; Queyrel et al., 2016; Lammoglia et al., 2017).

For Auzeville, the three models simulated some percolation of water each time it was observed (Fig. 1), except for specific periods: from 16 April to 4 June 2013 and from 14 March to 1 June 2014 in the LI cropping system, and from 1 June to 10 July 2014 in VLI. These gaps corresponded to heavy rainfall events on the 30 May 2013 (36 mm), 25–31 May 2014 (42 mm), 23–24 June 2014 (70 mm), and 6 July 2014 (18 mm) (Fig. S1). The dynamic of water percolation is different in LI and VLI despite identical meteorological conditions: differences in soil structures and dynamic of evapotranspiration due do different cropping systems could explain why a peak of water percolation was observed before 1 June in LI but after 1 June in VLI (Basset et al., 2023) (Fig. 1). In IWM_{RT} of Bretenière, almost all percolation events were simulated by the models, except some events exceeding 10 mm: 8–10 April 2013 (19 mm), 7–14 May 2013 (63 mm), 7–16 September 2013 (55.5 mm), and 1 November–6 December 2013 (94 mm) (Figs. 1 and S1). For IWM_{MW}, no rainfall event exceeding 10 mm were missed by the models but MACRO was most of the time the only model able to simulate percolation of water, especially in autumn and winter 2012–2013 (Fig. 1). In IWM_{RT}, from 14 to 21 May 2013, the three models simulated >25 mm of percolated water while there was 0 mm in the lysimeters. However, from 7 to 14 May 2013, 20 mm of water were recorded in the lysimeter (Fig. 1), following 50.5 mm of rain on the 2–3 May 2013. The models reproduced this event with approximately one week of delay compared to the observation maybe because the lysimeter plates impose a gradient of pressure head higher than the one simulated by the model for a “free drainage” case, resulting in slower water movement in the model than in reality (Fig. 1). Similar delays were also observed in October–November 2013 and in December 2013–January 2014 (Fig. 1). In IWM_{MW}, only

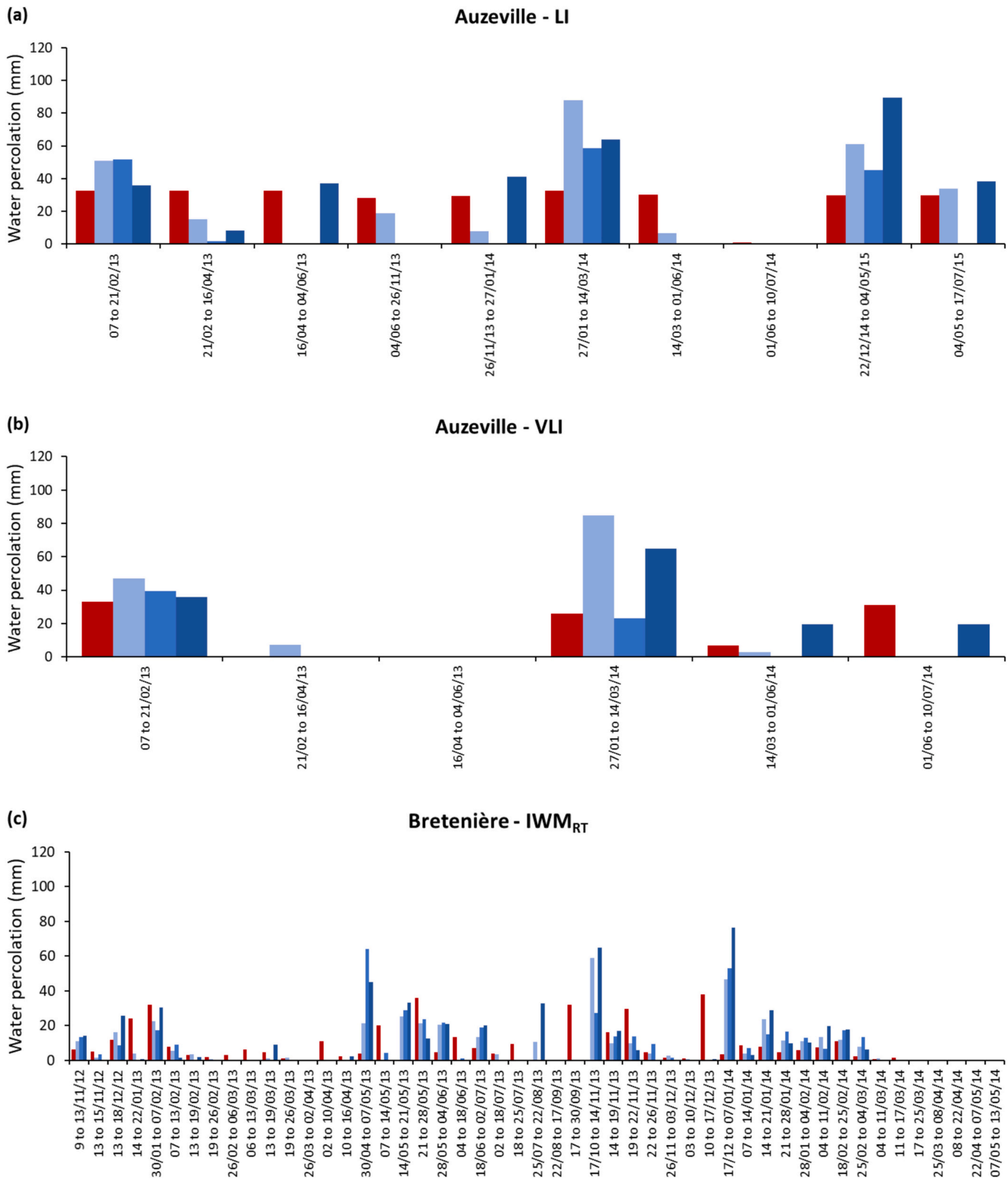

Fig. 1. Observed (in lysimeters) and simulated (with MACRO, PEARL and PRZM) water percolation in the durum wheat–sunflower based cropping systems of Auzeville: (a) LI — low input with cover crops system, (b) VLI — very low input system with intercrops and cover crops system; oilseed rape — winter wheat–winter barley based cropping systems of Bretenière: (c) IWM_{RT} — integrated weed management (IWM) reduced tillage system, (d) IWM_{MW} — IWM with mechanical weeding system; and maize monoculture based cropping systems of Lamothe: (e) M_{LIM} — low input maize monoculture system, (f) M_{IMR} — integrated maize rotation system. Observed (■), MACRO (■), PEARL (■), PRZM (■).

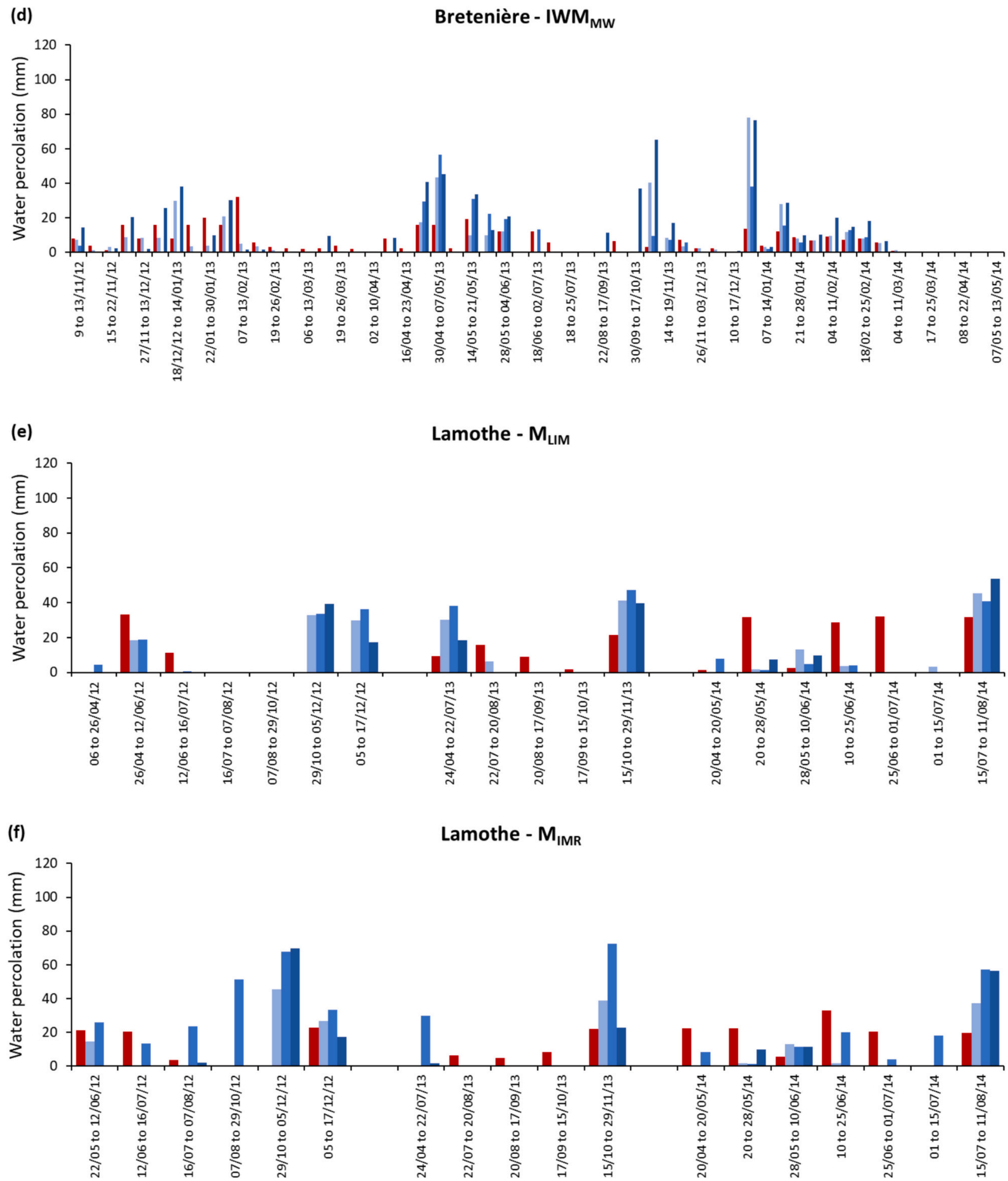

Fig. 1. (*continued*).

MACRO was able to simulate some water percolation from 13 November 2012 to 26 February 2013 (Fig. 1). In Lamothe, in both M_{LIM} and M_{IMR}, the models strongly underestimated the percolated water in May, June and July 2014 (Fig. 1), corresponding to 34 mm, 16 mm and 10 mm amounts of rain (Fig. S1). This could be explained by an overestimation of the evapotranspiration of the crops at this period. On the contrary, they overestimated the amounts of percolated water from 29 October to 5 December 2012, 15 October to 29 November 2013 and 15 July to 11 August 2014, corresponding to 92 mm, 131 mm and 107 mm of rain, respectively (Figs. 1 and S1).

As indicated by Lammoglia et al. (2017), several hypotheses could explain the underestimation of water transfer by the models: (1) the lateral flows above or just below the lysimeter are not simulated by the one-dimensional models (Marín-Benito et al., 2014); (2) the lysimeters may capture more water than expected, especially when initial conditions are very humid (Louie et al., 2000; Cattan et al., 2007); (3) in MACRO, the daily rainfall data are converted into hourly rainfall data, and the default average rainfall intensity (2 mm h^{-1}) may be inappropriate, resulting in macropores not being activated after intense rainfall events (McGrath et al., 2009; Moeys et al., 2012; Spill and Gassmann, 2022); and (4) tension plate and wick lysimeters will start percolating at a lower tension (less saturated) than in a free drainage lysimeter as simulated by MACRO where water percolates only when soil is almost saturated. Thus the former will collect more water. On the contrary, the overestimation of some percolation events by the models may be due to slower infiltration in the field due to soil sealing following heavy rainfall. The lack of accurate representation of the dynamic of water percolation could also be due to the fact that the soil hydraulic properties were considered constant in the three models, whereas they might vary with time and space, as observed by Ugarte-Nano et al. (2015) in Bretenière and by Alletto et al. (2015) in Lamothe. In addition, they might also vary as a function of temperature, wetting-drying cycles, and agricultural management (Bodner et al., 2013; Alletto et al., 2015; Gao and Shao, 2015; Lammoglia et al., 2017). Overall, the simulation of the cumulative volumes of percolated water by MACRO, PEARL and PRZM in the tested low input cropping systems was acceptable but the models were not able to represent correctly the dynamic of water flows.

3.2.2. *Pesticide concentrations in leachates*

3.2.2.1. Parameterization of pesticide sorption and degradation. For each of the 12 pesticides quantified in the six cropping systems (representing 17 scenarios "pesticide × cropping system × site") (Tables 2 and 4), the best parameterizations are summarized in Table S7.

In general (11 scenarios out of 17), for MACRO, the "worst-case" values, *i.e.*, the lowest Kf, and the highest nf and DT50 values, which represent the conditions favouring pesticide transfers, led to the best modelling efficiencies (Table 7). For the Kf value, the only exception was thiamethoxam for which the mean Kf had to be selected (Table S5). This insecticide has a very low minimum Kf value (Table S5), and since MACRO has high sensitivity to this parameter (Dubus et al., 2003b), a low value led to overestimation of pesticide concentrations (data not shown). Similarly, mean values of nf had to be selected for thiamethoxam and for bentazone (Table S7). Regarding DT50, exceptions were found for bentazone in IWM_{RT}, azoxystrobin and cyproconazole in IWM_{MW}, mesotrione and thiamethoxam in M_{LIM} for which mean values were used, and for boscalid in IWM_{RT} for which the minimum value was used (Table S7). Boscalid is the most persistent of the studied pesticides with high minimum, mean, typical, and maximum DT50 values (Tables S5 and S7). The use of such high mean and maximum values led to strong overestimation of the observed concentrations (data not shown). The five other pesticides (*i.e.*, azoxystrobin, bentazone, cyproconazole, mesotrione, thiamethoxam) requiring no "worst-case" values were either very persistent or very mobile (Tables S5 and S7). Whatever the sites or the cropping system, the parameterization of MACRO was the same for S-metolachlor and glyphosate, and almost the same for azoxystrobin and mesotrione, with only a slight difference in the choice of the DT50 (Table S7). Overall, for MACRO, the "worst-case" parameterization has to be retained (Tables 7 and S7).

For PEARL, more than half of Kf and nf values had to be parameterized as "worst-case" values, *i.e.*, minimum and maximum values, respectively. For the DT50, the mean values were generally found to be the most appropriate ones (Table S7). Unlike MACRO, only four scenarios needed to be completely parameterized with "worst-case" values in PEARL: glyphosate, S-metolachlor and mesotrione in M_{LIM}, and mesotrione in M_{IMR} (Table S7). For persistent pesticides (DT50 > 90 days, Regulation (EC) No 1107/2009, 2009) such as azoxystrobin, cyproconazole or imidacloprid, the maximum value of Kf had to be combined with the minimum or typical values of DT50 (Table S7). The remaining scenarios were mostly parameterized with mean values of Kf, nf and/or DT50 (Table S7). Contrary to MACRO, for PEARL, the parameterization of pesticides which were studied in different sites and cropping systems was different and varied according to them (Table S7).

Table 7
Modelling efficiency (EF), correlation coefficient (r), coefficient of residual mass (CRM) and relative root mean square error (RRMSE, %) of MACRO, PEARL and PRZM for pesticide concentrations (μg L^{-1}) in leachates in the low input cropping systems of Auzeville, Bretenière and Lamothe experimental sites. na: no calculation of r was possible because all simulated values were equal to zero. IWM: Integrated Weed Management.

Experimental site	Cropping system	Pesticide	MACRO				PEARL				PRZM			
			EF	r	CRM	RRMSE	EF	r	CRM	RRMSE	EF	r	CRM	RRMSE
Auzeville	Low input with cover crops (LI)	Imidacloprid	−0.50	na	1	173	−66.7	−0.15	−4.807	1164	−0.50	0.58	0.999	173
		S-metolachlor	−1.21	−0.18	0.283	219	0.29	0.89	−0.210	124	−0.61	−0.19	0.512	186
Bretenière	IWM reduced tillage (IWM_{RT})	2,4-D	−6.35	−0.13	0.829	91	−388	−0.16	−2.962	664	−8.22	−0.12	0.956	102
		Azoxystrobin	−5.53	0.32	0.999	109	−15.9	−0.44	−1.014	174	−8.69	−0.69	0.087	132
		Bentazone	−0.14	−0.11	0.179	301	−0.25	−0.23	0.224	315	−0.18	−0.23	0.443	305
		Boscalid	0.62	0.52	0.232	24	−193	0.71	−3.968	550	−3.31	−0.43	0.539	92
		Glyphosate	−0.28	−0.18	−0.070	283	0.02	0.06	0.088	248	−0.27	−0.29	0.117	282
	IWM with mechanical weeding (IWM_{MW})	Azoxystrobin	−2.62	0.06	0.859	101	−5.13	−0.56	0.157	131	−2.98	−0.03	0.913	106
		Cyproconazole	−4.57	na	1	110	−6.71	−0.44	0.048	130	−4.57	−0.74	1	110
		Florasulam	−15.1	0.53	0.735	75	−165	0.78	−0.745	241	−18.1	0.77	0.247	82
Lamothe	Low input maize monoculture (M_{LIM})	Glyphosate	−0.17	−0.07	0.932	262	−0.16	0.03	0.975	261	−0.17	0.11	0.992	262
		Mesotrione	−8.34	−0.11	−1.15	783	−7.15	0.01	−4.063	732	−1.33	0.34	−1.691	391
		Nicosulfuron	−0.03	0.06	0.454	278	0.02	0.11	0.266	271	−0.24	0.21	−0.656	304
		S-metolachlor	−0.76	−0.14	−0.196	396	−0.32	0.41	−1.775	342	−0.11	−0.09	0.906	314
		Thiamethoxam	−0.32	−0.08	0.084	210	−0.52	−0.19	−0.010	226	−0.61	0.21	0.069	232
	Integrated maize rotation (M_{IMR})	Mesotrione	−0.08	−0.08	1	361	−0.08	−0.08	0.999	361	−0.08	0.96	0.999	361
		S-metolachlor	−0.14	−0.07	0.999	286	−0.14	−0.09	0.993	286	−0.09	0.09	0.835	280

For PRZM, most of the pesticides had to be parameterized with the “worst-case” minimum Kf values and maximum nf values (Table S7). For DT50, the mean values were in general found to be the most suitable ones to obtain the best simulations of observations (Fig. S2, Table S7). Six out of 17 scenarios required a complete set of “worst-case” values: imidacloprid and S-metolachlor in LI, cyproconazole in IWM_{MW}, glyphosate and S-metolachlor in M_{LIM}, and mesotrione in M_{IMR} (Table S7). For persistent pesticides such as azoxystrobin, bentazone, boscalid or thiamethoxam, minimum or mean values of DT50 had to be selected (Table S7). In PRZM, the parameterization of S-metolachlor was similar in LI of Auzeville and M_{LIM} of Lamothe but different in M_{IMR}, and the parameterization of glyphosate and azoxystrobin varied according to the site and cropping system (Table S7).

For the three models, in 60 % of the case studies, the parameterization of Kf, nf and DT50 which resulted in the highest model efficiencies was based on “worst-case” values (Tables 7 and S7, Fig. S2). Exceptions were observed for 2,4-D, azoxystrobin, cyproconazole, imidacloprid, S-metolachlor in LI and M_{IMR} with PEARL; for 2,4-D and azoxystrobin in IWM_{RT}, mesotrione and nicosulfuron in M_{LIM}, and S-metolachlor in M_{IMR} with PRZM; and for bentazone, boscalid and thiamethoxam with the three models (Table S7).

As a general rule, testing the values of Kf, nf and DT50 originating from PPDB (Lewis et al., 2016) showed that: (1) MACRO can be parameterized with “worst-case” values of Kf, nf and DT50 (for persistent compounds with mean DT50 > 90 days, the mean value can be used); and (2) PEARL and PRZM can be parameterized with “worst-case” values of Kf and nf values, and mean values of DT50. However, as indicated in the Section 3.2.2.2 below, despite the use of “worst-case” values, pesticide concentrations in leachates often remain underestimated (Fig. S2; see Section 3.2.2.2), which is questionable for risk assessment.

3.2.2.2. Model performances to simulate pesticide concentrations in leachates. In general, the statistical indices indicated poor fits to measured pesticide concentrations in leachates for MACRO, PEARL and PRZM, confirming that it is quite challenging to simulate (Scorza Junior et al., 2007; Marín-Benito et al., 2014; Lammoglia et al., 2017; Dufilho and Falco, 2020) (Table 7). Excellent fit for simulations of pesticide leaching have rarely been reported, which is not surprising given the complexity of the system to be described (Dubus et al., 2003a; Beulke et al., 2001; Dufilho and Falco, 2020). Nevertheless, MACRO was found to perform better ($-15.1 < EF < 0.62$, $-0.18 < r < 0.53$) than PEARL ($-388 < EF < 0.29$, $-0.56 < r < 0.89$) then PRZM ($-18.1 < EF < -0.08$, $-0.74 < r < 0.96$) (Table 7). Indeed, several model comparison studies demonstrated that preferential flow pesticide models outperform models based solely on Richards' equation and capacity models (Köhne et al., 2009). MACRO and PRZM were mostly found to underestimate pesticide concentrations, as shown by positive CRM values, while PEARL either underestimated or overestimated the concentrations (Table 7, Fig. S2). The RRMSE ranged from 24 (boscalid) to 783 (mesotrione) for MACRO, from 124 (S-metolachlor) to 1164 (imidacloprid) for PEARL, and from 82 (florasulam) to 391 (mesotrione) for PRZM (Table 7). For the three models, the statistical indices, and especially RRMSE, were better for Bretenière than for Auzeville and Lamothe (Table 7). As indicated above, the variability of the performance of the models among different sites is well known (*e.g.* Moeys et al., 2012; Queyrel et al., 2016; Lammoglia et al., 2017).

In Auzeville, PEARL was the only model able to simulate the concentration of imidacloprid in LI while MACRO and PRZM simulations resulted in large underestimations (Fig. S2a). Scorza Junior et al. (2007) observed that MACRO underestimated imidacloprid leaching even though the model was calibrated using field measurements of water and bromide behavior. PEARL was also the only model able to simulate the transfer of S-metolachlor shortly after its application (Fig. S2b). However, the three models were all able to simulate the concentrations of the pesticide almost two years later (Fig. S2b).

In the IWM_{RT} system of Bretenière, none of the models were able to simulate the concentrations of 2,4-D which were underestimated all along the measurement period, with PEARL strongly overestimating the concentrations from January 2014 (Fig. S2c). Regarding azoxystrobin, PEARL reproduced the concentration observed one year after its application but it overestimated the concentration observed 1.5 years later by a factor of 5 as well as PRZM (factor of 3). MACRO underestimated all concentrations (Fig. S2d). For bentazone, all models failed to simulate the first peak of concentration because they were not able to simulate water flows at this date (see Section 3.2.1.2) (Fig. S2e). Conversely, MACRO simulated the second peak observed from August to December 2013 but the simulated concentration was 2.5 times lower than the observed one. Then all models overestimated the measured concentrations, except at the last point of the measurement from 11 to 17 March 2014 where they all simulated a concentration of zero although 0.068 $\mu g\ L^{-1}$ were observed. This is consistent with the findings of Scorza Junior et al. (2007) who observed that MACRO underestimated the leaching of bentazone. For boscalid, MACRO and PRZM represented the observed concentrations fairly well, while PEARL tended to overestimate the measures more than two years after the application of the fungicide (Fig. S2f). For glyphosate, the three models overestimated the measured concentrations by a factor 7 on average, except for the peak in May 2013 which was strongly underestimated because the models were not able to simulate water flows at the corresponding date (see above) (Fig. S2g). This rapid transfer of glyphosate is probably due to preferential flows which is a highly episodic process combined with cotransport (Brown et al., 2004; Marín-Benito et al., 2020; Carretta et al., 2022) which is not considered in the models. In some soils, rainfall or irrigation after application will also induce macropore flow (simulated by MACRO), which has the potential to rapidly transport some pesticides to the drainage system or to a depth where degradation is slower than in the topsoil (Jarvis et al., 2009). For IWM_{MW} of Bretenière, the concentrations of azoxystrobin were underestimated by MACRO and PRZM but were either underestimated or overestimated by PEARL (Fig. S2h). This is consistent with what was observed in IWM_{RT} for the same fungicide (Fig. S2d). The three models were not able to simulate the leaching of cyproconazole in 2013, but PEARL was able to represent the concentrations observed in 2014 (Fig. S2i). Finally, for florasulam, MACRO was found to be able to represent the concentrations acceptably, while PEARL and PRZM started to overestimate the concentrations before underestimating them (Fig. S2j).

In the M_{LIM} cropping system of Lamothe, the models were unable to simulate the observed concentrations of glyphosate, which were strongly underestimated, particularly the two peaks in spring 2013 and spring 2014 (Fig. 1, Fig. S2k) because the corresponding water flows were not simulated (see Section 3.2.1.2). The concentrations of mesotrione were poorly represented by the three models (Fig. S2l): they simulated some concentrations when none were observed and conversely. This is illustrated by poor statistical indices (Table 7). Regarding nicosulfuron, the models were unable to represent the first peak of concentration but they simulated the second one in 2014 though the concentration was underestimated with factors ranging from 2.5 (PEARL) to 12 (MACRO) (Fig. S2m). The remaining concentrations were strongly overestimated by the three models. For S-metolachlor, none of the models captured the dynamic of the concentrations (Fig. S2n). PEARL was able to represent the peak of June 2014 but it strongly overestimated the remaining observed concentrations. The three models did not simulate the first peak of concentration of thiamethoxam in May–June 2012 (Fig. S2). However, MACRO represented the second peak in July–August 2013, though the concentration was underestimated by a factor of 5.5, and the third peak in June 2014 with an underestimation factor of 2.5, as well as PEARL. PRZM overestimated this third peak by a factor of 1.5. The other measurement dates showed concentrations lower than the LOQ, while the three models simulated some concentrations. Finally, in M_{IMR} of Lamothe, none of the models simulated the peak of mesotrione (Fig. S2p) because water flows were not simulated (Fig. 1). Similarly, S-metolachlor concentrations were not simulated by any model except by PRZM, but with an underestimation of a factor of 3 (Fig. S2q). In the conventional maize monoculture system of the Lamothe experimental site, Marín-Benito et al. (2014) also observed that the three models tended to underestimate mesotrione and S-metolachlor concentrations in leachates.

From the extensive assessment of the performance of MACRO, PEARL and PRZM to simulate pesticide leaching based on three experimental sites and various low input cropping systems, this work demonstrated that modelling the fate of pesticides is still challenging. Indeed, the behavior of compounds in the environment is influenced by a wide range of physical, chemical and biological processes, some of them probably unknown. The multiplicity of factors affecting the fate of pesticides introduces uncertainties into the modelling through (1) model error (also referred as structural error or model inadequacy), *i.e.*, the non-inclusion or inappropriate representation of significant processes in the model such as preferential flows, co-transport or plant uptake. The fact that the models tested in this study do not include "fixed tension" as bottom boundary condition belongs to that category of errors; (2) acquisition of primary data in the field or in the laboratory (site characteristics, soil properties, weather conditions, pesticide properties); and (3) derivation of model input parameters from basic data or by other means (Dubus et al., 2003a; Jarvis and Larsbo, 2012; Moeys et al., 2012; Gamble and Bruccoleri, 2016; Vereecken et al., 2016; Ullucci et al., 2022; Li, 2023). The difficulty to simulate pesticide peak concentrations with MACRO, PEARL and PRZM has been already observed by several authors (Garratt et al., 2003; Scorza Junior et al., 2007; Köhne et al., 2009; Steffens et al., 2014; Spill and Gassmann, 2022). Accurate prediction of early solute breakthrough depends on the ability of generic routines to accurately estimate parameters and on the ability of the models to accurately simulate water flows soon after solute application (Moeys et al., 2012), however they generally failed (see Section 3.2.1). As stated by Köhne et al. (2009) and Jarvis and Larsbo (2012), some calibration will always be necessary since not all parameters are measurable, they vary spatially and also temporally, and it is impossible to fully characterize a field site by measurements alone, especially in the subsoil. In this work, the calibration of pesticide DT50, Kf and nf was restricted to the values from regulatory reports (Lewis et al., 2016), which are within realistic range, but other values could also be tested. For pesticides with weak sorption for which leaching was overestimated, such as mesotrione and 2,4-D (Fig. S2c, l and p), including aged sorption in the models could decrease the simulated concentrations (Boesten, 2017). The knowledge of the processes governing the fate of certain pesticides is also probably inadequate which could explain why the models do not simulate their behavior correctly. Finally, some of the discrepancy between observations and simulations may be due to tillage operations which redistribute solutes present in the upper soil layers prior to cultivation. This physical redistribution is likely to modify subsequent leaching behavior, and it will be relevant particularly to pesticides that persist in soil at the start of the cropping season following application, such as azoxystrobin or cyproconazole (Tables 2 and S5) (Summerton et al., 2023), but this is not simulated by the three models. The simulation of pesticide concentrations in leachates could be improved by considering some of these processes in future versions of the models.

4. Conclusion

To ensure the sustainability of agricultural systems, new cropping systems reducing the dependency on pesticides have to be designed. Given the vast number of systems to explore and the scarcity of field experiments, *in silico* tools are needed to assess the impacts on the environment of the pesticides that are used in these new cropping systems. This work assessed and compared water flows and pesticide leaching in six low input cropping systems, and the performances of MACRO, PEARL and PRZM models to simulate the observations. The models were parameterized using a pesticide property database and generic parameter estimation routines as done for regulatory risk assessment, and a method allowing to parameterize intercrops, not explicitly represented in the models, was developed. This method uses the mean of crop factors, maximum LAI, maximum crop height and maximum rooting depth of the crops constituting the intercrop as inputs. The best systems to reduce pesticide losses in water were the very low input system for the durum wheat–sunflower system, the integrated weed management with mechanical weeding system for the oilseed rape–winter wheat–winter barley based cropping systems, and the integrated rotation for maize systems. In general, MACRO was found to perform better than PEARL and PRZM for simulating water flows and pesticide leaching, but the use of the three models without any calibration is likely to underestimate pesticide leaching in several situations. Further works should therefore focus on characterizing the calibration required to ensure that the models correctly represent the observations. They should also focus on simulating the concentrations of the pesticides which were not observed in the lysimeters to determine if the model results are consistent with the lack of observations. This work also showed the need to improve the understanding of the processes driving the fate of pesticides in soils, and to consider in the models processes such as co-transport and enhanced description of plant uptake. To be able to fully estimate the long-term pesticide leaching risk in low input cropping systems, one would also need to use a model of pest-pressure and computer-based decision rules for pesticide treatment.

CRediT authorship contribution statement

Laure Mamy: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Jesús M. Marín-Benito:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Lionel Alletto:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Eric Justes:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Marjorie Ubertosi:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Nicolas Munier-Jolain:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Bernard Nicolardot:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Catherine Bonnet:** Writing – review & editing, Methodology, Investigation. **Julien Moeys:** Writing – review & editing, Software. **Mats Larsbo:** Writing – review & editing, Software, Methodology. **Valérie Pot:** Writing – review & editing, Methodology, Conceptualization. **Carole Bedos:** Writing – review & editing, Conceptualization. **Pierre Benoit:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Enrique Barriuso:** Writing – review & editing, Methodology, Investigation, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177607.

Data availability

Data will be made available on request.

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