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Application date as a controlling factor of pesticide transfers to surface water during runoff events

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ABSTRACT

In agricultural watersheds, pesticide contamination in surface water mostly occurs during stormflow events. When modelling pesticide fate for risks assessment, the application timing input is one of the main uncertainty sources among all the parameters involved in the river network contaminations process. We therefore aimed to assess the sensitivity of the river network pesticide concentration patterns to application timing shifts within a plausible range of application dates, considering two pre-emergence herbicides (metolachlor and aclonifen) characterised by two different octanol/water partition coefficients (K_{ow}). The Soil and Water Assessment Tool (SWAT) was applied in the 1110 km^2 agricultural watershed of the river Save (south-western France), where wheat, maize, sorghum and sunflower are intensively grown. The pesticide application date was changed within a one-month interval and the pesticide concentration at catchment outlet was simulated from March to June 2010. Total metolachlor concentration prediction could be improved by an application timing shift to 3 days later (Daily $R^2 = 0.22$ and PBIAS = -57%). By testing the behaviour of the two molecules, it was shown that sorption processes were influencing the control of application timing on the transfer to surface water: metolachlor concentration in the channel depended on both discharge and delay between application date and first stormflow event whereas the transfer of aclonifen depended on rainfall intensity for exportation with suspended sediments through surface runoff. At last, the study discusses the potential implications of the sensitivity in terms of regional agricultural management practice design.

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1. Introduction

The detrimental effect of intensive agriculture on surface water and groundwater quality has been shown by various authors (Burt, 2001; Cullum, 2009; Ulrich et al., 2013; Zalidis et al., 2002; Zeiger and Fohrer, 2009). The transfer of excessive pesticide loading from cultivated land to surrounding surface water, either dissolved or sorbed onto particles, may be harmful to terrestrial and aquatic ecosystems (Martin et al., 2011; Niemi et al., 2009; Polard et al., 2011). The partition between both dissolved and particulate fractions controls the bioavailability of the chemical for living organisms' contamination. Pesticide exportations, from either point losses (e.g. through leaking tools) or diffuse sources (i.e. mostly through runoff and droplet drift) (Holvoet et al., 2005; Müller et al., 2003), may make stream water and groundwater unfit for human consumption. Drinking water quality European Maximum Permissible Level (MPL) is of 0.1 μg L^{-1} for an individual pesticide concentration and 0.5 μg L^{-1} for all pesticide concentration (EC, 1998). Recent studies showed the role of one-off and intense events, such as floods, on water quality degradation regarding pesticides, including in the south-western France area (Boithias et al., 2011, 2014a; Taghavi et al., 2010, 2011). Intensity and timing of rain and irrigation were shown to be the main inducers of pesticide transfers (Chiovarou and Siewicki, 2008; Vryzas et al., 2009). Short-term (5-day) precipitation and antecedent soil water deficit were identified as the two most important explanatory variables for maximum pesticide concentrations in drainflow (Lewan et al., 2009). Reichenberger et al. (2007) listed the shift of the pesticide application to an earlier or later date as an efficient mitigation strategy. Modelling studies corroborated observations for runoff incidence on pesticide exportation (Boithias et al., 2011; Chu and Mariño, 2004; Zhang and Zhang, 2011) and for application timing role at seasonal scale (Luo et al., 2008) and at rainfall event scale (Fohrer et al., 2014; Holvoet et al., 2005; Neitsch et al., 2002; Vazquez-Amabile et al., 2006). Dubus et al. (2003) highlighted the uncertainties inherent in pesticide fate modelling, including application timing, which depends on the farmer and varies from year to year

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(Beernaerts et al., 2002; Campbell et al., 2004). Indeed, large-scale surveys with farmers often do not give precise enough information about application sites, application dates and pesticide doses, i.e. pesticide application rates, for catchment-scale daily time-step modelling purpose (Boithias et al., 2011).

In south-western France, spring floods (i.e. spring flushes) were shown to be the main inducers of pre-emergence herbicide stream network contamination, as they are mostly applied on bare soils in the most rainy periods (Boithias, 2012; Macary et al., 2013, 2014). When applied, pesticide doses are assumed to be at the most equal to manufacturer recommendation. Thus, for contaminant fate modelling and possible catchment-scale risk assessment, uncertainty lies in temporal and spatial patterns of pesticide application. Boithias et al. (2011) concluded that the Soil and Water Assessment Tool (SWAT—Arnold et al., 1998; Gassman et al., 2007) was an appropriate catchment-scale model to simulate the fate of dissolved and sorbed phases of pesticides at a daily time-step. To our knowledge, no studies were yet published that related the impact of the application timing to the hydrophobicity of applied chemicals. As a first step to assess the uncertainty of the pesticide inputs (application site, timing, and dose) when modelling pesticide fate at catchment-scale with SWAT, the aims of this study were twofold: (1) to assess the sensitivity of the river network pesticide concentration patterns to application timing shifts within a plausible range of application dates, considering two herbicides characterised by two different octanol/water partition coefficients, and (2) to discuss the potential implications of the sensitivity in terms of agricultural management practice design.

2. Material and methods

2.1. Study area

The river Save is located in south-western France and drains an area of 1110 km^2 (Fig. 1). Altitudes range from 663 m at its source in the Pyrenees piedmont to 92 m at the confluence with the river Garonne after a 140 km course at a 0.4% average slope. The catchment is monitored at the Larra gauging station, whose elevation is 114 m (Fig. 1). The geological substratum is built from impermeable molassic deposits stemming from the erosion of the Pyrenees Mountains during the end of the Tertiary period. Calcic soils stem from molasses and represent 61% of the whole catchment area with a clay content ranging from 35% to 50%. They are located on the top of the hills and on their slopes. Non-calcic silty soils represent 30% of the soil in this area (40–60% silt). They are mainly located downstream, close to the Garonne alluvial plain. Alluvial deposits are found along the streams and represent 9% of the catchment area (Boithias et al., 2014b). Top soil organic matter content is about 2% (Veyssy et al., 1999).

The climate is temperate oceanic. The river Save hydrological regime is mainly pluvial with a maximum discharge in May and low flows lasting from July to October (1998–2010). The annual precipitation is 600–900 mm and the annual evapotranspiration is 500–600 mm (1998–2010). Mean annual discharge is about 6.1 m^3 s^{-1} (1998–2010). During low flows, river flow is sustained upstream by the Neste canal (about 1 m^3 s^{-1}) (data from Compagnie d'Aménagement des Coteaux de Gascogne—CACG).

About 90% of the catchment surface is devoted to agriculture. The upstream part of the catchment is a hilly agricultural area mainly covered with pasture and forest with cereals and maize on small plateaus. The downstream part is devoted to intensive agriculture with mainly both maize grown as monoculture and a 4-year crop rotation alternating winter wheat with sunflower and maize, sorghum or soybean. Water supply for irrigation is 210 mm for maize from July to September (Boithias et al., 2014b). A Cemagref/Irstea-ADBX 3-year survey (2007–2009) was performed anonymously with catchment farmers in order to avoid any risk for them to be identified. The survey reports 3-year average spatial and temporal information about site, timing and dose of pesticide application. The most applied pesticides are metolachlor and aclonifen, both are pre-emergence herbicides. Each year, 28 tonnes of metolachlor, a highly soluble and poorly hydrophobic chemical (solubility in water $S_w = 480$ mg L^{-1}, and hydrophobicity expressed by log(K_{ow}) = 2.9), and 56 tonnes of aclonifen, a poorly soluble and highly hydrophobic chemical ($S_w = 1.4$ mg L^{-1}, log(K_{ow}) = 4.37) (Tomlin, 2009), are applied throughout the catchment. On average, metolachlor is applied each year to maize and sorghum around the 5th of April, whereas aclonifen is applied each year to maize and sorghum around the 5th of April and to sunflower around the 20th of April. In 2009, sunflower fields covered 9% of the catchment (100 km^2), maize covered 10% of the catchment (112 km^2) and sorghum covered 6% (70 km^2).
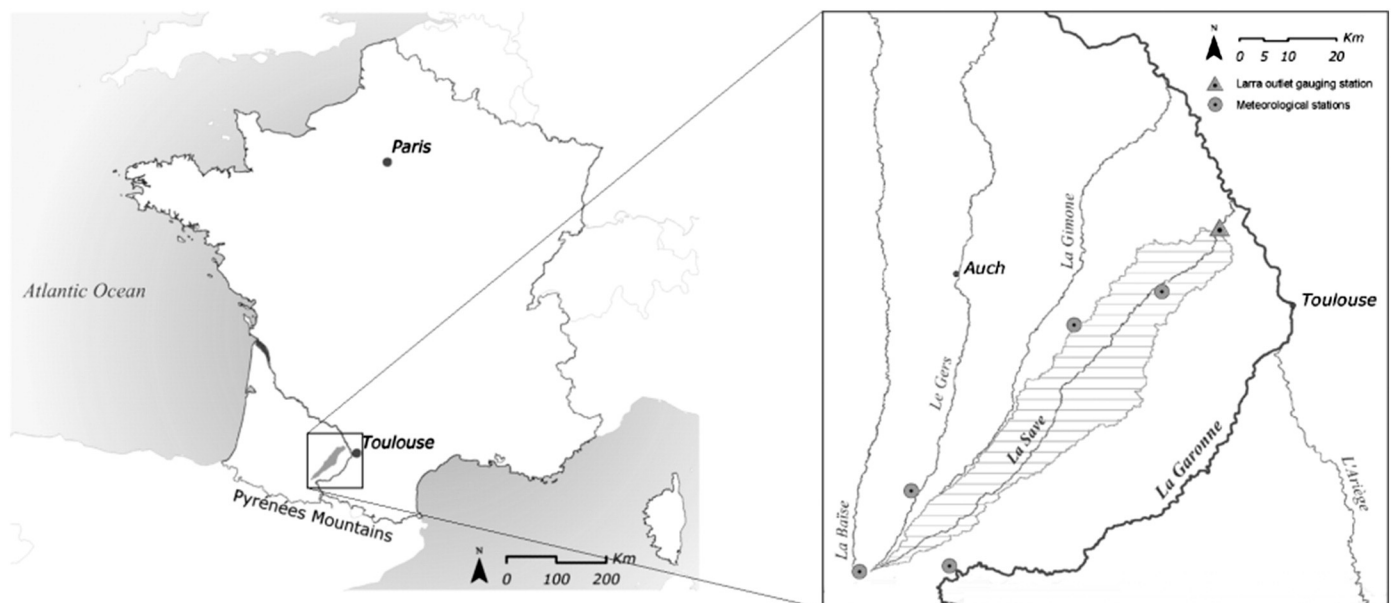

Fig. 1. Location of the Save catchment, the Larra gauging station and the 5 meteorological stations.

The present study focuses on the 4-month spring high flow period of 2010, lasting from March to June.

2.2. Measured data

The river Save discharge was monitored from July 2009 to June 2010 at the Larra hydrometric station. Hourly discharges (Q) were obtained from CACG. The hourly discharge was plotted by the rating curve $Q = f(H)$ in which the water level (H) was measured continuously and then averaged for each day.

Suspended sediments and pesticides were monitored from July 2009 to June 2010, both manually and automatically, as described in previous studies on Save catchment (Boithias et al., 2011, 2014a; Oeurng et al., 2010): an automatic water sampler, connected to the probe, was programmed to activate pumping water for 30 cm water level variations during high flows, for the rising and falling stages (from 1 to 29 river water samples of 1 L were grabbed per stormflow event depending on its intensity). Grab sampling was also undertaken near the probe position at weekly intervals during low flow. In addition, continuous suspended sediment data were collected by turbidity measurements. Samples of 1 L-river water were not aggregated before analysis. Pesticide laboratory analyses were performed as described by Taghavi et al. (2010, 2011) on both filtered and unfiltered extracts of the same sample of water with a limit of detection ranging between 0.001 and 0.003 µg L^{-1} depending on the molecule. Dissolved and particulate concentrations of pesticides were then summed up to get the total concentration. In case of sub-daily samplings, daily concentrations were calculated as an average concentration balanced by the instantaneous discharge. Thus, 89 daily concentration data were available for the June 2009–July 2010 period, including 43 daily concentration data for the March–July period.

2.3. Modelling approach

2.3.1. The SWAT model

The Soil and Water Assessment Tool (SWAT—Arnold et al., 1998; Gassman et al., 2007) is a physically-based agro-hydrological model. It was chosen because its daily operating time-step was appropriate for the modelling of floods on the Save catchment, and because it simulates pesticide fate in both dissolved and sorbed phases in land and in river channel (Boithias et al., 2011). SWAT discretises catchments into sub-basins. Sub-basins are then further subdivided into Hydrological Response Units (HRUs). HRUs are areas of homogenous land use, soil type and slope. HRU outputs are inputs for the connected stream network. One sub-basin is drained by one reach. Pesticide processes in SWAT are divided into three components:

(1) pesticide processes in land areas, including biotic and abiotic degradation, volatilisation from plant and soil surface, infiltration, and leaching;
(2) transport of pesticides from land areas to the stream network in both the dissolved and the sorbed phases, depending on the soil adsorption coefficient K_{oc} normalised for soil organic content (Table 1). Dissolved pesticides are transported with surface and subsurface runoff, while sorbed pesticides are transported with surface runoff only;
(3) in-stream pesticide processes, including degradation, volatilisation and settling. The processes depend on the pesticide's phase, based on the partition coefficient CHPST_KOC (Table 1).

SWAT predicts both dissolved and sorbed concentrations of pesticides: total simulated concentration is obtained by adding up both dissolved and sorbed simulated concentrations. Authors refer to Neitsch et al. (2009) for detailed description of the model's equations.

2.3.2. SWAT data inputs

Inputs maps are (1) a digital elevation model with a 25 m × 25 m resolution from Institut Géographique National, France (BD TOPO R); (2) a land use map from the classification of three 2009 Landsat 5TM images with associated management practices provided by Cemagref/Irstea-ADBX: spatial and temporal 3-year averages of planting and seedling dates, amounts, type and dates of fertilisation, pesticide application, irrigation, grazing, tillage, and harvest operations, including crop rotations, stemming from a 3-year survey (2007–2009) with catchment farmers; and (3) a soil map digitised and aggregated by Cemagref/Irstea-ADBX, from paper maps prepared by soil scientists of the CACG in the 1960s with associated soil layer properties. Climate data from 5 stations (Fig. 1) were provided by Météo-France. 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 by the Penman–Monteith method. Daily discharge data for the Neste canal, supplying water as an upstream point source to the Save river network, was contributed by CACG. Version 2009.93.7a of ArcSWAT and SWAT Editor were used to set up SWAT inputs and run the model. The catchment was discretised into 73 sub-basins whose minimal area was 5 km^2. 2985 HRUs were generated integrating 23 land uses classes, 6 soil classes and 5 slope classes (%: 0–2, 2–5, 5–10, 10–15 and above 15) (Boithias et al., 2014b).

2.3.3. Model calibration and validation

Pesticides can be transported in solution or attached to suspended matter. Therefore, calibration and validation of dissolved phase (e.g. nitrate) and particulate phase (e.g. suspended matter) were of major concern. This study used a SWAT project which was validated for discharge, nitrate loads and concentrations, crop yields and biomasses from 2007 to 2010 (Boithias et al., 2014b). For this study, suspended matter and both dissolved and sorbed phases of pesticide concentrations (metolachlor and aclonifen) were calibrated at the outlet from July 2009 to June 2010 (12 months) and without recalibrating hydrological parameters. The performance of the model was evaluated using the coefficient of determination (R^2) and the percentage of bias (PBIAS) computed with daily suspended matter concentration and daily total metolachlor and aclonifen concentrations, both simulated and observed, for both the 4-month (March–June 2010) and the 12-month (July 2009–June 2010) periods. We deemed daily R^2 satisfactory when higher than 0.5 (Green et al., 2006) and daily PBIAS satisfactory if within ± 55% for suspended matter and ± 70% for pesticides (Moriasi et al., 2007). We assumed that the average pesticide application date surveyed in the previous years (2007–2009) would also match the farmers' decisions of 2010. Survey average values of pesticide application date and applied amounts are reported in Fig. 2, shown as red bars. Parameters values are given in Table 1.

2.4. Application date scenarios

Based on the average values of application date given in Fig. 2 (the "0" scenario), 10 application date scenarios were run by shifting the

Table 1
Physicochemical properties and mass-transfer calibrated coefficients for metolachlor and aclonifen in the SWAT model: partition in soil and channel, half-life and degradation rate in the channel water and in the sediment bed (respectively CHPST_REA and SEDPST_REA).

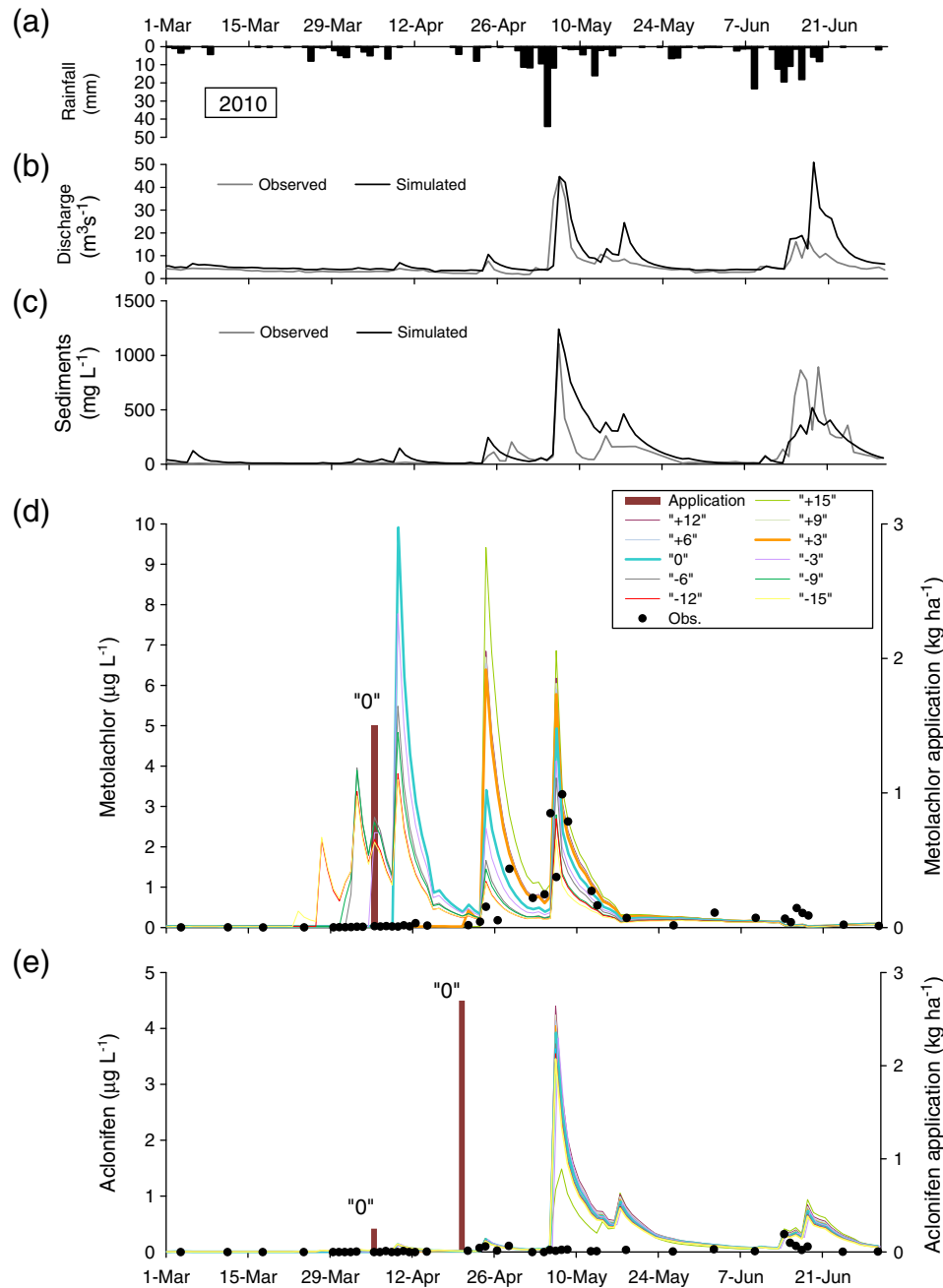| Parameters	Name in SWAT		File	Metolachlor	Aclonifen
Partition in soil	K_{oc}	L kg^{-1}	pest.dat	200	8203
Partition in channel	CHPST_KOC	L kg^{-1}	.swq	2.5×10^{-4}	7.2×10^{-3}
Soil half-life	HLIFE_S	days	pest.dat	90	90
Degradation rate	CHPST/SEDPST_REA	days^{-1}	.swq	0.025	0.025
Volatilisation	CHPST_VOL	m day^{-1}	.swq	0.3	0.3

Fig. 2. Simulations at the outlet of the Save catchment from March to June 2010: (a) catchment average SWAT interpolated rainfall; (b) observed and simulated discharge (m³ s⁻¹); (c) observed and simulated suspended sediment concentration (mg L⁻¹); (d) simulated total metolachlor concentration (µg L⁻¹) for 11 application date scenarios and observed concentrations; and (e) simulated total aclonifen concentration (µg L⁻¹) for 11 application date scenarios and observed concentrations. In (d) and (e), bars represent the amount of respective pesticide applied for initial "0" scenario (kg ha⁻¹).

application dates by steps of 3 days, down to 15 days before average "0" scenario and up to 15 days after average "0" scenario. Simulated pesticide total (dissolved + sorbed) concentration patterns were analysed at the outlet during the 2010 spring flood (March to June 2010). Each simulation scenario's performance was evaluated using R^2 and PBIAS computed with daily total metolachlor and aclonifen concentrations, both simulated and observed. The latter performances were then compared to the performances of the "0" scenario.

2.5. Sensitivity analysis

The sensitivity of the application date input was assessed for both metolachlor and aclonifen total load at catchment outlet (2010 spring flood). It was calculated as the average (S) of 10 relative sensitivity

indices (S_i), each of them calculated as shown in Eq. (1) (Melching and Yoon, 1996):

$$S_i = \frac{\partial P}{\partial I} \cdot \frac{I}{P(I)} \tag{1}$$

With P the prediction (total load at outlet) and I the input value (application date). I was -15, -12, -9, -6, -3, $+3$, $+6$, $+9$, $+12$ and $+15$ days.

3. Simulation results

For the 4-month period, the R^2 and the Nash-Sutcliffe Efficiency (NSE) of the daily discharge were 0.64 and 0.48 respectively (they

were of 0.74 and 0.62 respectively during the 12-month period and of 0.70 and 0.61 respectively during the 2007–2010 period). The R^2 and the PBIAS of the daily suspended sediment concentration were 0.50 and −35% respectively (they were of 0.45 and −43% respectively during the 12-month period). Fig. 2 shows average SWAT catchment-scale interpolated rainfall, observed and simulated discharge, observed and simulated suspended sediment concentration, and the concentration at outlet of total observed and simulated metolachlor and aclonifen for the 11 pesticide application date scenarios, from March to June 2010. Suspended sediment concentration was correlated to discharge ($R^2 = 0.77$, $n = 122$), itself responding to rainfall with runoff peaks. The concentration patterns of both pesticides are different: metolachlor concentration peaks are distributed depending on the application date, whereas aclonifen peaks are concentrated around the same date (the 4th of May). For total metolachlor concentration, scenario "+3" fitted observations the best (Table 2), where R^2 for dissolved and sorbed concentrations were 0.21 and 0.10 respectively (4-month period). For aclonifen, the best scenario was "+15", where R^2 for dissolved and sorbed concentration is 0.03 and 0.05 respectively (4-month period). Goodness-of-fit indices for the 12-month calibration period were slightly higher than the ones for the 4-month period for both molecules (Table 2).

Shifts in application date had the highest impact on metolachlor total load exportation at outlet during the spring flood period: exported fluxes from the 1st of March to the 30th of June were ranging between 38 and 82 kg for metolachlor, but were ranging between 36 and 59 kg for aclonifen (Table 3). Metolachlor exportation rates (input/output ratio) were ranging between 1.4‰ and 2.9‰. Aclonifen exportations rates were ranging between 0.7‰ and 1.1‰. Metolachlor concentration exceeded the MPL of 0.1 µg L^{-1} during 43% to 68% of the time depending on the application date, whereas aclonifen concentration exceeded the same MPL during 39% to 44% of the time (Table 3). In addition, the sensitivity S of metolachlor was −0.20 whereas it was −0.06 for aclonifen.

4. Discussion

Simulation of pesticide concentration was improved by shifting the application date, although simulations of pesticides did not meet all satisfactory standards. The quality of the simulation for both molecules was in the range of the previous daily time-step modelling pesticide fate study in the Save catchment of Boithias et al. (2011). The quality of the simulation was however lower than other previous modelling pesticide fate studies at daily time step, e.g. recently Fohrer et al. (2014), who benefited from detailed flufenacet and metazachlor input data in the 50 km² Kielstau catchment.

Hydrological processes, that drive pesticide transfers, were satisfactorily modelled although the goodness-of-fit indices during the 4-

Table 3
For 11 application date scenarios: fluxes (kg) of total metolachlor and aclonifen at the outlet of the river Save from March the 1st to June the 30th, 2010; fraction (%) of spring flood duration with a concentration of pesticide exceeding the EU water quality standard of 0.1 µg L^{-1}.

	Metolachlor		Aclonifen	
	Flux (kg)	[Met] > 0.1 µg L^{-1} (% of days)	Flux (kg)	[Acl] > 0.1 µg L^{-1} (% of days)
"−15"	38	68	46	40
"−12"	42	65	48	40
"−9"	44	61	49	41
"−6"	52	61	50	41
"−3"	57	57	51	42
"0"	66	54	52	43
"+3"	66	44	54	42
"+6"	68	44	56	42
"+9"	69	44	57	43
"+12"	71	44	59	44
"+15"	82	43	36	39

month spring period were weaker than those of the 2007–2010 period. So was the suspended sediment transport, which drives sorbed pesticides transfers. Bias between observations and model predictions of pesticide concentrations may also come from inadequate values of the pesticide parameters (e.g. half-life and reaction coefficients, although their calibrated values were in the range of the pesticide properties inputs reported by Neitsch et al. (2002)), given that the uncertainty on their value is large (Dubus et al., 2003; Walker et al., 2002). Uncertainty also exists among observed data and laboratory analysis (Dubus et al., 2003). The spatial and the temporal patterns of pesticide applications are uncertain because of the limitations of the large-scale anonymous survey that provided average spatial and temporal values of application site and doses, together with application timing. The farmers did not actually apply pesticides on all their crops (e.g. sunflower, maize or sorghum) the same day: farmers staggered the application depending on the weed pressure and on the amount of rainfall announced by weather forecast, contrarily to simulation where only one application date per land use was considered (for that purpose Gevaert et al. (2008) suggested to describe application date input as a probability distribution). The metolachlor modelling results in Fig. 2 show concentration peaks immediately after application dates, which are not observed from the "−15" to "0" cases. As highlighted by the goodness-of-fit values reported in Table 2, metolachlor was probably actually applied later, from the 8th of April to the 18th of April. The aclonifen modelling results in Fig. 2 also show concentration peaks that are not observed. One explanation is that aclonifen, that has a K_{ow} higher than the one of metolachlor, is mostly sorbed to suspended matter and trapped with them when they sediment along the river course. In addition, given that pre-emergence

Table 2
Goodness-of-fit indices calculated for both the 4-month ($n = 43$) and the 12-month ($n = 89$) periods with metolachlor and aclonifen total observed and simulated concentrations for 11 application date scenarios.

	Metolachlor				Aclonifen			
	4 months (March–June 2010)		12 months (July 2009–June 2010)		4 months (March–June 2010)		12 months (July 2009–June 2010)	
	R^2	PBIAS (%)	R^2	PBIAS (%)	R^2	PBIAS (%)	R^2	PBIAS (%)
"−15"	0.01	−91	0.01	−69	0.01	−788	0.01	−478
"−12"	0.00	−100	0.01	−76	0.01	−810	0.01	−491
"−9"	0.00	−120	0.01	−93	0.01	−831	0.01	−504
"−6"	0.00	−137	0.02	−107	0.01	−851	0.01	−516
"−3"	0.00	−142	0.03	−111	0.01	−867	0.01	−526
"0"	0.01	−150	0.04	−118	0.01	−885	0.02	−538
"+3"	0.22	−57	0.25	−41	0.01	−893	0.02	−542
"+6"	0.22	−60	0.25	−42	0.01	−916	0.02	−557
"+9"	0.22	−64	0.25	−45	0.01	−940	0.02	−572
"+12"	0.22	−67	0.25	−48	0.01	−978	0.02	−596
"+15"	0.19	−104	0.22	−79	0.09	−535	0.09	−321

pesticide as metolachlor and aclonifen are usually applied before germination of seeds, there is little chance that aclonifen had been applied before the 21st of March and after the 22nd of April. Given the precipitation pattern, the latter suggests that aclonifen might not have been applied by farmers in 2010, or maybe in much lower quantity (dose and spread surface) than they did in average from 2007 to 2009. Indeed, farmers use to change the molecules they use from one year to the next in order to avoid weed resistance (e.g. Service, 2007). According to the 3-year survey, most of aclonifen was usually applied around the 20th of April. In 2010, if farmers missed the weather window lasting from the 8th to the 18th of April, they had no time to spread pesticide later as it had been raining every two days during the following weeks.

The latter suggests that if aclonifen had been applied in 2010, then aclonifen observations would have had a similar pattern to the simulated one. Application date shift had more impact on metolachlor considering the 2010 spring flood period. Because of its high solubility and low hydrophobicity, metolachlor was mostly found in the dissolved phases, thus allowing transfers with surface and sub-surface runoffs whatever the rainfall intensity (Müller et al., 2003; Ulrich et al., 2013). Its concentration in the channel therefore depended on both discharge and delay between application date and first stormflow event. Conversely, aclonifen was mostly sorbed to soil particles. Its transfer not only depended on the delay between application date and first stormflow event, but also on rainfall intensity for exportation with eroded suspended sediments through surface runoff (Jin et al., 2009; Otto et al., 2012). Therefore, the effect of application time on pesticide transfers itself depends on pesticide specific controlling factors, as their sorption ability, or hydrophobicity, that can be quantified by the partition coefficient K_d (Boithias et al., 2014a; Nakano et al., 2004), known in SWAT as K_{oc} and CHPST_KOC (Table 1). The transfer of pesticides in soil, and hence their bioavailability and transfer to other compartments, also depends on volatilisation, chemical and biological degradation processes, together with soil and suspended matter properties (Boulange et al., 2012). Considering the volatilisation rates similar for both pesticides (Table 1), the combined effect of application timing and hydrophobicity thus depends on the degradation rate in both soil and channel (Ghafoor et al., 2011): the role of application timing is only relevant for pesticide whose half-lifes are significantly longer than the duration of the period without rainfall. Therefore, the role of rainfall timing may either be reduced or increased in a climate change context. For instance in the south-western part of Europe, where occurrence of rainfall is likely to decrease and the intensity of the rainfall and subsequent runoff is likely to increase (García-Ruiz et al., 2011; Lehner et al., 2006), the effects of degradation on pesticide fate may exceed the effects of their mobility to river networks in both the dissolved and the sorbed phases.

5. Conclusion

Results suggest that the delay between pesticide application and first rain is a more significant driving factor of the transfer to surface water of molecules of low K_{ow} than of high K_{ow}. They imply that pesticide concentration signal at the outlet is a combination of spatial and temporal patterns of application date and dose, in addition to pesticide specific properties such as half-life and hydrophobicity. This study leads us to recommend assessing the uncertainty on pesticide application site, date and amount, as an integral part of the pesticide calibration process when modelling pesticide fate at catchment scale.

Therefore, future work will consist in testing all combinations of spatial and temporal application date patterns, together with a range of plausible doses, in an automatic spatially explicit expert system to get the combination fitting the best the observed signal at outlet. Tools such as SWAT-CUP (Abbaspour, 2008) are appropriate for that inverse modelling exercise: by comparing outputs with observed concentrations, they allow assessing the uncertainty and calculating the sensitivity

of a wide range of parameters including application site, date and amount and pesticide properties. Plausible scenarios stemming from best combinations may be later validated by spatially distributed extensive field surveys. The same approach could be later performed for point-source contaminations, including pharmaceuticals and hydrocarbon compounds. Applied to a regional scale, such a tool would later help water managers to localise the main contamination sources avoiding time- and money-consuming field campaigns and, in the case of pesticides, to assess the contamination risk and the environmental impacts of future agricultural practices changes. This will allow them to suggest farmers appropriate mitigation practices, i.e. best management practices (BMP) such as pesticide application date shifts or applied dose reduction during rainy periods, or such as tillage limitations in most erosion prone agricultural areas. Such measures will help to avoid excessive concentrations in surface water and achieve for example the objectives of water policies such as the Water Framework Directive in Europe.

References

Abbaspour, K.C., 2008. SWAT-CUP2: SWAT Calibration and Uncertainty Programs - A User Manual. 95.

Arnold, J.G., Srinivasan, R., Muttiah, R.S., Williams, J.R., 1998. Large area hydrologic modeling and assessment. I. Model development. J. Am. Water Resour. Assoc. 34, 73–89.

Beernaerts, S., Debongie, P., DeVleeschouwer, C., Pussemier, L., 2002. Het pilootproject voor het Nil bekken. Groenboek Belgaqua-Phytophar 2002, Belgium.

Boithias, L., 2012. Modélisation des transferts de pesticides à l'échelle des bassins versants en période de crue. PhD diss. Institut National Polytechnique de Toulouse, France (220 pp.).

Boithias, L., Sauvage, S., Taghavi, L., Merlina, G., Probst, J.L., Sánchez Pérez, J.M., 2011. Occurrence of metolachlor and trifluralin losses in the Save river agricultural catchment during floods. J. Hazard. Mater. 196, 210–219.

Boithias, L., Sauvage, S., Merlina, G., Jean, S., Probst, J.L., Sánchez Pérez, J.M., 2014a. New insight into pesticide partition coefficient Kd for modelling pesticide fluvial transport: application to an agricultural catchment in south-western France. Chemosphere 99, 134–142.

Boithias, L., Srinivasan, R., Sauvage, S., Macary, F., Sánchez-Pérez, J.M., 2014b. Daily nitrate losses: implication on long term river quality in an intensive agricultural catchment (south-western France). J. Environ. Qual. 43, 46–54.

Boulange, J., Kondo, K., Phong, T.K., Watanabe, H., 2012. Analysis of parameter uncertainty and sensitivity in PCPF-1 modeling for predicting concentrations of rice herbicides. J. Pestic. Sci. 37, 323–332.

Burt, T.P., 2001. Integrated management of sensitive catchment systems. Catena 42, 275–290.

Campbell, N., D'Arcy, B., Frost, A., Novotny, V., Sansom, A., 2004. Diffuse Pollution: An Introduction to the Problems and Solutions, First ed. IWA Publishing, London, UK.

Chiovarou, E.D., Siewicki, T.C., 2008. Comparison of storm intensity and application timing on modeled transport and fate of six contaminants. Sci. Total Environ. 389, 87–100.

Chu, X., Mariño, M.A., 2004. Semidiscrete pesticide transport modeling and application. J. Hydrol. 285, 19–40.

Cullum, R.F., 2009. Macropore flow estimations under no-till and till systems. Catena 78, 87–91.

Dubus, I.G., Brown, C.D., Beulke, S., 2003. Sources of uncertainty in pesticide fate modelling. Sci. Total Environ. 317, 53–72.

EC, 1998. Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Off. J. Eur. Communities L330.

Fohrer, N., Dietrich, A., Kolychalow, O., Ulrich, U., 2014. Assessment of the environmental fate of the herbicides flufenacet and metazachlor with the SWAT model. J. Environ. Qual. 43, 75–85.

García-Ruiz, J.M., López-Moreno, J.I., Vicente-Serrano, S.M., Lasanta–Martínez, T., Beguería, S., 2011. Mediterranean water resources in a global change scenario. Earth Sci. Rev. 105, 121–139.

Gassman, P.W., Reyes, M.R., Green, C.H., Arnold, J.G., 2007. The soil and water assessment tool: historical development, applications, and future research directions. Trans. ASABE 50, 1211–1250.

Gevaert, V., Van Griensven, A., Holvoet, K., Seuntjens, P., Vanrolleghem, P.A., 2008. SWAT developments and recommendations for modelling agricultural pesticide mitigation measures in river basins. Hydrol. Sci. J. 53, 1075–1089.

Ghafoor, A., Jarvis, N.J., Thierfelder, T., Stenström, J., 2011. Measurements and modeling of pesticide persistence in soil at the catchment scale. Sci. Total Environ. 409, 1900–1908.

Green, C.H., Tomer, M.D., Di Luzio, M., Arnold, J.G., 2006. Hydrologic evaluation of the soil and water assessment tool for a large tile-drained watershed in Iowa. Trans. ASABE 49, 413–422.

Holvoet, K., Van Griensven, A., Seuntjens, P., Vanrolleghem, P.A., 2005. Sensitivity analysis for hydrology and pesticide supply towards the river in SWAT. Phys. Chem. Earth 30, 518–526.

Jin, K., Cornelis, W.M., Gabriels, D., Baert, M., Wu, H.J., Schiettecatte, W., Cai, D.X., De Neve, S., Jin, J.Y., Hartmann, R., Hofman, G., 2009. Residue cover and rainfall intensity effects on runoff soil organic carbon losses. Catena 78, 81–86.

Lehner, B., Döll, P., Alcamo, J., Henrichs, T., Kaspar, F., 2006. Estimating the impact of global change on flood and drought risks in europe: a continental, integrated analysis. Clim. Chang. 75, 273–299.

Lewan, E., Kreuger, J., Jarvis, N., 2009. Implications of precipitation patterns and anteced-ent soil water content for leaching of pesticides from arable land. Agric. Water Manag. 96, 1633–1640.

Luo, Y., Zhang, X., Liu, X., Ficklin, D., Zhang, M., 2008. Dynamic modeling of organophos-phate pesticide load in surface water in the northern San Joaquin Valley watershed of California. Environ. Pollut. 156, 1171–1181.

Macary, F., Leccia, O., Almeida Dias, J., Morin, S., Sánchez-Pérez, J.-M., 2013. Agro-environmental risk evaluation by a spatialised multi-criteria modelling combined with the PIXAL method. Int. J. Geomatics Spatial Anal. 23, 39–70.

Macary, F., Morin, S., Probst, J.-L., Saudubray, F., 2014. A multi-scale method to assess pesticide contamination risks in agricultural watersheds. Ecol. Indic. 36, 624–639.

Martin, S., Bertaux, A., Ber, F., Maillard, E., Imfeld, G., 2011. Seasonal changes of macroinvertebrate communities in a stormwater wetland collecting pesticide runoff from a vineyard catchment (Alsace, France). Arch. Environ. Contam. Toxicol. 62, 29–41.

Melching, C.S., Yoon, C.G., 1996. Key sources of uncertainty in QUAL2E model of Passaic River. J. Water Resour. Plan. Manag. 122, 105–113.

Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Bingner, R.L., Harmel, R.D., Veith, T.L., 2007. Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. Trans. ASABE 50, 885–900.

Müller, K., Deurer, M., Hartmann, H., Bach, M., Spiteller, M., Frede, H.G., 2003. Hydrological characterisation of pesticide loads using hydrograph separation at different scales in a German catchment. J. Hydrol. 272, 1–17.

Nakano, Y., Miyazaki, A., Yoshida, T., Ono, K., Inoue, T., 2004. A study on pesticide runoff from paddy fields to a river in rural region—1: field survey of pesticide runoff in the Kozakura River. Jpn. Water Res. 38, 3017–3022.

Neitsch, S.L., Arnold, J.G., Kiniry, J.R., Williams, J.R., 2009. Soil and Water Assessment Tool theoretical documentation—version 2009 (TR406).

Neitsch, S.L., Arnold, J.G., Srinivasan, R., 2002. Pesticides fate and transport predicted by the Soil and Water Assessment Tool (SWAT)—atrazine, metolachlor and trifluralin in the sugar creek watershed. p. 96.

Niemi, R.M., Heiskanen, I., Ahtiainen, J.H., Rahkonen, A., Mäntykoski, K., Welling, L., Laitinen, P., Ruuttunen, P., 2009. Microbial toxicity and impacts on soil enzyme activ-ities of pesticides used in potato cultivation. Appl. Soil Ecol. 41, 293–304.

Oeurng, C., Sauvage, S., Sánchez-Pérez, J.-M., 2010. Dynamics of suspended sediment transport and yield in a large agricultural catchment, southwest France. Earth Surf. Process. Landf. 35, 1289–1301.

Otto, S., Cardinali, A., Marotta, E., Paradisi, C., Zanin, G., 2012. Effect of vegetative filter strips on herbicide runoff under various types of rainfall. Chemosphere 88, 113–119.

Polard, T., Jean, S., Gauthier, L., Laplanche, C., Merlina, G., Sánchez-Pérez, J., Pinelli, E., 2011. Mutagenic impact on fish of runoff events in agricultural areas in south-west France. Aquat. Toxicol. 101, 126–134.

Reichenberger, S., Bach, M., Skitschak, A., Frede, H.G., 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; a review. Sci. Total Environ. 384, 1–35.

Service, R.F., 2007. A growing threat down on the farm. Science 316, 1114–1117.

Taghavi, L., Merlina, G., Probst, J.L., 2011. The role of storm flows in concentration of pes-ticides associated with particulate and dissolved fractions as a threat to aquatic eco-systems. Case study: the agricultural watershed of Save river (Southwest of France). Knowl. Manag. Aquat. Ecosyst. 400, 11.

Taghavi, L., Probst, J.L., Merlina, G., Marchand, A.L., Durbe, G., Probst, A., 2010. Flood event impact on pesticide transfer in a small agricultural catchment (Montousse at Aurade, south west France). Int. J. Environ. Anal. Chem. 90, 390–405.

Tomlin, E., 2009. The Pesticide Manual, Fifteenth ed. C.D.S Tomlin.

Ulrich, U., Dietrich, A., Fohrer, N., 2013. Herbicide transport via surface runoff during intermittent artificial rainfall: a laboratory plot scale study. Catena 101, 38–49.

Vazquez-Amabile, G., Engel, B.A., Flanagan, D.C., 2006. Modeling and risk analysis of nonpoint-source pollution caused by atrazine using SWAT. Trans. ASABE 49, 667–678.

Veyssy, E., Etcheber, H., Lin, R.G., Buat-Menard, P., Maneux, E., 1999. Seasonal variation and origin of particulate organic carbon in the lower Garonne River at La Reole (southwestern France). Hydrobiologia 391, 113–126.

Vryzas, Z., Vassiliou, G., Alexoudis, C., Papadopoulou-Mourkidou, E., 2009. Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece. Water Res. 43, 1–10.

Walker, A., Bromilow, R.H., Nicholls, P.H., Evans, A.A., Smith, V.J.R., 2002. Spatial variability in the degradation rates of isoproturon and chlorotoluron in clay soil. Weed Res. 42, 39–44.

Zalidis, G., Stamatiadis, S., Takavakoglou, V., Eskridge, K., Misopolinos, N., 2002. Impacts of agricultural practices on soil and water quality in the Mediterranean region and proposed assessment methodology. Agric. Ecosyst. Environ. 88, 137–146.

Zeiger, M., Fohrer, N., 2009. Impact of organic farming systems on runoff formation processes—a long-term sequential rainfall experiment. Soil Tillage Res. 102, 45–54.

Zhang, X., Zhang, M., 2011. Modeling effectiveness of agricultural BMPs to reduce sedi-ment load and organophosphate pesticides in surface runoff. Sci. Total Environ. 409, 1949–1958.