Shifting application dates on cereal reduces pesticide transfer via subsurface drainage based on water flow forecasts during autumn applications

Julien Tournebize, Alexis Jeantet, Jonathan Marks-perreau, Alain Dutertre, Julie Maillet-mezeray

Julien Tournebize (Orcid ID: 0000-0001-9294-839X)
Jeantet Alexis (Orcid ID: 0000-0002-3197-6693)

Shifting application dates on cereal reduces pesticide transfer via subsurface drainage based on water flow forecasts during autumn applications

Authors

Tournebize Julien, Alexis Jeantet, Jonathan Marks-Perreau, Alain Dutertre, Julie Maillet-Mezeray

1 HYCAR Research Unit, INRAE-Univ. Paris-Saclay, Antony

2 ARVALIS, Ouzouer-le Marché

3 ARVALIS, La Jaillière

4 BAYER CROP SCIENCE, Lyon

Corresponding author: Julien.tournebize@inrae.fr

Abstract

BACKGROUND: Thanks to the changes in aquatic risk assessment within the Marketing Authorization (MA) process in France, the contamination of surface water through the subsurface drainage network is better accounted for. The measure adopted by Risk Regulations is to prohibit any use of selected pesticides on drained plots. Herbicide solutions on subsurface-drained plots are becoming scarce due to a limited number of innovations combined with the re-approvals process. Autumn weed management then becomes a major issue for winter cropping systems on drained plots. Unlike runoff prevention, few risk management measures are available to prevent the risks associated with drained plots.

RESULTS: We analyzed data from La Jaillière, an ARVALIS experimental site (9 plots, 1993 to 2017), representative of scenario D5 from EU FOCUS Group, for four herbicides (isoproturon, aclonifen, diflufenican, flufenacet). Our study first demonstrates the relevance of the time application management measure by showing the decreasing trend in the transfer of pesticides in drained plots. The second result is to validate, still on the La Jaillière site, the hypothesis of a management measure based on an indicator of soil profile saturation before drainage flow (Soil Wetness Index).

CONCLUSIONS: A conservative measure consisting in restricting pesticide applications during autumn, when the SWI is < 85% of saturation, reduces the risk by a factor of 4–12 for quantification above the predicted no-effect concentration (PNEC) and values of maximum or flow weight average concentrations (Cmax and CMP) by 70- and 27-fold, ratio of exported

pesticide (Rexp) by 20-fold, and total flux by 32. This measure based on SWI threshold appears to be more efficient than those using other restriction factors. SWI could be easily calculated considering local weather data and soil properties for any drained field.

Key words

1   Introduction

Subsurface drainage in field soils is one of the water routes among surface runoff, leaching and spray drift, contributing to pesticide transport from fields to surface waterbodies [1,2]. In France, subsurface drainage pipes are installed on 2.9 million ha corresponding to about 10.6% of total arable land (data from RGA 2010[3]) with the main aim of controlling exceeding winter water levels in waterlogged soil.

Despite the fact that subsurface drainage is occasionally considered as a mitigation measure compared to surface runoff[4], and provides several ecosystem services[5] (reducing about 30–90% of overland flow and up to 50% of pesticide losses), it is a fact that subsurface drainage contributes at least slightly to pesticide transport into surface water bodies. On the other hand, subsurface drainage is also seen as a giant lysimeter[6] or an "early warning" of groundwater contamination by pesticides[7] by making accessible agricultural water at the outlet of pipes. Excepted for specific pesticides and events, the overall exportation rate is less than 1%, and very often less than 0.1% of the applied amount[6,8]. Variations in hydrological field properties can explain the large variation in pesticide losses. Several authors[1,6,8,9] have highlighted the fact that pesticide losses can be explained by two different transport routes in subsurface drained plots: (1) vertical preferential flow through macropores from top soil to drain pipe depth or below, which is often responsible for the fastest transport and highest concentrations, and (2) horizontal micropore flow from the temporary perched water table contribution between the mid-space and pipe area.

In France, the two main periods with the highest risk of pesticides transfer by drainage flow, especially for cereal crops, are in autumn between October and November and in spring (March/April). Among others, the time interval between pesticide application and the occurrence of the first drainflow event is reported, by several studies, to be an important factor in the risk of pesticide transport[10,11,12,13,14,15,16]. The risk of transport can be managed through the timing of autumn pesticide applications. Additionally the soil water content at application date, even more than timing, is a more powerful indicator to prevent application during wet conditions and thereby significantly reduces pesticide losses from subsurface drained plots (up to 10-fold reduction reported by Willkommen et al., (2019)[14], or by a factor of 2–3 according to Lewan et al., (2009)[17]).

To reduce pesticide transport in drained areas, Zajicek et al. (2018)[18], Trajanov et al. (2015)[11], and Brown and Van Beinum (2009)[1] recommend restricting the application to periods when no drainage water is flowing and establishing rules for appropriate application using the soil

water content status or antecedent moisture conditions (e.g., in early autumn or late spring), without giving any threshold. Moreover, application restrictions based on the actual water content would be more acceptable for farmers than a total ban or restriction in full-time periods[17].

Changes in aquatic risk assessment during the regulatory registration process in issuing Marketing Authorisations (MA) for pesticides in France led to a better accounting of the contamination of surface water through the drainage network. The initially proposed measures to mitigate risk in regulatory assessments led to Risk Phrases prohibiting every use on drained fields. This would have consequences on the ability to control chemically weeds especially those developing resistance to herbicides. Other agronomic measures could be applied to control weeds such as tillage, late seeding. Nevertheless, studying the relationship between rainfall, antecedent soil water content, pesticide application, drainage discharge, and leaching should give information for the optimization of application timing, which was considered by Lewan et al. (2009)[17] as the only practical mitigation strategy helping farmers to reduce the risk of pesticide transfer.

A proposal could be made to apply herbicides in autumn or winter only before the drainage water starts to flow in drainage pipes. This would need to consider the water content in the soil profile in order to define low-risk periods for pesticide transfer after application. Drainage experiments at La Jaillière offer the advantages of being one of the EU FOCUS drainage scenarios (D5) for MA[19], and a long time series (1993–2017) of pesticide application coupled with drainage assessment gathering data on a diversity of hydrological and agronomical situations. In other words, we would like to answer the following question: Will shifting the pesticide application date in cereals to pre-drainage periods reduce the overall quantity of pesticides transferred into surface water via subsurface drainage and thereby contribute toward reducing the risk of pesticide transfer? And how could soil water content, as indicator, control pesticide transport, applied in autumn?

2 Material and methods

The study area (Figure 1) is one of the six representative agricultural experimental sites in the EU chosen for the purpose of assessment of the Predicted Environmental Concentration in surface water of active substances (FOCUS surface water) under Directive 91/414/EEC and regulation (EC) N° 1107/2009[19]. The La Jaillière site (N 47.456457- W 0.953768) is then representative of subsurface drainage on loamy soil in temperate climate, named as scenario D5. The experimental station (since 1987) is located in the Loire-Atlantique region and is under the influence of an oceanic climate. The average annual rainfall is 734 mm, while the mean annual potential evapotranspiration (PET) is 738 mm and the mean annual temperature is 11°C (see [11] for more detailed in climatic data). The soil at La Jaillière is a hydromorphic brown soil, stagnic luvisol[20], resulting from alterite shale formation[21]. Luvisol is representative of French subsurface drained soils for large areas of arable land, accounting for about 80% of French drained area[22]. The crop rotation system in La Jallière is a sequence of maize, winter wheat, and spring or winter pea. Thus, several experiments have been conducted since its installation, providing an important dataset covering almost 30 years.
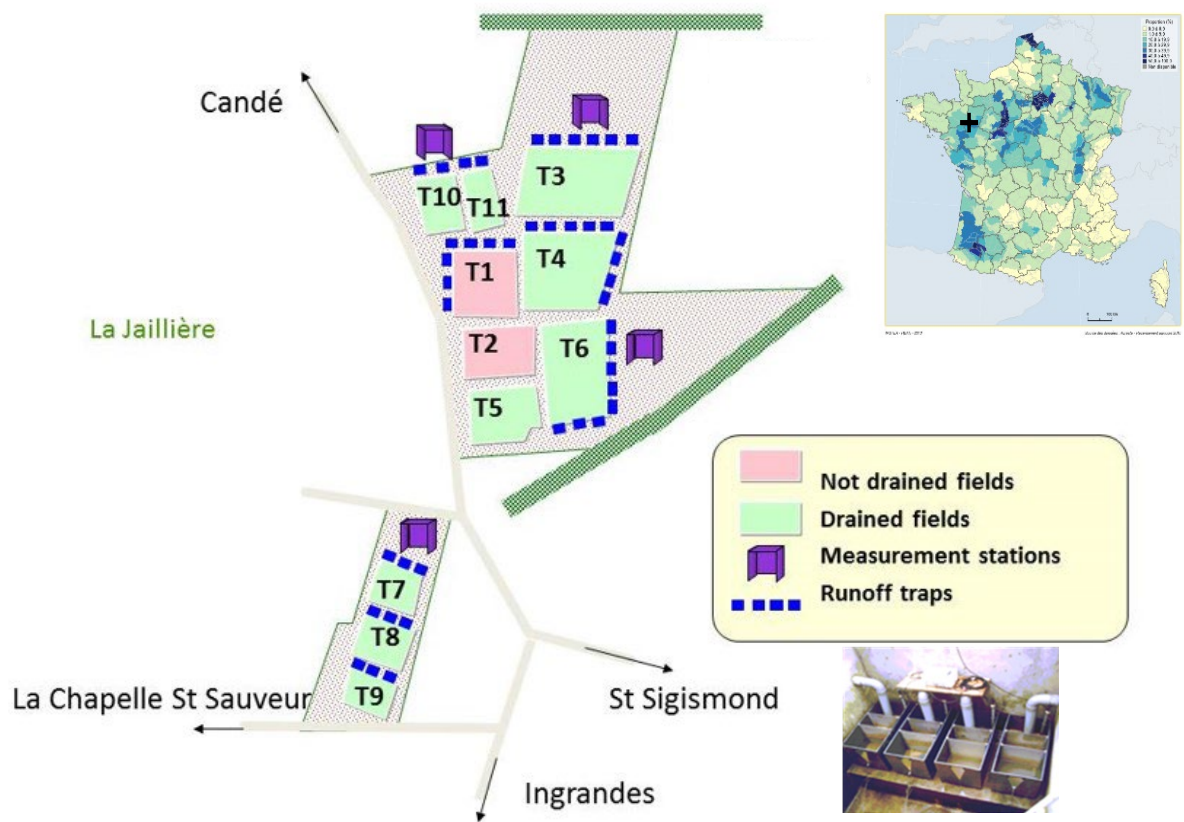
Figure 1: Experimental study site of La Jaillière (left), including distribution of drained fields as percentage of arable land at Canton scale (a French territorial subdivision; top right; AGRESTE, 2010), and location of La Jaillière experimental site (black cross); bottom right: picture of measurement chamber collecting individual plot flow.

2.1 Data description

The dataset used in this study includes data on meteorological and agronomical features. Meteorological data (minimum, maximum, and average daily temperature, daily rainfall, average daily evapotranspiration) were collected from the meteorological station in La Jaillière from the year 1982 onward. Agronomic data were taken from the PCQE (Water Quality and Agricultural Practices) database maintained by ARVALIS. ARVALIS as applied agricultural research organization focusing on agronomic, technological performance of cereals, corn, manages the experimental field of La Jaillière since 1987. ARVALIS follows rules of best management practices and reports all activities in the PCQE database. PCQE contains field-level data on the agricultural practices applied (e.g., tillage, sowing, fertilization, pesticides used, and their application dates), the amount of water outflow of drainage and runoff (daily time step), the concentration of mineral nutrients in the water outflow, and the concentration of pesticides in the water outflow (weekly sampling). From the recorded applied pesticides, 60% were herbicides, 37% fungicides, and 3% insecticides on average per year for the full monitored period (1993-2017). In this study, four herbicides were considered – aclonifen, isoproturon, diflufenican, and flufenacet – for a sequence of 18 campaigns ranging

from 1993 to 2017. An agricultural campaign is a 1-year period, starting on 1 September and ending on 31 August. As mentioned by Trajanov et al. (2018)[12], surface runoff from drained experimental plots is negligible, accounting for less than 10% of annual drained flow volume (27 mm vs. 224 mm/year on average, during wet winter and mainly out of pesticides application period).

2.2 Hydrology and water monitoring input

The experimental site La Jallière consists of nine agricultural plots (T3 to T11) of 0.5–1 ha each, where drainage and runoff water are collected separately. Each drained plot is equipped with an individual drainage network (10–12 m drain spacing, installed at 0.8–1-m depth), which is connected to a non-perforated collector joining the measurement chamber (Figure 1). Discharges were recorded hourly, using an ultrasound probe once flow had settled. The sampling strategy is based on flux quantification instead of time flow event dynamics. Consequently, flow-weighted mean samples were composed of several subsamples taken every 5 m^3/ha of drained water. The weekly samples were then stored at −18 °C for pesticide analysis in order to get representative mean concentrations and to calculate total pesticide export. Analyses were carried out by a subcontractor using accredited methods (classic on-line LC-MS/MS or GC-MS/MS via direct injection or after SPE). The uncertainty of pesticide concentrations within a measurement was in a range of 20%, determined by the subcontractor (limit of detection (LOD) = 0.01 µg/L and limit of quantification (LOQ) = 0.02 µg/L). Each measured concentration of pesticide was compared with its corresponding predicted no-effect concentration (PNEC in water) (Technical Guidance Document 93/67/EC, 97/67/EC, 793/93/EC). PNEC represents the concentration of pesticide in water that has no predicted adverse effect on aquatic ecosystems.

2.3 Experimental design

The plot characteristics are summarized in Table 1.

Table 1: Agronomic characteristics and plot history

Plot	Surface (ha)	Water holding capacity, (mm)	Tillage	Crop	Establishment year
T3	1.04	84	Yes	Wheat, corn	1987
T4	1.08	104	Yes	Wheat, corn	1987
T5	0.85	114	Not since 1989	Wheat, corn	1987
T6	1.01	103	Not since 2007	Wheat, corn (meadow until 1995)	1987
T7	0.43	116	Yes	Corn (meadow until 1995)	1989
T8	0.43	111	Not since 1996	Corn (meadow until 1995)	1989
T9	0.34	96	Yes	Corn (meadow until 1995)	1989
T10	0.42	95	Yes	Rapeseed, wheat, peas or field beans, wheat	1991
T11	0.42	99	Yes	Rapeseed, wheat, peas or field beans, wheat	1991

Different pesticides were applied on crops at the La Jallière plots. The total number of applications per pesticide is highly variable from one pesticide to another, as shown in Table 2 (detailed applications in SM), mainly depending on the number of monitoring years. Isoproturon and diflufenican are the most quantified and researched pesticides.

Table 2: Pesticide properties (Field DT50: soil degradation; Koc or Kfoc soil sorption; GUS index: groundwater ubiquity score; PNEC: predicted no-effect concentration) and total number of applications in drainage water per active substance (data from ARVALIS, compound properties from Pesticide Property Data Base[42]).

	Isoproturon	Flufenacet	Diflufenican	Aclonifen
Field DT$_{50}$ (d)	23	39	64	80
Koc[1] or Kfoc[2] (L/kg)	122[2]	401[1] – 273[2]	5504[1] - 2215[2]	7126[2]
GUS index (-)[31]	2.61	2.49	1.19	0.28
PNEC (µg/L)	3.45	2.4	0.167	0.5
Application dose (g/ha)	500–1250	150–480	20–156.25	300-2400
Number of applications	37	21	38	15

2.4 Description of available data on the four pesticides

The pesticides practices, recorded in PCQE database, are in the form of formulated products, available on the plant protection market (these are the same products used by farmers). The application rates always respect the maximum rates defined by the registration, and are always used at full-dose or 1/2 dose or 1/3 dose or 1/4 dose. However, as regulations evolve, application rates also take this evolution into account, which may explain, in part, the changes over time. The study focuses on the analysis of pesticide fluxes after the application of selected autumn-applied herbicides over a long hydrologic record. Note that we consider also late application of aclonifen and flufenacet in winter or spring for plots 7, 8, 9 in 2001, 2008, and 2012 (see AppliDay in Table 3). As ARVALIS is an applied research institute, different strategies were tested (always below maximum allowed application rate) to study agronomic and economic performances (not shown here).

The whole period gathers a large set of data on representative hydrological years (Table 3). The cumulative drained flows (LD, in mm/year) are staggered between dry years (<10 mm/year) and wet years (>400 mm/year). The average drained flows vary from 203 and 283 mm/year between the 9 experimental plots. These hydrological variations impact the beginning and length of the drainage season. Drained flows started from 21 September to 6 February, with a mean date around the beginning of December (termed "StartDrain"). Further time periods were evaluated: the time between application day and day of drainage start (named D_LD, in d), and the time between application day and day when the soil wetness index SWI reaches a threshold to be determined (see detail in section 2.5 and 3.3, named D_SWI, in d). The numerous hydrological samples for the period 1993–2017 reinforce the robustness of the experimental approach.

From the primary data, extracted from PCQE database, we calculated, for each agronomic period and for every plots: annual pesticide losses called Flux (in mg/ha), maximum concentrations (Cmax in µg/L), flow-weight average concentration (CMP in µg/L), percentage of analyzed samples above LOQ, percentage of quantified concentrations above PNEC, 0.1 and 2 µg/L (considering the drinkable limit and maximum concentration of pesticides in raw water before treatment), application rates (in g/ha), application dates (AppliDay), and starting dates of drainage based on flow (D_LD) and based on soil wetness index SWI (D_SWI).

Table 3: Summary of pesticide arithmetic mean data for IPU (isoproturon), FLU (flufenacet), DFF (diflufenican), and ACLO (aclonifen) from 1993 to 2017 at the La Jaillière ARVALIS experimental site. (d*=day from 1 September; Min and Max values are indicated in bracket; SWI$_{RC}$ correspond to value of threshold of the soil wetness index)

	Pesticides			
Variable	ISOPROTURON (n=36)	FLUFENACET (n=21)	DIFLUFENICAN (n=38)	ACLONIFEN (n=15)
Annual cumulated drained flow (mm/y)	263 [9-512]	203 [10-483]	283 [10-803]	281 [150-554]
Soil Wetness Index at application day (%)	0.95 [0.74-1.00]	0.62 [0.35-1.00]	0.87 [0.35-1.00]	0.75 [0.28-1.00]
Application rate (g/ha)	884 [500-1250]	269 [150-480]	92 [20-156]	1487 [300-2400]
Application Day	Dec 12 [Oct 19-Feb 28]	Dec 30 [Oct 31-May 18]	Dec 7 [Nov 10-Feb 28]	Jan 25 [Oct 28-May 18]
Day of drainage start	Nov 15 [Sep 21-Jan 23]	Dec 11 [Oct 14-Feb 06]	Dec 3 [Sep 23-Feb6]	Dec 2 [Sep 21-Jan 6]
Delta date between application and drain start day (d*)	-28 [-138;69]	-19 [-174;84]	-4 [-137;84]	-54 [-186;59]
Delta date between application and date reaching SWI$_{RC}$ (d*)	-52 [-141;1]	-48 [-184;25]	-36 [-141;25]	-81 [-225;28]
Weekly Concentration (µg/L)	23 [0-220]	0.62 [0-6.3]	0.47 [0-5.57]	0.337 [0-3.01]
Exported ratio (%)	0.52 [0.00066-3.23]	0.059 [0-0.84]	0.0136 [0-1.26]	0.0127 [0-0.135]
Annual Flux (mg/y)	4727 [7-31827]	102 [0-1311]	175 [0-1975]	269 [0.3247]

Pesticides applications
Diflufenican was applied 38 times with 11 different doses from 20 to 156.25 g/ha. Overall, 21 applications were made before winter drained flow and 17 applications were made during winter drained flow. Flufenacet was applied during 21 campaigns, on both wheat and maize. A total of 13 doses of flufenacet, from 150 to 480 g/ha, were tested before winter drained flow and eight doses after winter drained flow. Aclonifen was applied during 15 campaigns, on both wheat and maize. Six doses from 300 to 2400 g/ha were tested before winter drained flow and nine during winter drained flow. Isoproturon was applied 14 times before drained flow started and 22 times after drained flow, with doses ranging from 500 to 1250 g/ha.

Pesticides chemical quantification
The diflufenican quantification frequency in drainage water is 23.2% (221 analyses out of 951 > LOQ). The threshold of 2 µg/L is rarely exceeded (0.6% of cases > LOQ). The PNEC threshold (0.167 µg/L) is exceeded, with 13.8% of cases over the LOQ.

The flufenacet quantification frequency in drainage water is 7.3% (32 analyses out of 438 are > LOQ). Both thresholds, 2 µg/L and 2.4 µg/L (PNEC), were rarely exceeded, with 0.9% and 0.7% of the cases, respectively, over the LOQ.

Aclonifen was quantified in drainage water with a frequency of 16.1% (47 analyses out of 292 > LOQ). It hardly exceeded the PNEC (0.5 µg/L) or 2µg/L threshold, with only 0.7% of the analyses above the threshold for both parameters.

Isoproturon was detected with a frequency of 39.5% (281 analyses out of 711 > LOQ). The thresholds of 2 µg/L and 3.4 µg/L (PNEC) were exceeded in 28% and 14% of cases, showing the highest potential of transfer through drained water of the four pesticides analyzed.

2.5   Soil Wetness Index

Drained flow was analyzed in terms of annual cumulative drained flow (LD, in mm/ha). Additionally, we introduce a soil wetness index (SWI), as proposed by Saleem and Salvucci (2002)[23], in order to obtain the relationship between the land–atmosphere water fluxes and changes in the moisture storage of the soil that influences the transport properties under climatic forcing. The degree of the relative soil wetness is a key factor for soil hydraulic characterization and, in particular, for pollutant transport processes. The choice of SWI is motivated by the fact of being a proxy of soil water saturation. The SWI represents the level of water saturation compared to available water content (in soil profile through the concept of soil water holding capacity). SWI takes into account water soil properties by defining the value as

$$SWI(t) = \frac{Water\_Storage(t)}{AWC} \quad (1)$$

with

$$AWC = (\theta_{FC} - \theta_{WP}) * z_s$$

and $Water_{Storage(t+1)} = Water_{Storage}(t) + NetPrec(t+1)$

where AWC (in mm) is available water content in soil profile (z_s) considering θ_{WP} and θ_{FC} the moisture contents at wilting point and field capacity, respectively. $\theta_{FC} - \theta_{WP}$ is the water holding capacity of the soil profile (available water for plants). $Water_{Storage}(t)$ is the soil water content at time t (in day), integrated along soil depth (z_s in mm) and using NetPrec(t) (net precipitation at time t), calculated from weather data (Precipitation and Evapotranspiration, generally calculated by Penman-Monteith equation).

SWI, ranging between 0 and 1, thus represents the degree of saturation of the pore capacity. SWI is calculated daily using the observed weather data.

2.6   Standardized data and statistical analysis

Another analysis performed in this study consists in statistically assessing whether modifications of the pesticide application time have an effect on reducing the pesticide loss rates. To do so, the variability in annual pesticide use and exportation can be evaluated by normalizing the annual exported pesticide flux or losses through drain pipes with the total

amount of pesticide applied annually (termed "exported ratio" labelled R$_{exp}$). Principal component analysis was applied on the full matrix as presented in SM, using the "Ade4" R package[24].

Furthermore, the relation $R_{exp} = f(SWI\ at\ day\ of\ application)$ is analyzed in order to extract the shifting value of SWI called "SWI$_{RC}$" above which the pesticide transport via drainage is promoted, i.e., when SWI > SWI$_{RC}$. To find this shifting value, the relation $R_{exp} = f(SWI)$ is set as a piecewise function (see Eq. (2)):

$$R_{exp} = \begin{cases} a * SWI + b & 0 \leq SWI < SWI_{RC} \\ a' * SWI + a * SWI_{RC} + b & SWI_{RC} \leq SWI \leq 1 \end{cases} \tag{2}$$

with a, a' and b are parameters of the piecewise function. To estimate these parameters by iterative method, all the available R$_{exp}$/SWI couples from the observed data (110 couples gathering the four studied pesticides) are used. First, each R$_{exp}$/SWI couple is considered as a potential shifting point. Second, the parameters a, a' and b are estimated by linear regression for each couple. Third, the Wilcoxon non-parametric test[25,26] is applied to extract only the couples allowing to obtain two significantly different regimes from the linear regimes extracted from Eq. (2), with a required p-value ≤ 0.01. This test is performed using the "stats" R package[27]. Eventually, the R$_{exp}$/SWI couple allowing to obtain the best determination coefficient r^2 among the previous selected couples is set as the shifting point. The corresponding SWI value is set as SWI$_{RC}$.

3 Results

3.1 Correlation between maximum concentration and annual exported pesticide flux

In preliminary, we studied the relation between annual exported pesticide flux and its maximum concentration in drained water to restrict our analysis on annual flux or exported ratio (Figure 2). For all pesticides, the correlation between annual exported flux and maximum concentration is high with r^2>0.8. Independent of application rates and hydrological years, the slope of the regression curve is very specific for each of the pesticides applied: 0.0053 for IPU and FLU, 0.003 for DFF, and 0.0009 for ACLO. This confirms that reducing annual exported pesticide fluxes also helps to reduce peak concentrations in drained water.
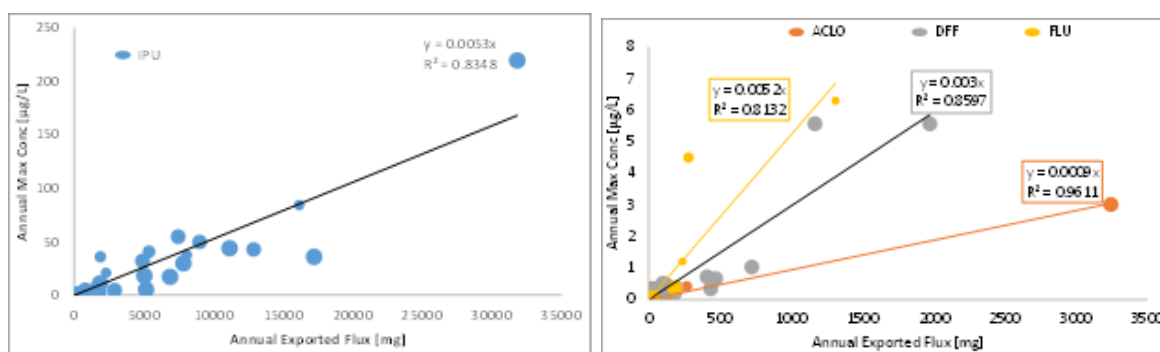

Figure 2. Annual exported pesticide flux vs. annual maximum concentration in drained flow for isoproturon (IPU; left) and aclonifen (ACLO), diflufenican (DFF), and flufenacet (FLU;

right), at the La Jaillière experimental site for the period 1993–2017. Size of circles is weighted by application amount.

3.2 Influence of hydrology on pesticide exportation

The range of values of the maximum exported flux were 4 700 mg, 100 mg, 170 mg, and 270 mg for IPU, FLU, DFF, and ACLO, respectively, corresponding to 3.23%, 0.84%, 1.26%, and 0.135% of the application dose (Figure 3). Based on hydrological interpretation, it appears that by applying pesticide after the start of drainage, the pesticide exportation ratio R_{exp} increases for all pesticides independently of the amount applied (Wilcoxon-Mann-Whitney test with p-value<0.0025). Additionally, as expected, the data show a correlation with the mobility properties of the pesticides, i.e., IPU with a K_{foc} of 122 L/kg is exported with a higher exported ratio than ACLO with a higher adsorption potential (K_{foc} = 7126 L/kg). Despite higher sorption properties, annual fluxes of DFF were superior to FLU, due to a joint application with IPU mainly during flowing period.
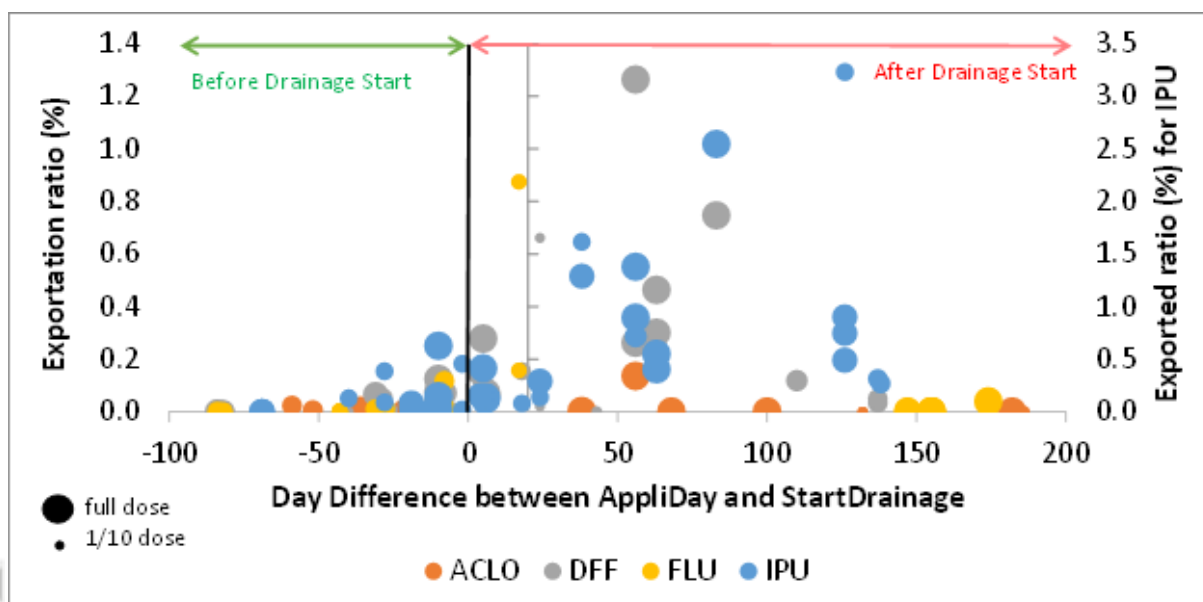

Figure 3. Pesticide exported ratio R_{exp} related to time difference between application date (AppliDay) and date of drainage start (StartDrainage) (all plots; size of circles is related to height of application rate compared to full dose; all hydrological years for the period 1993–2017, La Jaillière site). ACLO: aclonifen, DFF: diflufenican, FLU: flufenacet, IPU: isoproturon

3.3 Soil wetness index

Figure 4 compares the evolution of exported ratio R_{exp}, measured at the pipe outlet during the drainage season, with the corresponding values of the SWI on the date of pesticide application. As described in section 2.5, all pesticides studied here are gathered to constitute one unique sample of 110 R_{exp}/SWI couples. The graphic shows that there are two distinct groups of points, separated at a SWI ranging from 80 to 90%. The parameters from the piecewise function (cf. Eq. (2)) were estimated according to this sample (see Eq. (3)):

$$R_{exp} = \begin{cases} 0.088 * SWI - 0.026 & 0 \leq SWI < SWI_{RC} \\ 1.9 * SWI + 0.088 * SWI_{RC} - 0.026 & SWI_{RC} \leq SWI \leq 1 \end{cases} \quad (3)$$

with the shifting point SWI_{RC} = 85% between these two groups. The corresponding p-value from the Wilcoxon test is below 0.01, attesting that the two linear regimes (one per group) described by Eq. (3) are significantly different. Furthermore, the determination coefficient r^2 from the linear regression is 0.11, showing that the regression does not match the observed data very well, but this is the best obtained r^2 value from the 110 analyzed R_{exp}/SWI couples. Below SWI_{RC} = 85%, the exportation ratio is less than 0.2%. Above this threshold, the values of the exportation ratio range up to 3.23%. The higher the SWI on the date of application, the larger the range of exported ratio R_{exp} is.
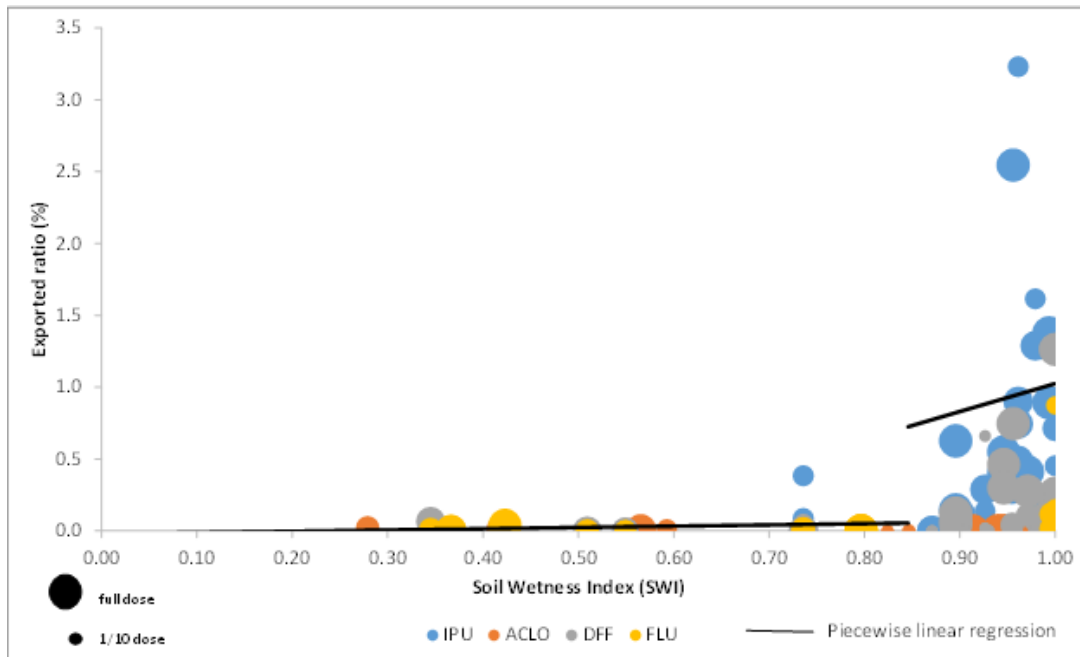

Figure 4. Pesticide exported ratio R_{exp} related to soil wetness index (SWI) on date of pesticide application, at La Jaillière, during the period 1993–2017. ACLO: aclonifen, DFF: diflufenican, FLU: flufenacet, IPU: isoproturon. Black lines represent linear tendencies as defined by a piecewise function. Size of circles is a function of adimensional application rate compared to full dose.

3.4 Principal component analysis

The statistical analysis of the data is presented in two parts (Figure 5), detailing the results of the PCA (principal component analysis) for all pesticides combined (left) and for exported ratio separately (right).

The explained variance is greater than 66% for all pesticides combined (Figure 5) or for individual pesticides (see SM) with two explanatory factors (the third factor ranged about 13%). The axes can be explained by the temporal dimension for the x-axis, and a dimension on hydrological and agronomic conditions for the y-axis. The projection of R_{exp} on the two axis (right side of Figure 5) showed that the highest values are linked to Application dose, SWI and LD variables.

For all pesticides combined, even if the correlation shown in Figure 5 is not very strong, the annual exported pesticide flux (Flux All) depends mainly on three close factors: the applied

pesticide dose (Application), the cumulative water drained flow (LD), and the SWI at application (relative soil moisture). A fourth factor, StartDrain, is slightly anticorrelated. The projection of the adimensional fluxes (called "R_{exp}") shows that the lowest values are related to the latest starting dates for the drainage season, while the highest fluxes (>0.5% of applied amount) are related to the three variables: application dose, SWI, and cumulative drained flow LD. Neither the application date (AppliDay) nor the time between application and the starting date for the drainage season (D_LD) seems to explain the annual exported pesticide flux or ratio. The projections on the two axes do not show any clear influence on plot location (including tillage), and also not on the agronomic year, which could be excepted for plots 8 and 9, where application dates were late (after 20 April, see SM).

However, the results differ on a pesticide-by-pesticide basis (see SM). In the case of IPU, the annual exported flux is related to the date of application (AppliDay) and to the time between the application date and the date when SWI_{RC} is exceeded (D_SWI). In the case of FLU, the annual exported flux is correlated with the cumulative drained flow LD, and has a less strong correlation with the SWI at application. Similarly for DFF, annual exportations show significant correlations with cumulative drained flow LD, beginning of drainage season StartDrain, soil wetness index SWI and date of application AppliDay. ACLO annual exportations are correlated with the application rate as well as with the cumulative drained flow LD.
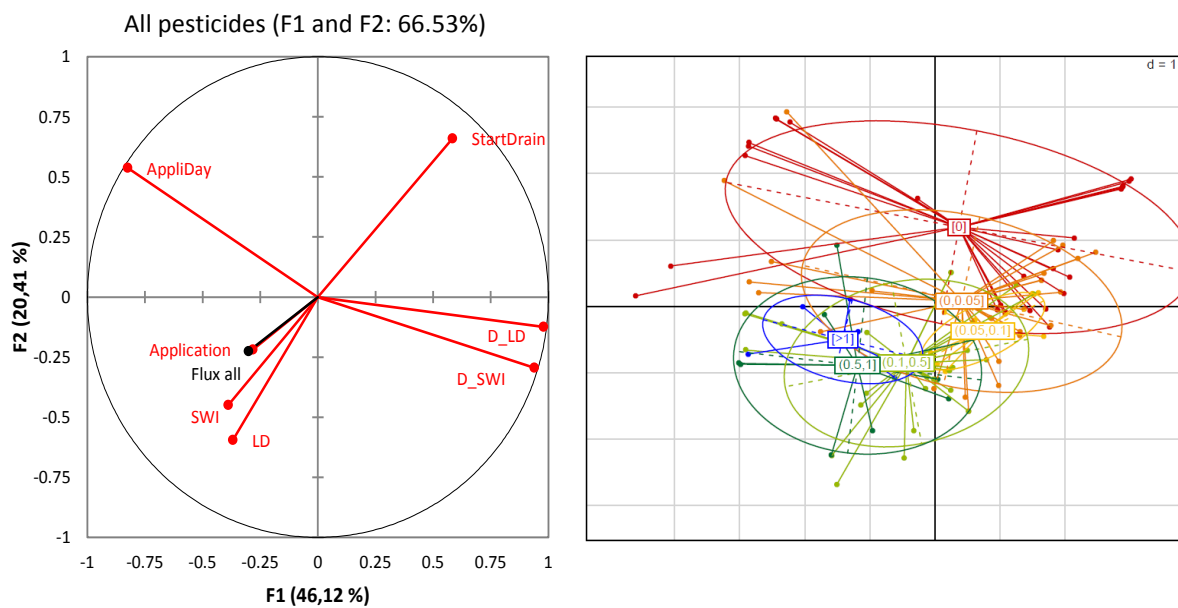

Figure 5. PCA results for all combined (left) and individual pesticides (right) for annual exported pesticide flux and projection of "R_{exp}" variable, ranged per interval (color corresponds to interval in brakets), on axis 1. AppliDay= date of application, StartDrain= date of beginning of drained flow, Application= amount of applied pesticide, SWI= soil wetness index, LD= cumulated drained flow, D_LD= time between application date and date of beginning of drained flow, D_SWI= time between application date and date when SWI_{RC} is exceeded, Flux= all annual exported pesticide by drained flow.

The correlation values between the annual exported pesticide fluxes and the selected variables are presented in Table 4. The correlation values confirm that the driving factors are different for the different herbicides. For IPU, the day of application (AppliDay) and the cumulative drained flow (LD) are positively correlated (>0.5) with the annual exported flux, whereas the time between application and the start of the drainage season (D_LD) are negatively correlated (<-0.5). This means that when application is largely planned before the drainage season, the exported flux is lower. For DFF, an additional factor plays a strong role, i.e., the SWI at application (0.374). For ACLO, which is a more sorptive pesticide, the main factor governing the transfer is the start of the drainage season, StartDrain (-0.528). For FLU, moderately sorptive pesticide, the SWI at application and the start of the drainage season, StartDrain, are significant factors (0.471 and -0.558, respectively). The SWI at application is found to have a significant correlation for two of the four pesticides.

Table 4. Correlation matrix from PCA analysis. IPU = isoproturon, FLU = flufenacet, DFF = diflufenican, ACLO = aclonifen, LD = annual cumulative drained flow (mm/a), SWI = soil wetness index at application, Application = application rate (g/ha), AppliDay = application date, StartDrain = number of days from 1 September to day of drainage start, D_LD = time between application day and day of drainage start (d), D_SWI = time between application day and day when soil wetness index reaches SWI_{RC} (d). Bold values are significantly correlated with the dependent variable at $p<0.05$.

Flux	LD	SWI	Application	AppliDay	StartDrain	D_LD	D_SWI
IPU	**0.524**	0.162	**0.332**	**0.529**	-0.198	**-0.492**	**-0.535**
FLU	0.121	**0.471**	-0.206	-0.172	**-0.558**	-0.029	0.063
DFF	**0.476**	**0.374**	-0.228	**-0.392**	**-0.492**	0.219	0.243
ACLO	0.332	0.239	0.295	-0.296	**-0.528**	0.057	0.161
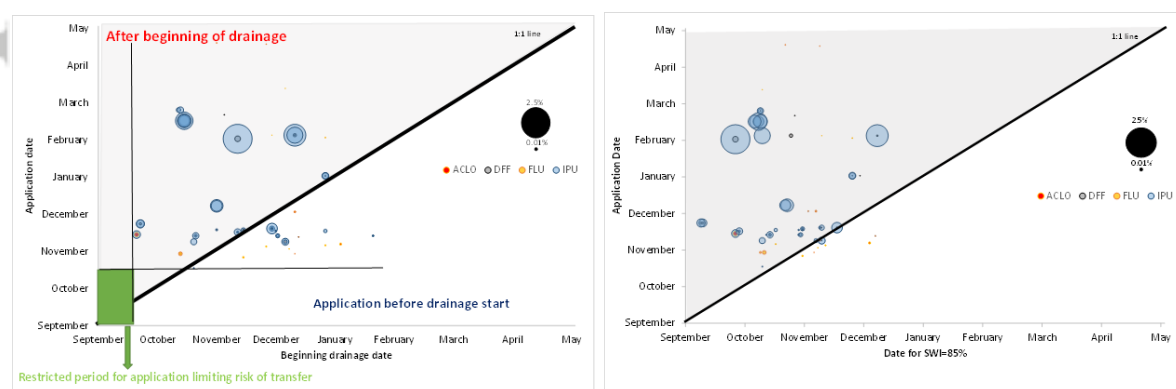
Figure 6. Application date versus date of drainage start (left) and versus date when soil wetness index (SWI) reached the threshold 85% (right) for the four selected pesticides (ACLO: aclonifen, DFF: diflufenican, FLU: flufenacet, IPU: isoproturon. Size of circles is proportional to the annual exported pesticide ratio. Green box description corresponds to the restricted period for application limiting the risk of pesticides transfer..

In Figure 6, all annual exported pesticide ratios are set in relation to their application dates (y-axis) as well as to the corresponding date of drainage start (x-axis). Below the 1:1 line, the application occurs before drainage start, and above this line, application occurs during drained flow. We observed that the higher above the 1:1 line, the more pesticide mass is exported within the drained flow, and the inverse was observed for below the 1:1 line. The same approach can be applied, using the date, when the SWI_{RC} threshold is reached (85%, determined for La Jaillière; y-axis). In this case (right, Figure 6), the annual exported pesticide ratio reaches a mean of 0.4% (SD=0.6) and a median of 0.1%, if the application is made at SWI > SWI_{RC} (above 1:1 line), and a mean of 0.02% (SD=0.06) and a median of 0% if the application is made at SWI < SWI_{RC} (below 1:1 line).

4 Discussion

4.1 Pesticide transfer

Complementary to agricultural practices aiming to reduce pesticide transfer (i.e. tillage, late seeding), optimum date of pesticide application considering hydrological functioning of subsurface drainage, is discussed. 110 drainage events, from 1993 to 2017, were analyzed for different moisture conditions and weather situations. A detection period was limited to the crop season following the application. We did not notice any remaining pesticides from one year to the following year. We should also mention that no metabolites of the four pesticides were analyzed.

At La Jaillière, the majority of annual exported pesticide fluxes are below 0.1% of the applied amount, independent of the agricultural years. This result is congruent with the review of Kladivko et al. (2001)[6], and of Willkommen et al. (2019)[14] in the case of flufenacet (mean R_{exp} = 0.059%), but much lower than the results reported by Ulen et al. (2013)[8] (R_{exp} 0.7%) or Dousset et al. (2004)[28] (0.28%) for spring herbicide applications. For flufenacet, the results are similar to those reported by Willkommen et al. (2019)[14], linking exported ratio to the status of soil moisture. The ratio increased, in the case of application during the saturated period, to 0.84% for La Jaillière compared with 0.7% for Willkommen et al. (2019)[14]. For isoproturon, the annual exported ratio is higher due to its high solubility and weak sorption potential (K_{foc}=122 cm^3/g), including a wide range at La Jaillière from 0.0006% (similar to the results of Doppler et al. (2014)[29], with 0.005%) to 3.2% (similar to the results of Jones et al., (2000)[15], with 2%).

One other interesting result is the correlation between annual exported pesticide fluxes and maximum pesticide concentrations sampled in the drained flow (Figure 2). Despite a flow weighted sampling and a weekly sampling strategy, the correlation values are very high, demonstrating that reducing annual exported flux will also impact favorably on the maximum concentration in drainage water, as described by Brown and van Beinum (2009)[1]. As highlighted in several studies[6,21,30], the first drainage event in a drainage period after application delivers a significant proportion of the annual exported flux and generates the maximum monitored pesticide concentration due to flushing out from the soil surface just after application. A strong relationship could also be drawn between the chemical properties of the four pesticides studied (i.e., Koc, DT50) included in the GUS index (groundwater ubiquity score[31]) and the dynamic pesticides transport. Figure 7 shows the slope of Cmax / annual

exported flux (with the slope reported in Figure 2) and the corresponding GUS index (r^2=0.97),. As several authors have reported (e.g.[28]), these results confirm that pesticides with a lower GUS index are generally less sensitive to being exported by subsurface drainage. This should support farmers in their strategic decision-making through the selection of less mobile pesticides. However, as highlighted in several other studies[15,30,32], chemical properties of pesticides are not the only sensitive factors controlling annual exported pesticide fluxes.
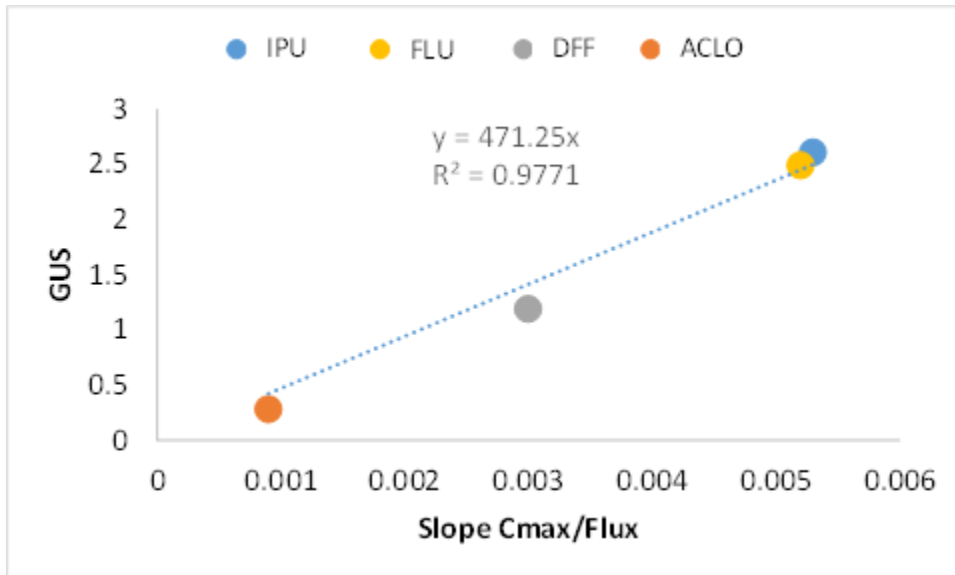

Figure 7. Relationship between the slope of Cmax / annual exported pesticide flux and GUS index (Groundwater Ubiquity Score; Gustafson 1989) for the four pesticides tested (IPU: isoproturon, FLU: flufenacet, DFF: diflufenican, ACLO: aclonifen) at La Jaillière experimental site during the period 1993-2017.

4.2 Managing the date of application as an effective way of controlling drainage risk

The statistical analysis (PCA) did not provide clear evidence of key factors driving pesticide drainage fluxes. The factors vary from one pesticide to another. Nevertheless, maximum pesticide fluxes are linked to high application rates, high SWI (relative moisture) at application, and high annual cumulative water drained flow. Whereas minimum pesticide fluxes are linked to late-starting drainage seasons.

Dousset et al. (2004)[28] observed that the timing of rainfall and of the first drainage events relative to the date of herbicide application was significant for pesticide leaching into drain pipes. An early application of autumn herbicides would, in most years, be beneficial in reducing pesticide losses due to drained flow, although there may be important agronomic reasons to delay the application[2,6,15,30]. Knowing that drainage flow can begin as early as the beginning of October (in La Jaillière), a conservative solution would be to restrict pesticide application times to no later than October the 11th for instance (dark green box in Figure 6, example). The measure with the highest mitigation potential, in theory, would be to limit the date of application. Of course, this option is agronomically not favorable for farmers. In practice, its potential for farmers is limited because of several other constraints, such as limited time windows according to the crop growth stage, weed development, frequent

rainfall events, or logistical reasons. However, in terms of environmental considerations, the experimental results from La Jallière clearly showed that the higher above the 1:1 line (i.e., the more pesticide is applied within the drainage period), the more pesticide mass is exported with the drained flow (Figure 6). From an empirical point of view, the dataset (Figure 3) showed that herbicide transport into drainage is strongly reduced (Ratio R_{exp} <0.1%) when applying 40 days before or 140 days after the start of the drainage period (140 days after is generally over the winter flowing period). This is congruent with results of Jones et al. (2000)[15]. However, transport is not only controlled by the time interval between application and the start of drained flow. It can also be determined by the water saturation status.

4.3 Mitigation of drainage risk by consideration of SWI

The threshold SWI_{RC} (Soil Wetness Index at risk change) determined by the piecewise function (Eq. 3) characterizes the degree of soil water saturation or relative soil moisture at the breakpoint when the pesticide transport via drainage starts to be enhanced. When the soil is saturated, i.e., an SWI close to 1, drainage flow starts. Using the SWI_{RC} value of 85% allows to anticipate the start of the drainage season. The definition of drainage start is different from the one used by Trajanov et al. (2018)[12], who considered a threshold of 5 mm cumulative drained flow to quantify the start of the drainage season.

This approach, based on the SWI at application in combination with the threshold SWI_{RC} (85 %, in La Jallière), may allow to reduce the risk of herbicide transport into drainage. An exported ratio R_{exp} below 0.1% for the four pesticides, when applying on a day with $SWI < SWI_{RC}$, based on a large number of situations, hydrological years, and application rates, makes this mitigation approach robust (Figure 8). The SWI seems to be a relevant indicator for estimating the hydraulic drainage flow and for explaining the hydrological processes in drained plots, as underlined by Klaus et al. (2014)[33]. From subsurface hydraulic interpretations, the threshold of 85% below saturation is explained by the preferential flow that could hydraulically connect the soil surface directly with the drain[34]. Close to soil water saturation, the connected soil matrix "macropore to drain" makes the transfer easier[35,36]. There is indeed a link between the hydraulic functioning of the drainage and the export of pesticides. In particular, Kung et al. (2000)[37], through a temporally staggered method of tracing, showed that more than the delay, it is the saturation of the profile that accelerates the preferential transfer from the surface to the drain. Kohler et al (2003)[38] and Willkommen et al. (2019)[14] drew attention to the transfer of pollutants when the soil profile is saturated. The experimental data from this study confirmed the simulated results of Lewan et al. (2009)[17]. Using the transport model MACRO (incl. micro- and macropores), the authors emphasized the role of the soil water deficit on the application date to limit pesticide transport into drain pipes by a factor of 2–3. The threshold of 85% was determined for the La Jaillière experiment, representative of 80% of French drained soil[22]. The threshold depends on soil properties and could be determined, for instance, for other soils using the parameter S_{inter}, an intermediate water status of the SIDRA-RU model (Simulation of Drainage model) developed by Hénine et al. (2022)[39] and spatialized by Jeantet et al. (2021)[40], managing the beginning of the drained season. In the case of La Jaillière, Hénine et al. (2022)[39] set S_{inter} to the value of 110 mm, which is close to the SWI (85% corresponding to 100 mm) threshold determined in this project. They also showed that the beginning of the drainage season is not sensitive to the type of winter crop seeded on drained

plot due to lower evapotranspiration during autumn. More research is needed to test this assumption.
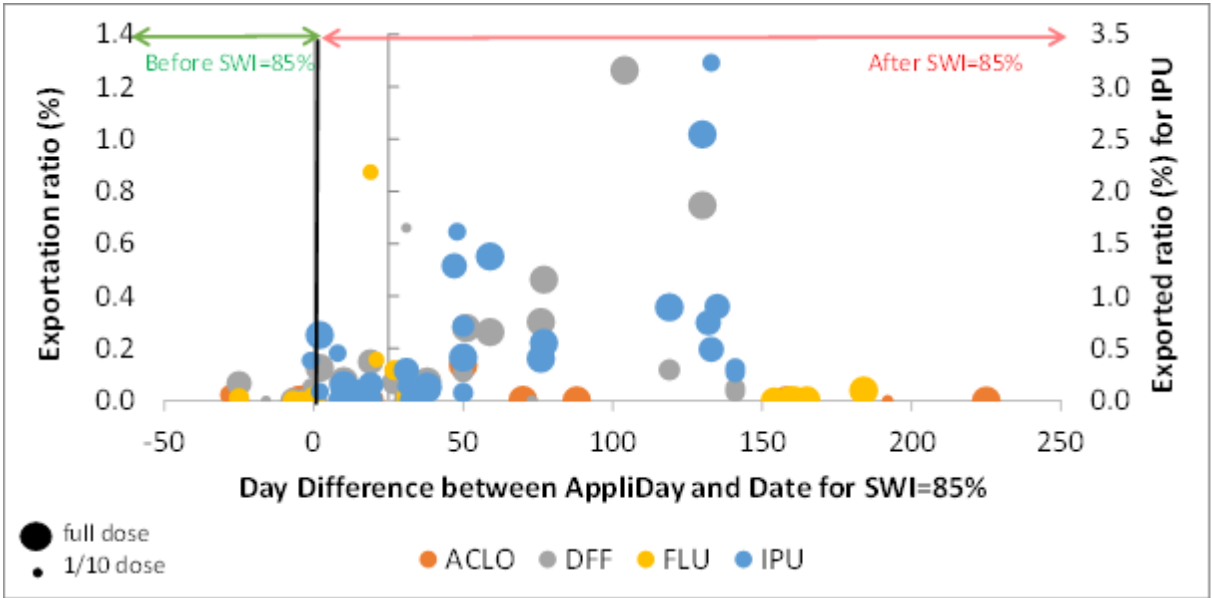

Figure 8. Annual exported pesticide ratio R_{exp} related to the time between application day and day when soil wetness index (SWI) reaches the threshold of 85% (all plots; size of circles is related to height of adimensional application rate compared to full dose; all hydrological years during the period 1993–2017, La Jaillière site). ACLO: aclonifen, DFF: diflufenican, FLU: flufenacet, IPU: isoproturon.

The SWI_{RC} threshold of 85% was reached on average on 31 of October in La Jaillière (Figure 9). From the period between 1993 and 2017, the application period representing a low risk of pesticide transfer by subsurface drainage based on SWI < 85%, ranges between October, the 11th to November the 20th in 50% of the cases, and between September the 10th to December the 12th in 3–97% of the cases, respectively.
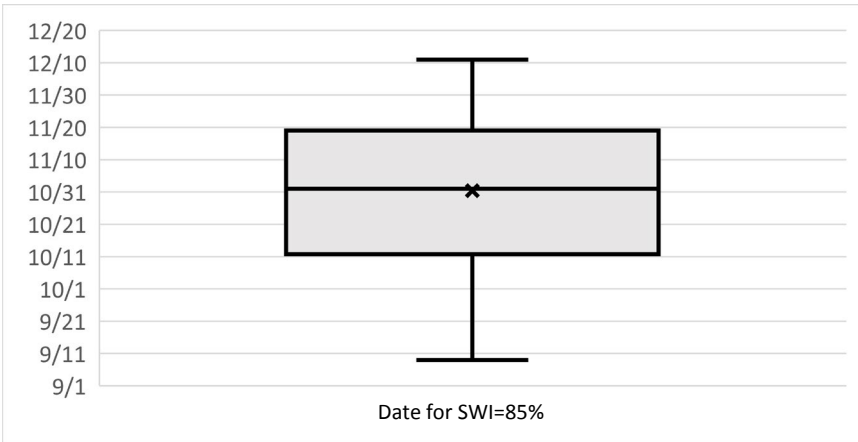
Figure 9. Box and whisker plot of the date reaching the threshold SWI=85%, in La Jaillière, 1993–2017 (*y* axis date: mm/dd). (cross indicate the mean, horizontal bar the median, the whiskers indicate 95th percentile).

Applying this SWI$_{RC}$ approach and evaluating the experimental data for its SWI on the day of application shows that the distribution of the variables of interest (annual exported flux, Cmax, concentrations > threshold 0.1 μg/L, 2 μg/L or PNEC; Figure 10) are all significantly different from the reference without application restriction: all *p* values are <0.00025. In comparison (in SM 1.3), the same approach made with time consideration (L_LD) shows less significant difference (p value<0.002, 10 fold higher). Thus, an agricultural management measure taking into account the SWI may make it possible to manage better the risk of annual exported pesticide flux and environmental pesticide concentrations in drain pipes. The SWI could be easily calculated considering local weather data (daily rainfall and potential evapotranspiration) and soil properties (field capacity and residual water content) for any field.
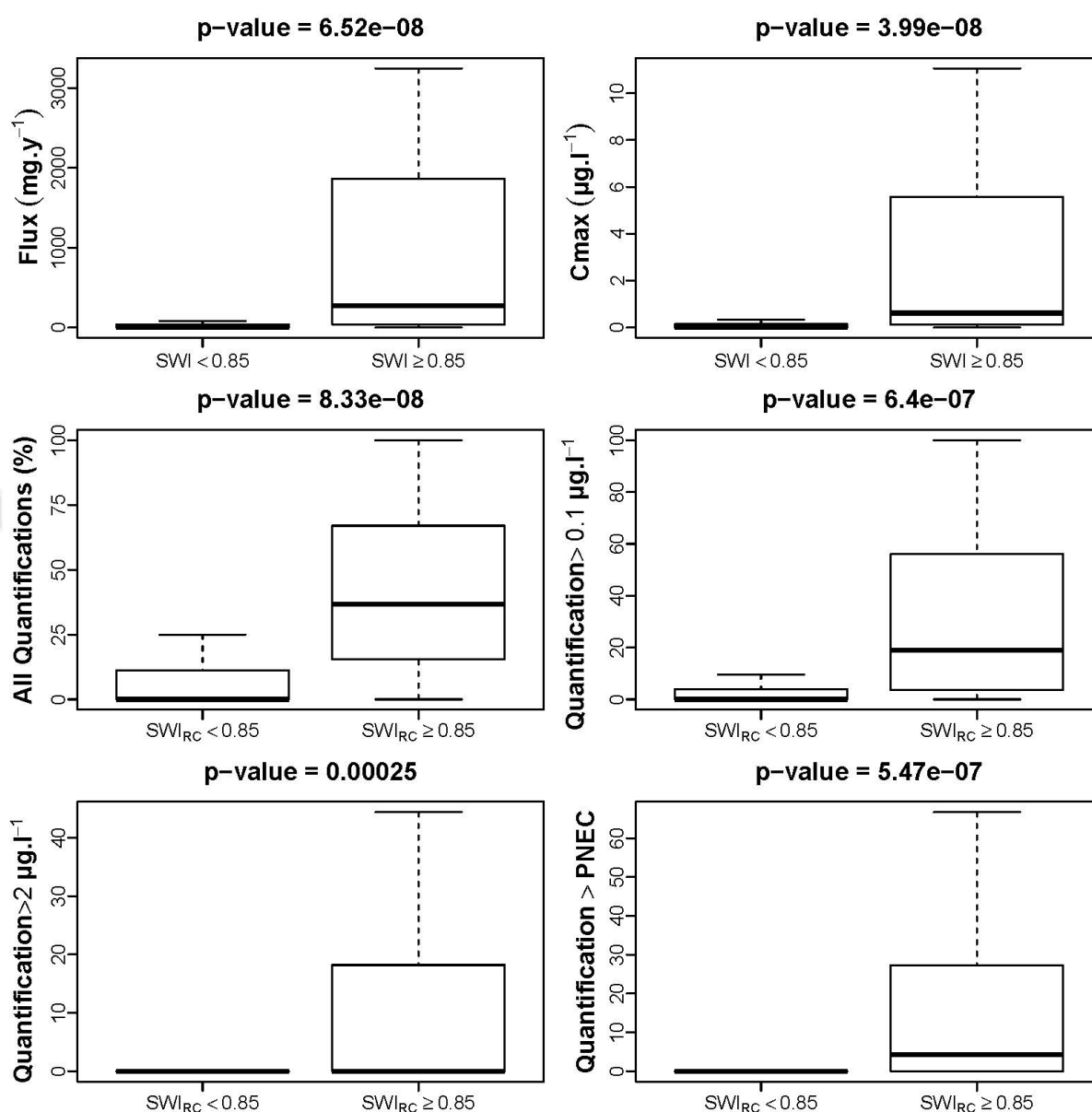
Figure 10. Box and whisker plots for annual flux, Cmax, quantification (percentage of analyzed samples > LOD), percentage of quantified concentrations > 0.1 μg/L, > 2 μg/L, > PNEC, clustering for SWI at application below (*N*=37) and above (*N*=73) the SWI$_{RC}$ threshold of 85%.

A conservative measure of restricting pesticide applications during autumn, when the SWI is < 85% of saturation, reduces the risk by a factor of 4–12 for quantification above PNEC and values of Cmax and CMP by 70- and 27-fold, R$_{exp}$ by 20-fold, and total flux by 32. This measure appears to be more efficient than those using other restriction factors as proposed by Willkommen et al. (2019, 10-fold)[14]. The SWI$_{RC}$ could be easily calculated as an indicator using water holding capacity, rainfall, and evapotranspiration data from national weather networks that consider the local climate and provide farmers with some flexibility in agricultural practices.

5 Conclusions

The experimental site at La Jaillière, also the basis for scenario D5 in regulatory FOCUS surface water assessments for pesticides[19,41], provides long time series of drainage water and pesticide fluxes and data on pesticide applications from 1993 to 2017. This large dataset includes different hydrological and agronomical conditions (incl. the four studied herbicides) allowing for a robust evaluation.

In general, controlling or mitigating the risk of pesticide transfer into drainage water is very challenging. This evaluation is focused on autumn applications for winter cereals, as this period is considered vulnerable to the risk of pesticide transport into drainage water. The evaluation of the experimental data led to the conclusion that the amount of annual exported pesticide flux is related to the soil moisture at the time of application (relative soil moisture, SWI). If a pesticide compound was applied during drier soil conditions with the SWI threshold of 85% (SWI$_{RC}$), the exported pesticide flux was reduced (< 0.1 % exported flux / application rate). A soil-moisture-based indicator (SWI) may enable the reduction of pesticide drainage transport, if taken into account for the timing of pesticide application.

Nevertheless, a risk of zero is not reachable. Farmers have to accept that certain pesticides cannot be applied throughout the year. In La Jailliere, the SWI-based approach (SWI < SWI$_{RC}$ = 85%) would provide a window of pesticide application, before October the 31st (median, in 50% of the cases) compatible with crop stage and weed management.

For future options, the soil moisture indicator SWI could be calculated for any field, based on its soil properties and daily weather data. The comparison with a SWI$_{RC}$ threshold may provide advice for application dates with a reduced drained flow risk. This could form part of a decision support tool for farmers. This mitigation risk measurement could be integrated into MA for recommendations to farmers.

6 Acknowledgments

7 References

1   Brown, C.D. and van Beinum, W. (2009) Pesticide transport via sub-surface drains in Europe. Environ Pollut 157(12), 3314-3324.

2   Sandin, M., Piikki, K., Jarvis, N., Larsbo, M., Bishop, K. and Kreuger, J. (2018) Spatial and temporal patterns of pesticide concentrations in streamflow, drainage and runoff in a small Swedish agricultural catchment. Science of the Total Environment 610-611, 623-634.

3   AGRESTE, 2010. Agricultural Census. Ministry of Agriculture, Food and Forestry, France

4   Tang, X., Zhu, B. and Katou, H. (2012) A review of rapid transport of pesticides from sloping farmland to surface waters: Processes and mitigation strategies. Journal of Environmental Sciences 24(3), 351-361.

5   Chalhoub, M., Gabrielle, B., Tournebize, J., Chaumont, C., Maugis, P., Girardin, C., Montagne, D., Baveye, P.C. and Garnier, P. (2020) Direct measurement of selected soil services in a drained agricultural field: Methodology development and case study in Saclay (France). Ecosystem Services 42, 101088.

6   Kladivko, E.J., Brown, L.C. and Baker, J.L. (2001) Pesticide transport to subsurface tile drains in humid regions of North America. Critical Reviews in Environmental Science and Technology 31(1), 1-62.

7   Ippolito, A. and Fait, G. (2019) Pesticides in surface waters: from edge-of-field to global modelling. Current Opinion in Environmental Sustainability 36, 78-84.

8   Ulén, B., Alex, G., Kreuger, J., Svanbäck, A. and Etana, A. (2012) Particulate-facilitated leaching of glyphosate and phosphorus from a marine clay soil via tile drains. Acta Agriculturae Scandinavica Section B: Soil and Plant Science 62(SUPPL. 2), 241-251.

9   Leu, C., Schneider, M.K. and Stamm, C. (2010) Estimating catchment vulnerability to diffuse herbicide losses from hydrograph statistics. Journal of Environmental Quality 39(4), 1441-1450.

10   Nolan, B.T., Dubus, I.G., Surdyk, N., Fowler, H.J., Burton, A., Hollis, J.M., Reichenberger, S. and Jarvis, N.J. (2008) Identification of key climatic factors regulating the transport of pesticides in leaching and to tile drains. Pest Management Science 64(9), 933-944.

11   Trajanov, A., Kuzmanovski, V., Leprince, F., Real, B., Dutertre, A., Maillet-Mezeray, J., Džeroski, S., and Debeljak, M. (2015) Estimating Drainage Periods for Agricultural Fields from Measured Data: Data-Mining Methodology and a Case Study (La JailliÈRe, France). Irrig. and Drain., 64: 703- 716. doi: 10.1002/ird.1933.

12   Trajanov, A., Kuzmanovski, V., Real, B., Perreau, J.M., Džeroski, S. and Debeljak, M. (2018) Modeling the risk of water pollution by pesticides from imbalanced data. Environmental Science and Pollution Research 25(19), 18781-18792.

13   Pierlot, F., Marks-Perreau, J., Réal, B., Carluer, N., Constant, T., Lioeddine, A., van Dijk, P., Villerd, J., Keichinger, O., Cherrier, R. and Bockstaller, C. (2017) Predictive quality of 26 pesticide risk indicators and one flow model: A multisite assessment for water contamination. Science of the Total Environment 605-606, 655-665.

14   Willkommen, S., Pfannerstill, M., Ulrich, U., Guse, B. and Fohrer, N. (2019) How weather conditions and physico-chemical properties control the leaching of flufenacet,

diflufenican, and pendimethalin in a tile-drained landscape. Agriculture, Ecosystems and Environment 278, 107-116.

15   Jones, R., J. S. Arnold, D., L. Harris, G., W. Bailey, S., J. Pepper, T., J. Mason, D., D. Brown, C., B. Leeds-Harrison, P., Walker, A., H. Bromilow, R., Brockie, D., H. Nicholls, P., C. C. Craven, A. and M. Lythgo, C. (2000) Processes affecting movement of pesticides to drainage in cracking clay soils. Pesticide Outlook 11(5), 174-179.

16   Renaud, F.G. and Brown, C.D. (2008) Simulating pesticides in ditches to assess ecological risk (SPIDER): II. Benchmarking for the drainage model. Science of the Total Environment 394(1), 124-133.

17   Lewan, E., Kreuger, J. and Jarvis, N. (2009) Implications of precipitation patterns and antecedent soil water content for leaching of pesticides from arable land. Agricultural Water Management 96(11), 1633-1640.

18   Zajíček, A., Fučík, P., Kaplická, M., Liška, M., Maxová, J. and Dobiáš, J. (2018) Pesticide leaching by agricultural drainage in sloping, mid-textured soil conditions - the role of runoff components. Water Science and Technology 77(7), 1879-1890.

19   FOCUS, 2001: FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EC. Report of the FOCUS Working Group on Surface Water Scenarios. EC Document Reference SANCO/4802/2001-rev2. 245 pp

20   FAO (2006) Guidelines for soil description. Food and Agriculture Organization of the United Nations, Rome, p. 110

21   Dairon, R., Dutertre, A., Tournebize, J., Marks-Perreau, J. and Carluer, N. (2017) Long-term impact of reduced tillage on water and pesticide flow in a drained context. Environmental Science and Pollution Research 24(8), 6866-6877.

22   Lagacherie, P., Favrot, J.C., 1987. Synthèse générale sur les études de secteurs de référence drainage. INRA

23   Saleem, J. A., & Salvucci, G. D. (2002). Comparison of Soil Wetness Indices for Inducing Functional Similarity of Hydrologic Response across Sites in Illinois, Journal of Hydrometeorology, 3(1), 80-91

24   Dray, S. and Dufour, A.-B. (2007) The ade4 Package: Implementing the Duality Diagram for Ecologists. Journal of Statistical Software 22(4), 1 - 20.

25   Bauer, D.F. (1972) Constructing Confidence Sets Using Rank Statistics. Journal of the American Statistical Association 67(339), 687-690.

26   Hollander, M. and Wolfe, D.A. (1973) Nonparametric Statistical Methods, Wiley.

27   Team, R.C. (2021) R: A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna, Austria.

28   Dousset, S., Babut, M., Andreux, F. and Schiavon, M. (2004) Alachlor and Bentazone Losses from Subsurface Drainage of Two Soils. Journal of Environmental Quality 33(1), 294-301.

29   Doppler, T., Lück, A., Camenzuli, L., Krauss, M. and Stamm, C. (2014) Critical source areas for herbicides can change location depending on rain events. Agriculture, Ecosystems & Environment 192, 85-94

30   Kobierska, F., Koch, U., Kasteel, R., Stamm, C. and Prasuhn, V. (2020) Plant protection product losses via tile drainage: A conceptual model and mitigation measures. Agrarforschung Schweiz 11(6), 115-123.

31   Gustafson, D. I. (1989) Hazard assessment groundwater ubiquity score : A simple method for assessing pesticide leachability, Environ. Tax. Chem. 8, 339-357

32   Chow, R., Scheidegger, R., Doppler, T., Dietzel, A., Fenicia, F. and Stamm, C. (2020) A review of long-term pesticide monitoring studies to assess surface water quality trends. Water Research X 9, 100064.

33   Klaus, J., Zehe, E., Elsner, M., Palm, J., Schneider, D., Schröder, B., Steinbeiss, S., van Schaik, L. and West, S. (2014) Controls of event-based pesticide leaching in natural soils: A systematic study based on replicated field scale irrigation experiments. Journal of Hydrology 512, 528-539.

34   Jacobsen, O.H. and Kjær, J. (2007), Is tile drainage water representative of root zone leaching of pesticides?. Pest. Manag. Sci., 63: 417-428.

35   Petersen, C.T., Holm, J., Koch, C.B., Jensen, H.E. and Hansen, S. (2003) Movement of pendimethalin, ioxynil and soil particles to field drainage tiles. Pest Management Science 59(1), 85-96.

36   Kjær, J., Ernsten, V., Jacobsen, O.H., Hansen, N., de Jonge, L.W. and Olsen, P. (2011) Transport modes and pathways of the strongly sorbing pesticides glyphosate and pendimethalin through structured drained soils. Chemosphere 84(4), 471-479.

37   Kung, K.-J.S., Kladivko, E.J., Gish, T.J., Steenhuis, T.S., Bubenzer, G. and Helling, C.S. (2000) Quantifying Preferential Flow by Breakthrough of Sequentially Applied Tracers Silt Loam Soil. Soil Science Society of America Journal 64(4), 1296-1304.

38   Kohler, A., Abbaspour, K.C., Fritsch, M. and Schulin, R. (2003) Using simple bucket models to analyze solute export to subsurface drains by preferential flow. Vadose Zone Journal 2(1), 68-75.

39   Henine, H., Jeantet, A., Chaumont, C., Chelil, S., Lauvernet, C. and Tournebize, J. (2022) Coupling of a subsurface drainage model with a soil reservoir model to simulate drainage discharge and drained flow start. Agricultural Water Management 262, 107318.

40   Jeantet, A., Henine, H., Chaumont, C., Collet, L., Thirel, G. and Tournebize, J. (2021) Robustness of a parsimonious subsurface drainage model at the French national scale. Hydrol. Earth Syst. Sci. Discuss. 2021, 1-33.

41   FOCUS, 2015: Generic guidance for FOCUS surface water Scenarios, version 1.4, May 2015. EU Document, 367 pp.

42   Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A. (2016) An international database for pesticide risk assessments and management, Human and Ecological Risk Assessment: An International Journal, 22:4, 1050-1064, DOI: 10.1080/10807039.2015.1133242