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Occurrence of metolachlor and trifluralin losses in the Save river agricultural catchment during floods

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ABSTRACT

Rising pesticide levels in streams draining intensively managed agricultural land have a detrimental effect on aquatic ecosystems and render water unfit for human consumption. The Soil and Water Assessment Tool (SWAT) was applied to simulate daily pesticide transfer at the outlet from an agriculturally intensive catchment of 1110 km^2 (Save river, south-western France). SWAT reliably simulated both dissolved and sorbed metolachlor and trifluralin loads and concentrations at the catchment outlet from 1998 to 2009. On average, 17 kg of metolachlor and 1 kg of trifluralin were exported at outlet each year, with annual rainfall variations considered. Surface runoff was identified as the preferred pathway for pesticide transfer, related to the good correlation between suspended sediment exportation and pesticide, in both soluble and sorbed phases. Pesticide exportation rates at catchment outlet were less than 0.1% of the applied amount. At outlet, SWAT hindcasted that (i) 61% of metolachlor and 52% of trifluralin were exported during high flows and (ii) metolachlor and trifluralin concentrations exceeded European drinking water standards of 0.1 μg L^{-1} for individual pesticides during 149 (3.6%) and 17 (0.4%) days of the 1998–2009 period respectively. SWAT was shown to be a promising tool for assessing large catchment river network pesticide contamination in the event of floods but further useful developments of pesticide transfers and partition coefficient processes would need to be investigated.

1. Introduction

Rising pesticide levels in stream waters draining intensively managed agricultural land have become a widespread problem throughout Europe in recent decades. Intensive agriculture is known to have a detrimental effect on soils, surface water and groundwater quality, leading to acute problems such as soil erosion and water contamination [e.g. 1–4]. Excessive loading of pesticides, transferred into the environment through various pathways (e.g. surface runoff, subsurface and groundwater flows) either in solution or sorbed onto particles, may be harmful to terrestrial and aquatic ecosystems [5–8], rendering stream water and groundwater unfit for human consumption.

In Europe, pesticides are considered hazardous substances in accordance with current directives regarding water [9,10]. Drinking water quality standard should not exceed 0.1 μg L^{-1} for an individual pesticide concentration and 0.5 μg L^{-1} for all pesticide concentration [11]. River basins were adopted as territorial management units and the scientific community was asked to provide reliable modelling tools to evaluate pesticide source contribution to water pollution and to quantify pesticide river loads. To model pesticide fate at catchment scale, spatially variable land management and landscape characteristics, temporally variable climatology and hydrology as well as dissipation processes in the river need to be taken into account. Therefore, the combination of watershed models and river water quality models is needed to calculate pesticide fluxes to the river and transformation processes in the river channel [12].

Various models describe the pesticide fate, allowing a better understanding of the processes involved. Among the very first, the Chemical Migration and Risk Assessment (CMRA) methodology [13] included the Agricultural Runoff Management (ARM) [14] and Chemicals, Runoff and Erosion from Agricultural Management Systems (CREAMS) [15] models. It simulates the transport and fate of both dissolved and sediment-sorbed contaminants and by predicting acute and chronic impacts, provides risk assessment on aquatic

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biota. Many one-dimension, river and catchment scale models simulating pesticide fate have been then developed [e.g. 16–19]. The Soil and Water Assessment Tool (SWAT, [20]) is a semi-distributed model that provides long-term continuous predictions, including hydrology, plant growth, nutrients and suspended sediments from the field to the catchment outlet at daily time-step. Two main processes describe the pesticide transfer in both the soluble and the sorbed phases: the pesticide load generated in the hydrological unit and the fate of the load in the river.

Few works have been published so far on pesticide fate modelling using the SWAT model. Molecules of a wide range of solubility were simulated (e.g. atrazine, metolachlor, trifluralin, diazinon and chlorpyrifos) in catchments ranging from 30 to 15,000 km^2 [21–24]. To our knowledge, no work has been published on pesticide modelling in both the dissolved and sorbed phases at flood-event scale, i.e. during a few days of high flow.

This study had four objectives: (i) to assess the performance of the SWAT model in the Save catchment (1110 km^2) in the Gascogne region, an agriculturally intensive area of south-western France, in predicting daily pesticide river loads and concentrations at the catchment outlet; (ii) to test the sensitivity of SWAT long-term response, in terms of pesticide exportations, to interannual hydrological constraint by using an 11-year constant pesticide supply; (iii) to hindcast earlier pesticide data in order to make the model reliable for predicting river network contamination (e.g. exceeding drinking water standards) depending on the climatic context and possible flood events; (iv) to identify factors controlling exportations and preferred pathways.

2. Material and methods

2.1. Study area

The River Save drains an area of 1110 km^2 which is mostly farmed with intensive agriculture. It is located in the Coteaux de Gascogne region (south-western France) near Toulouse (Fig. 1). The River Save has its source in the Pyrenees piedmont. It joins the River Garonne after a 140 km course at a 0.4% average slope. Altitudes range from 663 m in the piedmont to 92 m at the Garonne confluence. The Larra gauging station elevation is 114 m (Fig. 1).

The climate is oceanic. The Save river hydrological regime is mainly pluvial with a maximum discharge in May and low flows during the summer (July–September). Annual precipitation is 600–900 mm and annual evaporation is 500–600 mm (1998–2008). The hydrology is complex and subject to large climatic variations: annual average rainfall is 721 mm with a 99 mm standard deviation. The catchment lies on detrital sediments. Calcic soils represent over 90% of the whole catchment with a clay content ranging from 40% to 50%. Non-calcic silty soils represent less than 10% of the soil in this area (50–60% silt) [25].

Because of its high clay content, the catchment substratum is relatively impermeable. River discharge is consequently supplied mainly by surface and subsurface runoff and groundwater is limited to alluvial and colluvial phreatic aquifers. The mean interannual discharge (1965–2006) for the River Save is 6.1 $m^3 s^{-1}$. The annual discharge of 'dry' years is approximately 4.1 $m^3 s^{-1}$ whereas for 'wet' years it is about 8.1 $m^3 s^{-1}$. Low water discharge is about 1.3 $m^3 s^{-1}$ (data from the Compagnie d'Aménagement des Coteaux de Gascogne (CACG) at the Larra gauging station). During low flows, river flow is sustained upstream by the Neste canal (about 1 $m^3 s^{-1}$).

90% of the catchment area is used for agriculture. The upstream part of the catchment is a hilly agricultural area mainly covered with pasture – a 5-year rotation including one year of corn and 4 years of grazed fescue – and sometimes forest. The lower part is devoted to intensive agriculture with mainly a 2-year crop rotation of sunflower and winter wheat. Fertilizers are generally applied from late winter to spring. Average nitrogenous supply throughout the catchment is approximately 72 kg N ha^{-1}, i.e. 320 kg ha^{-1} nitrate-equivalents. About 150 mm of water is supplied by irrigation of corn.

Table 1
Spatial and temporal 3-year survey averaged management practices for sunflower grown on the Save catchment including metolachlor and trifluralin spreading.

Type of operation	Date of operation	Quantity (kg ha^{-1})
Pesticides spreading: trifluralin	05 April	0.874
Fertilizer: 15-15-15	05 April	193.3
Sowing	10 April	–
Pesticides spreading: metolachlor	15 April	1.12
Fertilizer: 15-15-15	16 May	193.3
Harvest	01 October	–

Various pesticides are applied in the catchment throughout the year depending on the crops. Our study focuses on the most applied pesticides: each year, 23 tons of metolachlor, a highly soluble chemical (S_w = 488 mg L^{-1}, log K_{ow} = 2.9), and 18 tons of trifluralin, a poorly soluble chemical (S_w = 0.221 mg L^{-1}, log K_{ow} = 4.83), are applied on the catchment. Both pesticides are herbicides. They are applied each year on sunflower in early April (Table 1). On average, sunflower fields cover 18.4% of the catchment (20,600 ha).

2.2. Observed discharge data

The River Save has been monitored for discharge since 1965. At the Larra hydrometric station, hourly discharges (*Q*) were obtained from CACG. The hourly discharge was plotted by the rating curve *H*(*Q*) in which the water level (*H*) was measured continuously and then averaged for each day.

2.3. Observed water quality data

2.3.1. Nitrate and suspended sediment monitoring

Nitrate loads and suspended sediment concentrations were monitored continuously from January 2007 to March 2009 at the Larra gauging station, both manually and automatically, as described previously in Oeurng et al. [26–28]: an automatic water sampler, connected to a probe, was programmed to activate pumping water on the basis of water level variations ranging from 10 cm (during low flows) to 30 cm (during high flows) for the rising and falling stages. Grab sampling was also undertaken near the probe position at weekly intervals.

2.3.2. Pesticide monitoring

Pesticides were monitored from March 2008 to March 2009 at the Larra station with weekly grab sampling during low flow and daily grab sampling during flood events. Laboratory analyses were performed as described in Taghavi et al. [29,30]. Additional data from Agence de l'Eau Adour-Garonne (AEAG) were used for long-term total pesticide concentration comparison (Source: Système d'Information sur l'Eau du Bassin Adour-Garonne, data exported in 2009).

2.3.3. Load calculation

Based on the high frequency of data collection, a linear interpolation method was applied between two neighbouring sampling points to construct the continuous nitrate, suspended sediment and pesticide concentration series and thus calculate continuous daily loads through the product of concentration and water volume. Yearly loads were calculated by totalling daily loads.

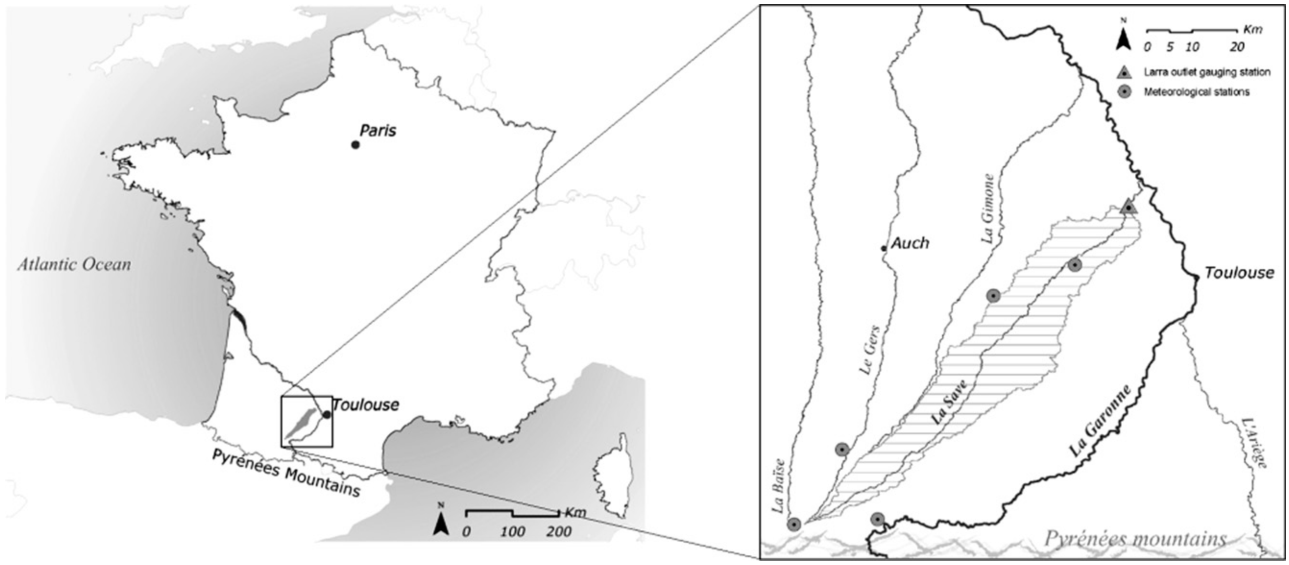

Fig. 1. Localisation of Save catchment, Larra gauging station and meteorological stations.

2.4. Modelling approach

2.4.1. The SWAT model

SWAT is a physically based agro-hydrological model [20]. It operates at a daily time-step and was designed to predict the impact of management practices on water quality in ungauged catchments. It allows the addition of flows by including measured data from point sources. SWAT discretises catchments into sub-basins. Sub-basins are then subdivided into Hydrological Response Units (HRUs). HRUs are areas of homogenous land use, soil type and slope. HRUs outputs are inputs for the connected stream network. One sub-basin is drained by one reach. Authors refer to Neitsch et al. [31] for detailed description of the model.

2.4.2. The pesticide component in SWAT

Pesticide processes in SWAT are divided into three components: (i) pesticide processes in land areas, (ii) transport of pesticides from land areas to the stream network, and (iii) instream pesticide processes.

SWAT uses algorithms from GLEAMS (Groundwater Loading Effects on Agricultural Management Systems) [16] to model pesticide movement and fate in land areas. The partitioning of a pesticide between the dissolved and sorbed phases is defined by a soil adsorption coefficient. Algorithms governing movement of soluble and sorbed forms of pesticide from land areas to the stream network were taken from the EPIC (Erosion-Productivity Impact Calculator) model [32]. The SWAT model incorporates a simple mass-balance method [33] to model the transformation and transport of pesticides in streams. Only one pesticide can be routed through the stream network in a given simulation. The fraction of pesticide in each phase is a function of the pesticide's partition coefficient and the reach segment's suspended solid concentration. Degradation is based on half-life. Authors refer to Neitsch et al. [31] for further details.

2.5. SWAT data inputs

Spatialised data used in this study were:

- Digital Elevation Model with a resolution of 25 m × 25 m from Institut Géographique National (IGN) France (BD TOPO R).
- Soil data on the scale of 1:80,000 from CACG and digitised by Cemagref de Bordeaux [34] and soil properties for the SWAT soil database [35].
- Land use data [34] from Landsat 2005 with associated management practices: spatial and temporal average of planting/seedling dates, amounts, type and date of fertilisation, pesticide application and irrigation, grazing, tillage and harvest operations dates from a 3 year survey (2003–2005) with catchment farmers, applied for each year of simulation.
- Meteorological data from 5 stations (Fig. 1) with daily precipitation from Météo-France. Missing data were generated by linear regression equation from data from the nearest stations with complete measurements. Two stations in the upstream section had a complete set of measurements of daily minimum and maximum air temperature, wind speed, solar radiation and relative humidity that were used to simulate the reference evapotranspiration in the model by Penman–Monteith [36,37] method.
- Point source data: the Save river network is connected upstream to the Neste canal. Daily discharge was given by CACG. Since it is water from a mountainous agricultural extensive area, concentrations of nitrate and pesticides were set constant and equal to 2 and 0 mg L^{-1} respectively. Since water is derived by a dam where sediments are trapped, suspended sediment concentration was set constant and equal to 10 mg L^{-1}.

In this study, version 2009.93.3 of ArcSWAT was used. The catchment was discretised into 73 sub-basins with a minimal area of 500 ha. 1642 HRUs were generated integrating 8 land uses classes, 23 soil classes and 5 slope classes (%: 0–1, 1–3, 3–5, 5–8 and 8 and over).

Whole simulation was carried out daily from January 1998 to March 2009 (excluding 4 years' warm-up from 1994 to 1997). The sensitivity of 15 parameters governing discharge, nitrate and suspended sediment dynamic was tested using the ArcSWAT2009 sensitivity analysis tool [38]. Calibration of discharge, nitrate, suspended sediment and pesticide at daily time-step was performed manually. Pesticide input values are given in Table 2.

2.6. Model evaluation

The performance of the model was evaluated using the Nash–Sutcliffe efficiency (E_{NS}) index [39] and the coefficient of

Table 2
Manually calibrated values of pesticides parameters: half-lifes, K_{oc} and CHPST_KOC and degradation rates in the channel water and in the sediment bed (respectively CHPST_REA and SEDPST_REA).

Parameters	Input file	Metolachlor	Aclonifen
Soil half-life Met/Tri (days)	pest.dat	90	60
K_{oc} Met/Tri (mg kg^{-1}/mg L^{-1})	pest.dat	667	13,196
CHPST_KOC Met/Tri (m^3 g^{-1})	.swq	0.1	2.6
CHPST/SEDPST_REA (days^{-1})	.swq	0.025	0.025

determination (R^2). E_{NS} ranges from negative infinity to 1 whereas R^2 ranges between 0 and 1. We refer to Krause et al. [40] for further discussion on these evaluation criteria.

Daily E_{NS} and R^2 were applied on daily discharge for low flows (below the 6.1 m^3 s^{-1} mean annual discharge), high flow (over 6.1 m^3 s^{-1}) and total (1998–2006 for calibration and 2007–2009 for validation). They were also calculated for nitrate loads and suspended sediment concentrations for the 2007–2009 period. Daily and monthly R^2 were calculated for dissolved, sorbed and total pesticides concentrations for calibration period (2008–2009). Due to data limitation, E_{NS} was not calculated on pesticide concentration. In this study we deemed E_{NS} satisfactory when higher than 0.36 [41] and R^2 satisfactory when higher than 0.5 [42].

2.7. Water quality simulation

2.7.1. Discharge, nitrate and suspended sediment simulation

Daily SWAT interpolated rainfall and simulated water yield (i.e. the amount of water flowing down the outlet) were totalled for each year. Daily simulated nitrate and suspended sediment loads at the Larra outlet were totalled for each year and for low flow and high flow (using the 6.1 m^3 s^{-1} threshold). Incoming suspended sediment in a given reach is the total of the amount of suspended sediments coming from the HRUs related to the reach, added to the amount entering from the upstream reach.

2.7.2. Pesticide simulation

Daily pesticide loads were totalled for each year, for April flood (11/04/08–30/04/08) and June flood (14/05/08–18/06/08), and for low flow and high flow (using the 6.1 m^3 s^{-1} threshold). Total pesticide concentration is the concentration of pesticide as measured in unfiltered water. Simulated total concentration is calculated as the total of dissolved and sorbed pesticide concentration. The particulate fraction is the fraction of pesticide in the sorbed phase and is calculated as the sorbed pesticide load divided by the total pesticide load. The exportation rate is calculated as the ratio from pesticide load exported at outlet and the amount of pesticide applied on the catchment. As pesticide toxicity is more relevant as concentration than as load, long-term simulation concentrations (1998–2009) were compared to European drinking water quality standards of 0.1 μg L^{-1} for a single pesticide and of 0.5 μg L^{-1} for both pesticides being modelled.

Correlation analyses were performed on 1998–2008 interannual-averaged metolachlor and trifluralin (both dissolved and sorbed) loads from reach and HRUs to relate them to reach and HRUs variables such as slope, soil classes, rainfall, water, suspended sediment and nitrate yields.

3. Results

3.1. Discharge, nitrate and suspended sediment simulation

According to sensitivity analysis, parameters governing discharge and nitrate were mostly parameters governing runoff and groundwater transfer (CN2, RCHRG_DP, GWQMN). Parameters governing suspended sediment were mostly parameters governing runoff (CN2) and in-stream processes (CH_N2, SPCON, SPEXP).

Table 3
Goodness-of-fit indices for daily discharge, nitrate load and suspended sediment simulation ($p < 0.05$).

	Periods	R^2	E_{NS}
Discharge – calibration	1998–2006	0.52	0.50
Discharge – validation	2007–2009	0.58	0.56
Low flow	1998–2009	0.02	0.02
High flow	1998–2009	0.51	0.54
Nitrate load	2007–2009	0.46	0.37
Suspended sediments concentration	2007–2009	0.36	0.27

Fig. 2 focuses on discharge simulated daily from January 2007 to March 2009. The goodness-of-fit indices for daily discharge were satisfactory during both calibration and validation period (Table 3). They were also satisfactory for high flow but unsatisfactory for low flow (Table 3).

Nitrate daily load predictions (Fig. 3(a)) were correlated to observations for the 2007–2009 period (Table 3). Observed and simulated cumulated nitrate loads in 2007 were 2514 and 2388 tons respectively, they were 3047 and 3018 tons respectively in 2008 (Fig. 3(b) and (c)). Considering daily and annual loads prediction on 2007–2009, the model was considered to hindcast past daily and annual nitrate loads back to 1998 with little error. Annual nitrate loads were correlated to annual water yield ($R^2 = 0.84$, $p < 0.05$).

Daily simulated suspended sediment concentrations fitted observations (Fig. 4(a)) although E_{NS} and R^2 were unsatisfactory (Table 3). Observed and simulated annual suspended sediment loads were 9000 and 15,000 tons respectively in 2007 and 58,000 and 64,000 tons respectively in 2008 (Fig. 4(b) and (c)). Considering concentration and load prediction on 2007–2009, the model was considered to reconstruct past annual loads back to 1998 with little error. Annual suspended sediment loads were correlated to annual water yield ($R^2 = 0.59$, $p < 0.05$). On average across the 73 reaches, the annual ratio of deposited/incoming suspended sediment in the reach is of 54%.

3.2. Pesticide simulation

Simulation results were shown to be poorly sensitive to application date change for both molecules (results not shown) although pesticide losses are known to be determined mainly by the period of time between application and the first rainfall event and by the application dose [43,44]. SWAT pesticide component parameters, including the soil adsorption coefficient (K_{oc}), were also poorly sensitive (results not shown) except the channel partition coefficient between water and suspended sediment (CHPST_KOC).

3.2.1. SWAT performances

The range of daily simulated concentrations of metolachlor and trifluralin followed the range of respective measurements during both the calibration 2008–2009 period (Fig. 5) and the long-term validation 1998–2009 period (Fig. 6). During the calibration period, simulated dissolved and sorbed molecule concentrations during low flow matched respective observations. Flood concentration peaks of dissolved metolachlor were predicted although overestimated during April and June flood events. Sorbed pesticide concentration peaks during the same period were underestimated. Trifluralin concentration peaks in May were skipped. The model did not simulate the trifluralin concentration peak in early 2009. Simulated partition between soluble and sorbed phases of both molecules roughly followed the observed partition.

In terms of loads, average simulated annual loads at outlet were in the range of observed annual loads (Table 4). The simulated

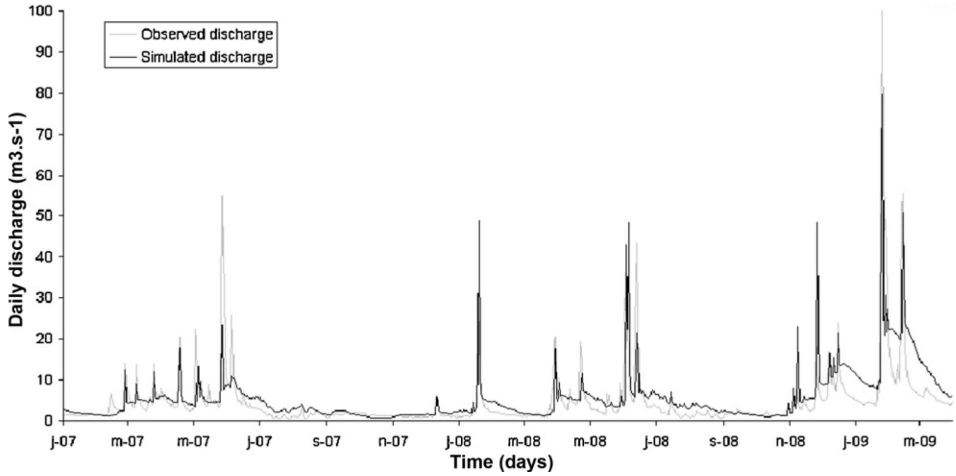

Fig. 2. Observed and simulated daily discharge ($m^3\,s^{-1}$) at the Larra gauging station (January 2007–March 2009).

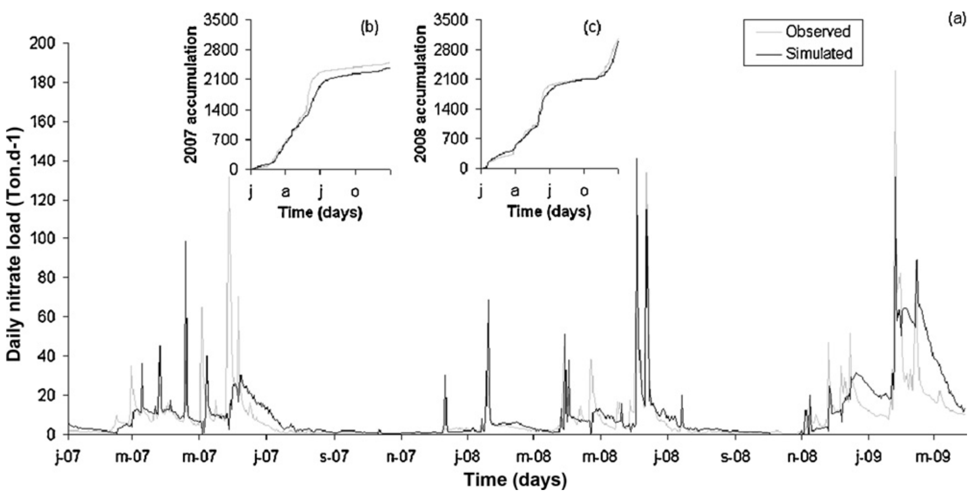

Fig. 3. Observed and simulated daily (a) nitrate load (tons) at the Larra gauging station (January 2007–March 2009), (b) 2007 accumulation (tons) and (c) 2008 accumulation (tons).

metolachlor and trifluralin particulate fractions at catchment outlet fitted the observed particulate fractions and were consistent with the fractions simulated in surface runoff out of the HRUs (Table 4). At flood scale, simulation followed the measured range of values (Table 5). However, metolachlor loads were underestimated whereas trifluralin loads were overestimated during the April flood and underestimated during the June flood. R^2 for monthly concentrations of metolachlor and trifluralin were over 0.38 except

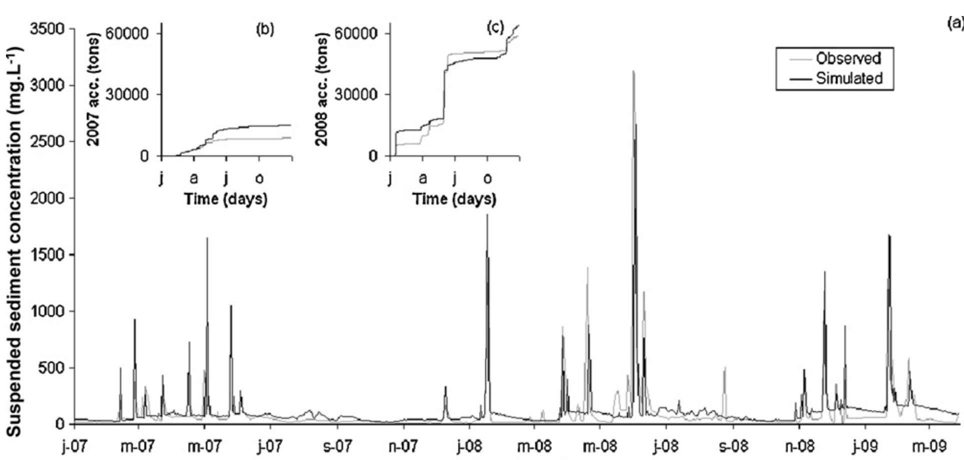

Fig. 4. Observed and simulated daily (a) suspended sediment concentration ($mg\,L^{-1}$) at the Larra gauging station (January 2007–March 2009), (b) 2007 accumulation (tons) and (c) 2008 accumulation (tons).

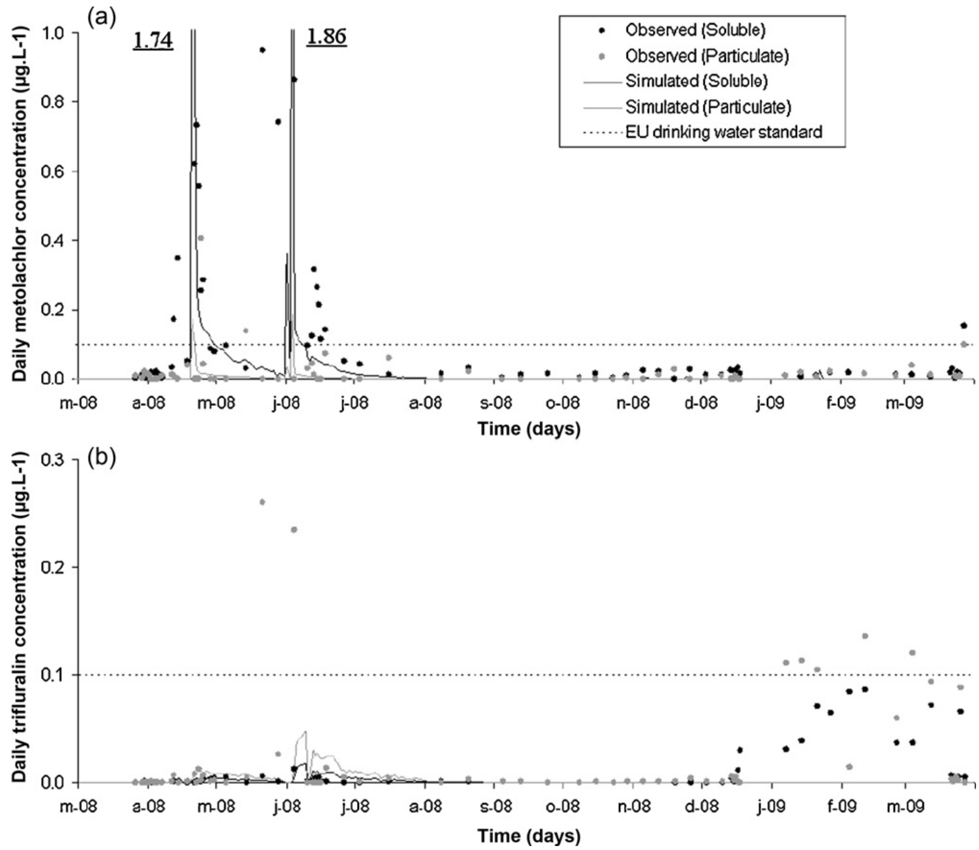

Fig. 5. Observed and simulated daily pesticide concentrations ($\mu g\,L^{-1}$) at the Larra gauging station (2008–2009): (a) metolachlor and (b) trifluralin.

Table 4
Observed (2008–2009) and simulated (1998–2008) average annual loads of metolachlor and trifluralin in each catchment compartment ($mg\,ha^{-1}\,yr^{-1}$) and particulate fraction out of HRUs and at catchment outlet.

	Metolachlor ($mg\,ha^{-1}\,yr^{-1}$)		Trifluralin ($mg\,ha^{-1}\,yr^{-1}$)	
	Observed	Simulated	Observed	Simulated
HRUs				
Runoff		Dissolved: 1653 Sorbed: 317 *Partition*: 0.16		Dissolved: 475 Sorbed: 1237 *Partition*: 0.72
Lateral flow		Dissolved: 200		Dissolved: 10
Outlet				
Flow water	Dissolved: 204 Sorbed: 27 *Partition*: 0.12	Dissolved: 135 Sorbed: 14 *Partition*: 0.09	Dissolved: 60 Sorbed: 195 *Partition*: 0.77	Dissolved: 2 Sorbed: 5 *Partition*: 0.72

Table 5
Total and dissolved metolachlor and trifluralin loads (g) during April and June 2008 floods at Larra outlet.

	Metolachlor		Trifluralin	
2008 floods	April (11/04–30/04)	June (14/05–18/06)	April (11/04–30/04)	June (14/05–18/06)
Measured total load (g)	5015	16,692	66	3285
Simulated total load (g)	3588	11,283	92	422
Measured dissolved load (g)	4591	16,178	13	186
Simulated dissolved load (g)	3262	10,257	26	117

Table 6
Daily and monthly R^2 for metolachlor and trifluralin concentration (dissolved, sorbed and total) at Larra outlet (2008–2009).

	Metolachlor		Trifluralin	
	Daily	Monthly	Daily	Monthly
Dissolved	0.25	0.43	0.21	0.60
Sorbed	0.01	0.38	0.01	0.15
Total	0.26	0.45	0.02	0.16

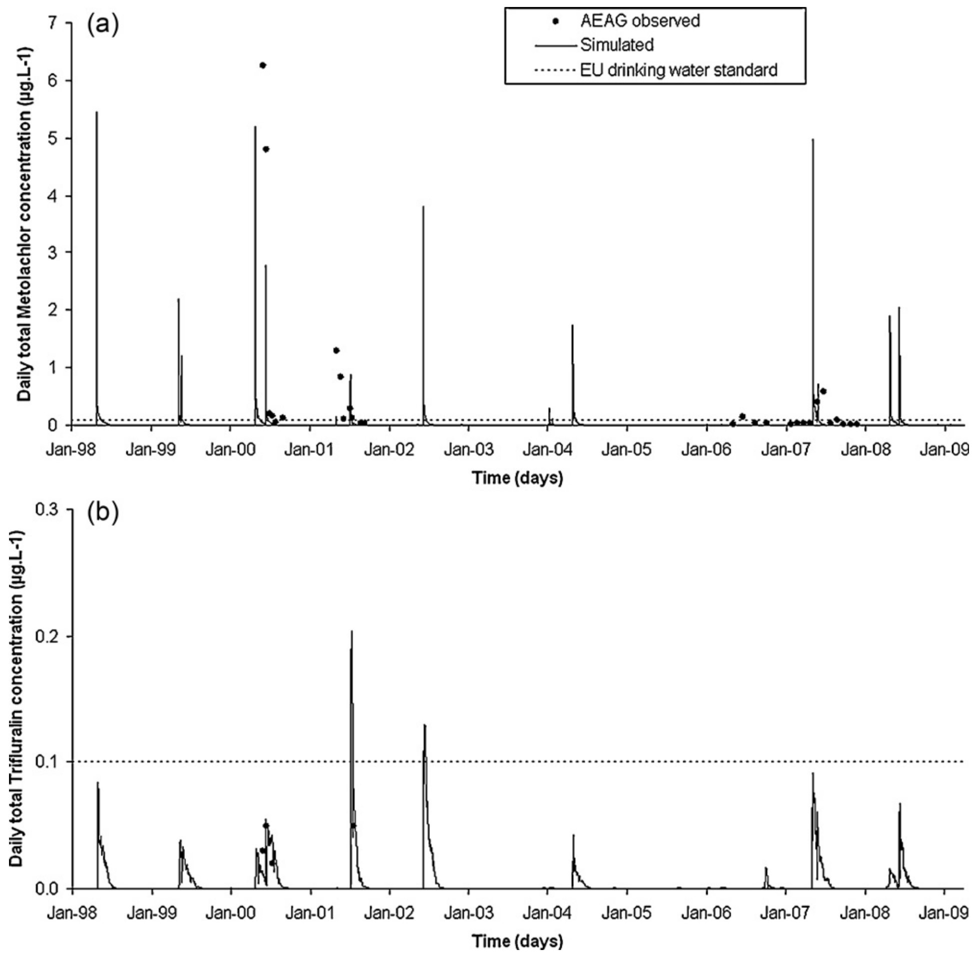

Fig. 6. Observed and simulated daily pesticide total concentrations (µg L^{-1}) at the Larra gauging station (1998–2009): (a) metolachlor and (b) trifluralin.

for sorbed and total trifluralin. R^2 for daily concentrations did not exceed 0.26 (Table 6).

3.2.2. Long-term pesticide exportation balances at outlet

During the 1998–2008 period, high flows represented 17% of the time considering the 6.1 $m^3 s^{-1}$ threshold. 50% of nitrate load and 57% of suspended sediment load were exported during high flow. Annual pesticide loads are shown in Fig. 7. The total metolachlor load varied between 0.1 kg yr^{-1} (2003) and 80 kg yr^{-1} (2000), whereas trifluralin varied between 0.01 kg yr^{-1} (2003) and 2.3 kg yr^{-1} (2000). Average total metolachlor and trifluralin annual loads were 16.7 kg (SD = 23 kg) and 0.8 kg (SD = 1 kg) respectively. The total metolachlor and trifluralin exported were around 0.072% and 0.005% of the applied amount respectively (exportation rate was 1% out of the HRUs for both molecules). At outlet 61% of the total metolachlor and 52% of the total trifluralin were exported during high flows (Table 7). Out of the 4108 simulated days (1998–2009), metolachlor at Larra outlet exceeded the European standard threshold of 0.1 µg L^{-1} for 149 days and trifluralin exceeded this same threshold for 17 days (3.6 and 0.4% of the time period respectively). Maximum metolachlor concentration was 5.4 mg L^{-1}, predicted in July 2001 whereas maximum trifluralin concentration was 0.2 mg L^{-1}, predicted in April 1998 (Fig. 6). Considering the sum of total metolachlor and total trifluralin concentrations, the threshold of 0.5 µg L^{-1} was exceeded during 24 days at catchment outlet.

3.2.3. Pesticide transfer controlling factors

At catchment scale, the simulated preferred pathway of pesticide transfer was surface runoff (Table 4) with associated nitrate and suspended sediment exportations. At sub-basin scale, trifluralin and metolachlor in the sorbed phase were correlated to suspended sediment loads (R^2 = 0.69 and 0.64, respectively). Trifluralin and metolachlor in the dissolved phase were poorly correlated to nitrate loads (R^2 = 0.21 and 0.16, respectively). Eventually, trifluralin and metolachlor in the dissolved phase were better correlated to suspended sediment loads (R^2 = 0.33 and 0.67 respectively). At HRU scale, the correlation analysis did not show any correlation between suspended sediment loads, metolachlor and trifluralin loads in the dissolved phase and catchment variables. Metolachlor and trifluralin loads in the sorbed phase correlated weakly to suspended sediment yields (R^2 = 0.24 and 0.43 respectively).

4. Discussion

4.1. Discharge, nitrate and suspended sediment simulation

Overall E_{NS} and R^2 for daily discharge were over the satisfactory threshold. However, gaps between observed and simulated values are explained by errors in observed and simulated values. Errors in observed values can stem from the precision of the sensor and from the use of a rating curve. Errors in simulated values can be attributed to (i) actual local rainfall storms that were not well represented by the SWAT rainfall data interpolation and (ii) the flow

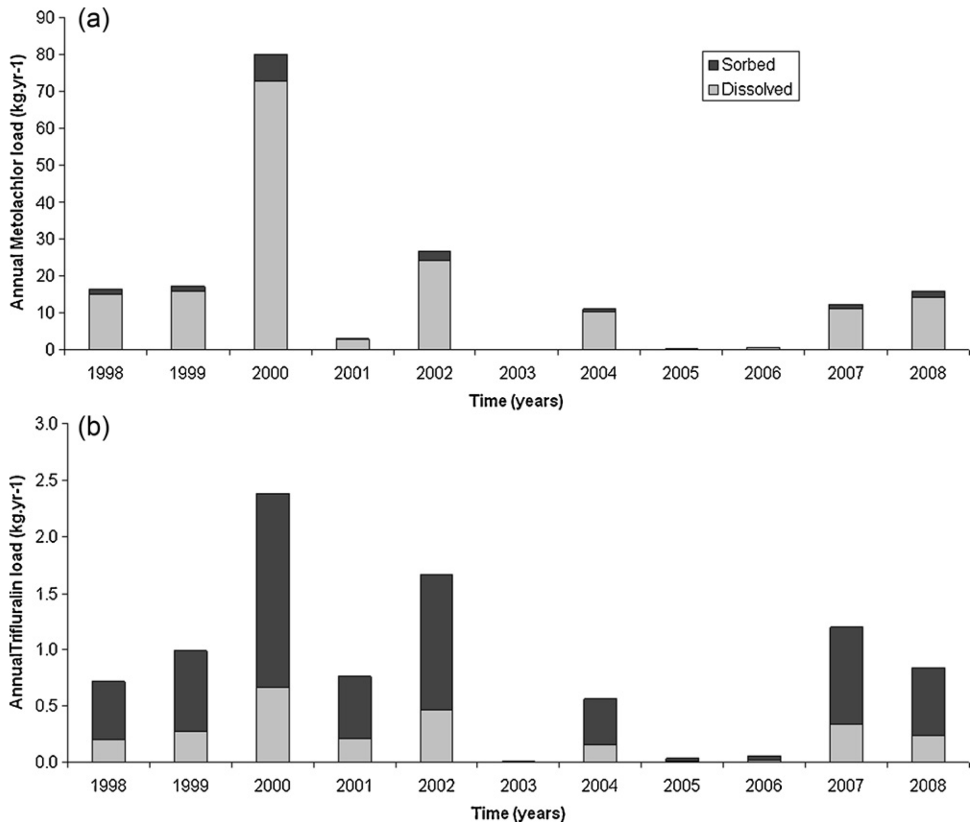

Fig. 7. Simulated annual dissolved and sorbed pesticide loads (kg yr^{-1}) at Larra outlet (1998–2008): (a) metolachlor and (b) trifluralin.

uncertainty in the dense network of canals diverted from the river network to bring part of river flow to many watermills. E_{NS} for low flow was below the satisfactory threshold. Low E_{NS} during low flow has to be related to its generally poor performance in periods of low flow: with only minor simulation errors the denominator of the equation tends towards zero and E_{NS} approaches negative infinity. Low E_{NS} is however of minor concern since pesticides were shown to be mostly exported during floods. Save river discharge simulation quality is however comparable to Oeurng et al. [45].

Daily nitrate prediction is related to daily discharge prediction, as it is a very soluble nutrient. Bias is therefore linked to the inaccuracy of discharge predictions mentioned above. Uncertainty in point-source nutrient input also explains bias. In addition, averaged land use and associated management practice inputs may not reflect well enough the actual and local land use and management practices. They also can evolve over the modelled period depending on agricultural policy trends.

E_{NS} and R^2 for daily suspended sediments concentration were below the satisfactory threshold. Calibration of sediment is difficult in the Save catchment considering the dense network of canals diverted from the river network. The succession of dams and gates traps sediments till their random emptying back to river network. Uncertainty in point-source suspended sediments input may also explain bias. Suspended sediment results were however consistent with Oeurng et al. [45].

4.2. Pesticide simulation

4.2.1. SWAT performances

R^2 of daily pesticide concentration was below the satisfactory threshold. As highlighted by Luo et al. [24] possible time shifts in the precipitation, agricultural activity, and measurements for flow and water quality data render daily pesticide statistics poor. Errors in pesticide concentration and load predictions may be related to (i) an inadequate calibration of the parameters governing flow and soluble (e.g. nitrate) and particulate (e.g. suspended sediment) phases transport and to (ii) an inadequate calibration of pesticide component parameters.

Sorbed pesticide underestimation has to be related to the high deposition rate of suspended sediment in the channel. Also, as K_{oc} was shown to be poorly sensitive and as CHPST_KOC is set as a constant value, both partition coefficients modelled in HRUs and in reaches vary depending on suspended sediment concentration. They may not reflect actual variations: metolachlor and trifluralin measurements at outlet show various inversions (i.e. [soluble] < [sorbed] for metolachlor and [soluble] > [sorbed] for tri-

Table 7
Average metolachlor and trifluralin daily loads (g d^{-1}) during high flow and low flow in dissolved and sorbed phases and percentage of pesticide load exported during high flow at Larra outlet (1998–2008).

	Dissolved			Sorbed		
	Low flow (g d^{-1})	High flow (g d^{-1})	Flood losses (%)	Low flow (g d^{-1})	High flow (g d^{-1})	Flood losses (%)
Metolachlor	19	137,118	61	2	13,712	61
Trifluralin	0.4	1805	52	1	4694	52

fluralin) of the partition coefficient *Kd*, as defined by Taghavi et al. [30] at catchment outlet, that were not modelled.

Regarding agricultural activity, i.e. land use and associated management practices, the model did not simulate any trifluralin concentration rise in early 2009. The land use input map was based on a 2005 land cover satellite image that may not reflect long-term actual operations: e.g. canola, representing 1% of the catchment land use in 2005, has been grown increasingly over the past five years in the northern part of the catchment. Up to 2009, canola was managed with an average spread of 1 kg ha^{-1} of trifluralin in August. This was not taken into account in the model because SWAT land use approximation was set to skip land use representing less than 10% of the sub-basin area. Reliable pesticide supply input data are therefore a necessary condition to achieve satisfactory simulation outputs.

A last source of error is the modelled transfer pathways: SWAT simulates pesticide transfers through surface runoff and subsurface lateral flow but not through groundwater flow, drainflow nor atmospheric deposition [31]. This may lead to additional errors in soluble pesticide simulation although leaching of pesticides into deep groundwater and a possible input of pesticides into surface waters by outflowing groundwater is known to be negligible [46,47]. In addition, no point-source, such as the cleaning of the equipment, was modelled in this study [12,48].

Finally, daily pesticide total concentrations R^2 were in the lower range of the values mentioned by Neitsch et al. [21]. They reported R^2 ranging from 0.41 to 0.28 for daily metolachlor total concentration and R^2 ranging from 0.51 to 0.02 for daily trifluralin total concentration.

4.2.2. Long-term pesticide exportation balance at outlet

Simulation showed that pesticides were exported mainly during flood events. Role of floods in pesticide exportation was previously shown at the Save catchment outlet [29]. As interannual average, exportation rates of both pesticides have to be related to their application time (April) and the month of maximum discharge (May). However, simulated values of exportation during a similar high flow period were less than measured values in a small catchment or at field scale [49,50]. The size of the drained area, but also the soil and the land use may modulate the exportation.

Pesticide exportations from land to outlet were less than 1% of applied amount. Such a value was reported by various studies on metolachlor in France, Switzerland and Québec [51–53] and on other pesticides [50,53,54]. About 93% and 99% of metolachlor and trifluralin respectively entering the stream network does not reach the outlet, suggesting high deposition (discussed above) and degradation in stream water. The latter would be consistent with the carbon consumption by river biota shown by Sánchez-Pérez et al. [55] on a similar catchment of Gascogne.

Trifluralin concentration exceeded the 0.1 $\mu g\,L^{-1}$ maximum permissible level less than metolachlor concentration. In the model, trifluralin was less applied than metolachlor among the catchment, its soil half-life was 60 days (instead of 90 days for metolachlor) and its transport was more likely depending on land and river bed erosion. It is worth noting that the European standard of 0.5 $mg\,L^{-1}$ was exceeded by a pool of only two molecules during 0.6% of the simulation time.

4.2.3. Pesticide transfer controlling factors

Runoff was shown to be the preferred simulated pathway for pesticide exportation. Luo et al. [24,56] already reported the control of runoff on pesticide transfer simulation. In the environment, pesticides may be sorbed onto mineral suspended matter, Particulate Organic Carbon (POC) and complexed by Dissolved Organic Carbon (DOC) [29]. Better correlation was found between dissolved phases and suspended sediment than between dissolved phases and nitrate. Although pesticide transfer through groundwater is not yet modelled in SWAT, contrarily to nitrate, the relationships highlighted a control of both surface and sub-surface runoffs during floods on dissolved phase exportation. This is consistent with the pesticides' actual ability to sorb onto DOC, i.e. smaller than the 0.45 μm mesh filter, and its transfer through sub-surface flow [29].

5. Conclusions

The SWAT model was applied to simulate pesticide transfer at the outlet of a large intensive agricultural catchment. Simulation results were deemed to be satisfactory, taking into account that the modelled transfer processes were simplified and do not represent all actual transfers. Further improvements of the SWAT model may be investigated. The transfer of pesticide in the dissolved phase from land to river through groundwater could be tested to assess possible water-table effect. Also, investigating the variations of the partition coefficient between observed dissolved and sorbed phases during floods in various points in the river (areas of rapid, deep, etc.) would help to assess the accuracy of the SWAT modelled partition at flood-event scale.

However, extrapolation to other chemicals is conceivable and SWAT was shown to be promising for providing a robust decision tool for water quality managers. Floods are quick events. Such a tool would help (i) to target 'what and when' to monitor, (ii) to highlight pesticide concentration peaks without cost-intensive field measurements and predict future peaks and (iii) to evaluate exported loads as contamination indicator. Suggestion of localised mitigation practices to reach water policy objectives such as the European Water Framework Directive is made possible.

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