How Should Agricultural Practices Be Integrated to Understand and Simulate Long-Term Pesticide Contamination in the Seine River Basin?

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Contents

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Abstract Modelling long-term pesticide transfer to rivers at the catchment scale is still difficult due to a lack of knowledge of agricultural practices and poorly adapted field observation. The Orgeval experimental catchment was first investigated to validate a modelling approach. In addition to pesticide practices investigated over 20 years, directly collected from farmers, monthly integrated river samples were analysed for 10 years. To explicitly integrate agricultural practices and crop rotation, the STICS crop model was adapted to simulate pesticide transfer in soil. Annual load simulations were compared to observed pesticide fluxes in rivers. To simulate the contamination of groundwater, the STICS-Pest model was coupled to the MODCOU hydrogeological model. The results are discussed at the subbasin scale in relation to available data. To upscale the approach at the Seine River basin scale, other strategies need to be developed.

Keywords eLTER, Modelling, Monitoring, Pesticide, Phytosanitary practices, PIREN-Seine, STICS-Pest, Zone Atelier Seine

1 Introduction

River contamination by pesticides is currently observed in the Seine basin. This is mainly due to long-term uses of such substances in agricultural areas. Still today, atrazine and its metabolite deethylatrazine (DEA) are one of the most frequently detected pesticides in the Seine basin, even though atrazine has been banned since 2003. In this context, we need to better understand and simulate pesticide fate in watersheds consistent with long-term uses.

Numerous pesticide fate models are available. The main differences between them are mostly related to water flow from simple water transfer such as PELMO [1] and PRZM [2] to more physically oriented models such as PEARL [3], MACRO [4] and RZWQM [5]. However, modelling pesticides requires understanding the relationship between land management practices and the dynamic of contaminants, and only a few models are able to take into account specific agricultural practices [6].

Pesticide transfer models need to know when each active ingredient (AI) is applied and the quantity applied. However, unlike the other data needed for implementing models (climate, soil characteristics or land use), there is no database available on phytosanitary practices that can directly feed the models [6–8]. In addition, there are few attempts to synthesise these practices at the catchment scale. This deficiency led to the development of new methods of acquiring and processing data [6, 7].

In the PIREN-Seine programme, studies were conducted to better define crop rotations and landscape diversity in the Seine catchment area. Agricultural practices were investigated, and the first models simulated nitrate contamination behaviour in groundwater [9] and surface water [10]. New developments have been carried out to integrate pesticide behaviour, taking into account farmers' phytosanitary practices. Pesticide contamination at the catchment scale was first investigated in two small

agricultural areas: the Orgeval and the Vesle. This paper is a synthesis of the work done in the PIREN-Seine research programme concerning the modelling of pesticide transfer. We present here how pesticide uses were collected, the modelling approach and the results for atrazine and its by-product DEA on two basins: the Orgeval and the Vesle. These studies highlight the difficulty of the spatio-temporal approach to modelling the fate of pesticides in the Seine basin.

2 Study Sites

The pesticide fate model was designed to gather input databases such as soil characteristics, climatic data, pesticide properties and phytosanitary practices. Given that the database is not available for the latter, an estimation of annual quantities of each AI, the application schedule and spatial distribution of application on the catchment must be at least documented. The effort needed for inquiries on pesticide applications is directly related to the size of the watershed. Therefore, the Orgeval site was considered for a long-term study, while the Vesle site was chosen for a spatial approach.

2.1 Presentation of the Orgeval and Vesle Basins

The Orgeval watershed (104 km^2) is located 70 km east of Paris (Fig. 1) where hydrological and biogeochemical cycles have been studied since 1962. It is situated on the Brie plateau, which is one of the most productive agricultural areas in France, between 140 and 180 m above sea level. The deep and low permeability clay loams result from the decomposition of limestones and millstones of the underlying Brie. Drainage has allowed intensive agricultural development of these silts of the Brie plateau. Consequently, this basin is dominated by agricultural areas (81%) and forests (18%). Roads and urban areas account for only 1% of the land area. Cereals are the main crops. Soft wheat accounts for more than 40% of crops and maize for about 14% for the 1988–2007 period. Some specific crops such as broad bean and flax are also cultivated in the Orgeval basin (5% and 4%, respectively), whereas sugar beet, barley and rapeseed are less widespread, compared to data for the Seine-et-Marne department.

The Vesle watershed (1,460 km^2) is located in one of the major agricultural regions of the Seine basin: the Champagne area (Fig. 1). Seventy-six percent of the basin is covered by agricultural lands, while the remaining surface is divided into forest (17%) and urban areas (7%). The city of Reims is situated in the downstream part of the basin. The basin is mainly covered by field crop systems: wheat (30%), barley (18%), sugar beet (13%) and alfalfa (12%). On this catchment, maize is mainly inserted into 5-year-long rotations such as beetroot (or pea or rapeseed) – wheat – maize – wheat – barley. Champagne grapes are a specific crop located on the
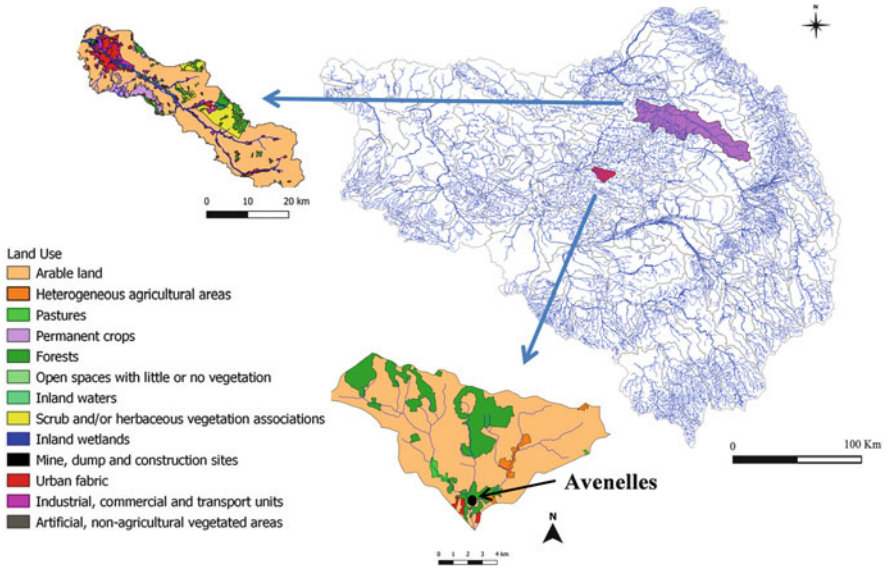
Fig. 1 Map of the Seine hydrographic basin, location and land use of the Orgeval and Vesle basins

slopes in the downstream part of the basin (Fig. 1). From a hydrogeological standpoint, two-thirds of the surface (upper and middle parts) is associated only with the Cenomanian limestone aquifer, while low-permeable tertiary formations have been deposited on top of it in the lower part of the basin. The Cenomanian aquifer is unconfined and drained by the Vesle River and its tributaries. The groundwater reservoir is located in a thickness layer ranging from 30 to 40 m [11] and is locally affected by fracture networks and karst systems, providing a good transmissivity. On top of the aquifer, the thickness of the unsaturated zone varies from a few metres in the valley to a few tens of metres underneath the plateau.

2.2 Data Acquisition

To study long-term contamination by pesticides, we focused on atrazine. In the Seine River and some aquifers of the basin, atrazine and its by-product DEA are currently detected in rivers and groundwater even after its ban in 2003. Atrazine is a herbicide widely used on maize as well as vineyards. It was also used on urban areas for weed control on roads and railways. In France, pesticides are monitored in rivers and aquifers for the European framework directive. However, such data is generally partial (monthly, half-yearly, annual or less), and further investigations were conducted.

In the Orgeval basin, within the PIREN-Seine programme, a flow-controlled refrigerated sampler has been installed since 2008 at the Avenelles station (see Fig. 1). Since then, samples have been collected once a week and then gathered monthly for pesticide analyses. A survey of the crop management techniques of the main farms was also carried out [12]. Pesticides were then extracted with an offline solid-phase extraction (SPE) technique with the Oasis hydrophilic lipophilic balance® (HLB, Waters) cartridge and analysed by liquid chromatography with tandem mass spectrometry (LC/MS/MS) [13, 14]. Detection limits are 1 ng L^{-1} for both atrazine and DEA.

In the Vesle basin, atrazine and DEA concentrations were extracted for 39 piezometers from the ADES database [15]. Additional specific sampling campaigns were carried out monthly from November 2003 to February 2005 on 11 piezometers by the Agence de l'Eau Seine-Normandie (Direction Territoriale des Vallées d'Oise, DTVO). This covered a larger geographic area and included more specific hydrogeological contexts.

3 Quantification of Past Pesticide Use

AIs provided at the watershed scale depend on phytosanitary practices (or treatment programmes) prescribed at the field scale by technical advisors. However, these uses vary greatly depending on pedoclimatic conditions acting on parasitism, types of crops and cultivated areas, farmers' phytosanitary strategies and regulations on pesticide use.

Most of the AI uses are registered for specific crops and often in a particular case (type of pest and/or disease). Crop rotations and their diversity (short rotations from 3 to 4 years to rotations of more than 10 years including alfalfa) ensure some diversity, except in the case of perennial crops such as vineyards. Each farmer has his/her own strategies in terms of phytosanitary practices based on the advice of technicians (cooperatives, technical institutes, etc.) and his/her personal choices (sowing date, crop variety, tillage practices, etc.) [16–18]. Then, for the same crop, pesticide use may differ from one farm to another or even from one field to another. This diversity could explain 40–60% of pesticide use [16]. Moreover, pesticide use evolves rapidly over time, depending on the regulations (banned or new AI), climate conditions (which cause diseases and pests to vary) and rotation crops [17].

The main source of information on crop rotation in the two study areas is the French Agricultural Census, which has been available at the municipal level since 1970. It is updated only every 10 years, but annual data were estimated by interpolation using annual data available at the regional scale between these dates [19–21].

With regard to pesticide use, there are few generic databases that can be used over a long time period and on large study sites. The E-Phy database [22] lists the plant protection products authorised in France, as well as their composition, homologation dates and actual registered uses and doses. However, these data cannot be directly

used because farmers can choose to use one AI or another. The national sales made by distributors' database (BNV-d), which includes pesticide sales, are another source. This database could be used to spatialise pesticide use [23, 24], but data have been available only since 2008.

To better define model inputs, a "hybridization approach" using national resources and local data was developed according to two methods [6]. Since the Orgeval catchment is only about 100 km^2, all agricultural practices were monitored over a period as long as possible for the whole watershed. The Vesle catchment is too large, and therefore only herbicide use has been investigated within a 30-year period on targeted practices (weeding vineyards and corn) for which the use of these AIs was approved. Data were collected at a municipal scale.

3.1 The Orgeval Case

For the Orgeval basin, other data were available to refine the spatial accuracy of the annual rotation. First, rotation tables were provided directly by farmers, describing their crop succession on their plots (771 plots accounting for 45% of the landscape area, dating from 1970 to 2005). Moreover, data from the French Land Parcel Identification System (LPIS) geographic database [25] has been available since 2006.

Here, we chose to collect records of their past practices directly from farmers located in the study area. These documents, called "lowland logbooks" or "field logs", help to get closer to farmers' "real" practices and to reconstruct the dynamics of phytosanitary practices over 20 years for a representative sample [26]. As an example, the chart in Fig. 2 shows that atrazine was long the main AI applied on maize until its ban in 2003. However, the chart still shows some applications beyond this date, showing the authenticity and low bias of the data recorded. High-resolution data could capture spatial variability but at the cost of intensive computing [27, 28]. Therefore, we assumed a type of simplification: to keep confidential and anonymous data and also to simplify modelling input; these data were averaged by crop and by year for the whole basin in the final database.

This APOCA (Agricultural Practices of the Orgeval Catchment Area) database was used to quantify the AIs applied per crop per year since 1990. It also includes a large number of indicators to monitor changes in phytosanitary pressures [26]. Comparison of these indicators shows that the phytosanitary pressure is not decreasing overall even if applied quantities per hectare are lower.

3.2 The Vesle Case

For the Vesle study, prescriptions issued by local agricultural development agencies were used to better indicate actual farmer pesticide use. The technical magazine *Le*
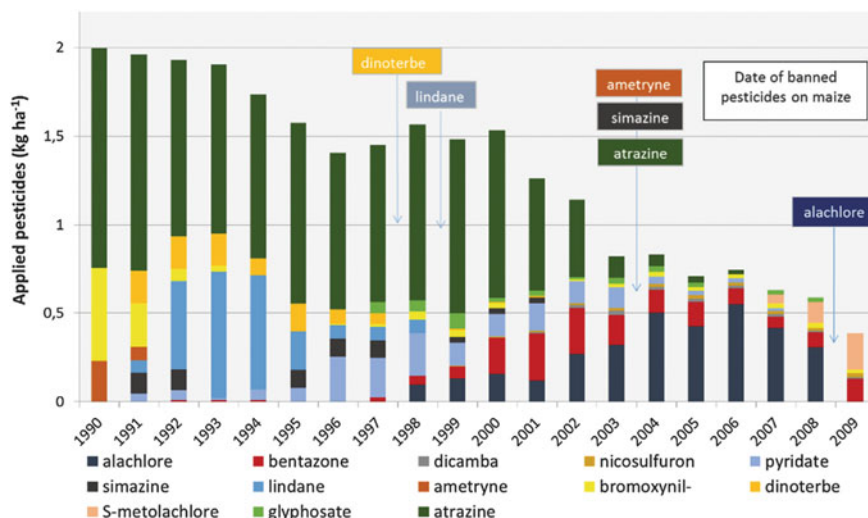
**Fig. 2** Application rates of pesticides on maize from 1990 to 2009 in the Orgeval catchment

Vigneron Champenois was especially useful for the reconstitution of phytosanitary practices on Champagne vineyards since the 1970s [29]. However, because of the large number of possible treatments, it was necessary to quantify and validate it with "experts" [19–21]. Furthermore, we obtained sales for corn weed control products since the 1970s from the main cooperative in the sector (Champagne Céréales). These data, compared to those of maize surfaces collected, allowed us to estimate the quantities of active ingredients applied per hectare. These averaged values, however, remain a relatively rough estimate of current practices in this catchment area but clearly reflect the complexity of determining pesticide inputs for modelling.

We created another database called ARSEINE for the identification of the major treatment programmes by period and crop as well as the percentage of product used for each programme in relation to the whole rotation crop. In both study areas, since phytosanitary practices were not differentiated within the watershed, it is the distribution of crops that allows to determine spatial treatments [30].

4 The Orgeval Catchment Over Time

4.1 Long-Term Observed Contamination

Pesticides have been studied since 1979 in the soils, river, groundwater, air, fallout, drainage and wetland of the Orgeval basin [31–36]. Organochlorinated pesticides and then triazines, phenylureas, chloroacetanilides, neonicotinoids, sulfonylureas, etc. were successively researched over time according to new uses and marketing
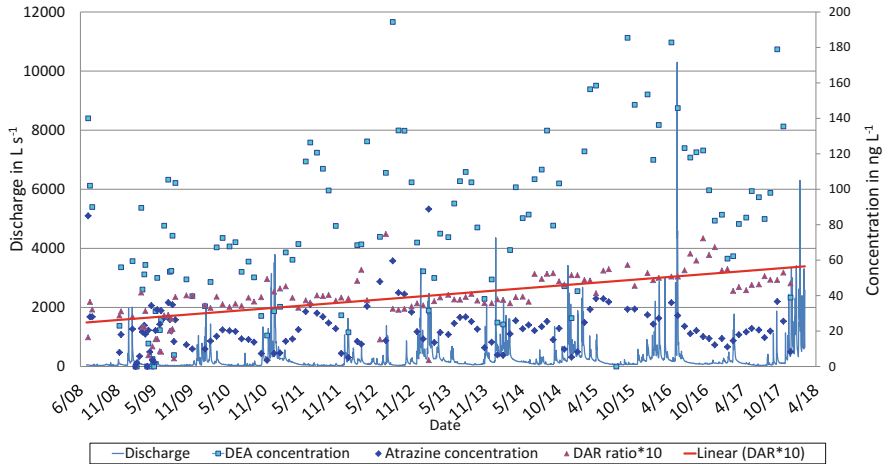
Fig. 3 Surface water flow over time (left axis), integrated monthly concentration of atrazine, DEA and DEA/atrazine ratio (DAR) with linear fitted correlation (right axis)

approval. Atrazine and its metabolite DEA were detected in all samples and were considered as the reference of past contamination for modelling.

To compare the simulations with the observed data, monitoring was adapted.

Unlike molecules still used in the watershed, atrazine found in surface river water has only slight fluctuations from 1 to 90 ng L^{-1} (Fig. 3). Since atrazine was banned in 2003, these detections correspond to the gradual elimination of stocks from soil and/or groundwater. Previous studies on groundwater contamination showed that DEA concentrations in rivers could be explained by Brie aquifer contamination where values were lower than 15 ng L^{-1} [37]. Furthermore, riverine seasonal fluctuations would also be related to the contribution of the Brie groundwater to surface water. However, the atrazine concentration is lower in groundwater than in the river, suggesting that another source could be suspected for atrazine. This could be due to desorption of atrazine from soils when the water table level rises. Although atrazine concentrations in rivers remain stable over the period studied, the DEA concentrations increase. DEA is still present in the river at concentrations up to 180 ng L^{-1}. The value of the DAR also increases and follows monotonic growth ($S = 1$, Mann-Kendall nonparametric test; [38]). Other studies also show that the maximum level of DEA contamination has not yet been reached, in particular through the gradual desorption of atrazine and its slow degradation and progression in soils [39].

To verify whether leaching of atrazine decreases over the period, annual fluxes were calculated for atrazine and DEA (Table 1). These results do not show any trend in how fluxes evolve. This is particularly due to hydrological hazards. Flows were the highest in 2016, corresponding to the exceptional flood in May 2016, which alone accounted for 35% of the annual flow. These high water flows were associated with higher concentrations, which explain the doubling of the atrazine and DEA fluxes between 2015 and 2016 (Table 1).

Table 1 Annual flow and fluxes of atrazine and DEA in g/year

Year	Flow (10^3 m^3 year^{-1})	Atrazine flux (g year^{-1})	DEA flux (g year^{-1})
2010	6,848	63.14	238.07
2011	5,698	65.89	265.62
2012	6,652	153.53	543.82
2013	9,710	286.84	528.85
2014	10,011	128.84	559.94
2015	8,164	172.05	838.84
2016	11,869	337.70	1,737.76
2017	8,012	130.19	637.58

These results demonstrate the need to develop a pesticide fate model to better forecast long-term contamination taking into account past pesticide use and soil and aquifer inertia.

4.2 Pesticide Fate Modelling with the STICS Crop Model

A pesticide transfer module was implemented in the STICS crop model [40] to better integrate cropping system specificity such as plant growth and specific agricultural practices in pesticide fate simulations. This STICS-Pest model [41] is able to simulate the main processes involved in pesticide fate, i.e. sorption, transformation and transfer through a soil profile. Liquid transfer is based on the STICS solute transfer formalism based on the mixing cell principle [42]. The model is original in that it includes a slow sorption kinetics formalism, following the Agriflux model equations according to [43]. The representation is based on the experimental works of [44, 45], who observed a time-dependent isotherm shape for sorption processes of organic compounds. This approach made it possible to better simulate long-term desorption from bound residues. A detailed description of the module is given in [41].

Five categories of parameters have to be described to implement the model: climate data, soil parameters, cultural practices (sowing and harvest dates, crop management), crop parameters (main crop rotations) and pesticide parameters. For the soil parameters, the field capacity, wilting point and bulk density are derived from the national database related to soil description and the characteristics of the French soil [46]. The organic carbon profile is related to field data and laboratory measurements [47].

Agricultural practices were extracted from the APOCA database. Atrazine inputs were calculated using phytosanitary practices provided by farmers (applied quantities on maize, application date) according to percentages of maize over the 1990–2009 period.

Pesticide characteristics are mostly extracted from international databases such as [48] or previous studies including field measurements with pedoclimatic conditions

similar to the Orgeval catchment [49, 50]. Moreover, the transformation of atrazine to its metabolite DEA is estimated with the first-order kinetics and maximum occurrence fraction estimated at 0.21 [48].

Several simplifications and assumptions were made in this study. The soil characteristics were assumed to be homogeneous at the catchment scale. Given that more than 80% of the area is artificially drained, we assumed that the residence time of water is equal to or less than 1 year. Consequently, the simulation and observed data were compared on an annual scale. Moreover, since we focused on atrazine behaviour, maize was the only crop considered. Soil water content, organic matter and nitrogen content were initialised with a 1-year warm-up, while a 14-year warm-up was used for pesticide initialisation in order to take into account a stock of atrazine and DEA in the soil at the beginning of the simulation.

Since water is the main vector of pesticide transfer, the ability of STICS-Pest to simulate water transfer was checked. Cumulated water transfers simulated with STICS-Pest were therefore compared to discharge observations at the outlet of the Orgeval catchment and showed a determination coefficient of 0.99, illustrating the ability of the model to represent water transfer and its interannual variations (Fig. 4).

Concentrations simulated by the model were compared with continuous monitoring of pesticides at the outlet of the catchment (Fig. 5). Observations represented with triangles and squares (Fig. 5, left) show higher concentrations during the period of atrazine application at the beginning of the simulation than after the banishment of the active substance. The simulated atrazine concentrations fluctuated during the first 14 years linked to water outflow fluctuation followed by a strong decrease in 2004 and finally tended to stabilise at the end of the simulation. From 2008 to 2016, simulations and observations were relatively similar and followed a similar trend, as
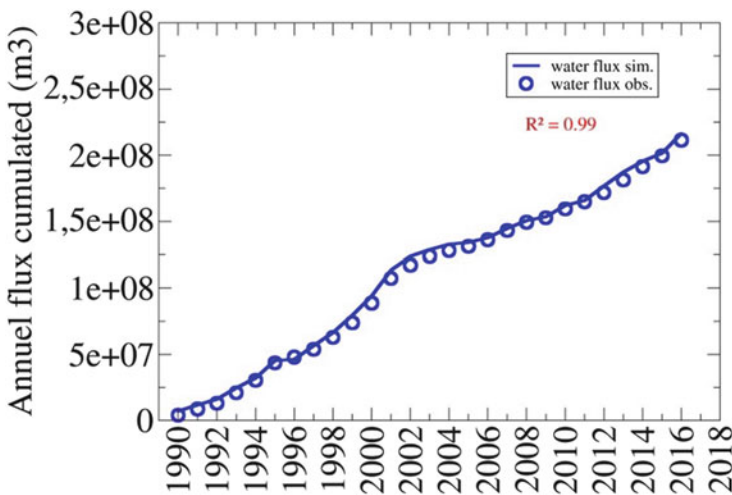
Fig. 4 Comparison of the cumulated water discharge simulated with STICS-Pest (continuous line) versus observations (circles) at the Orgeval catchment outlet
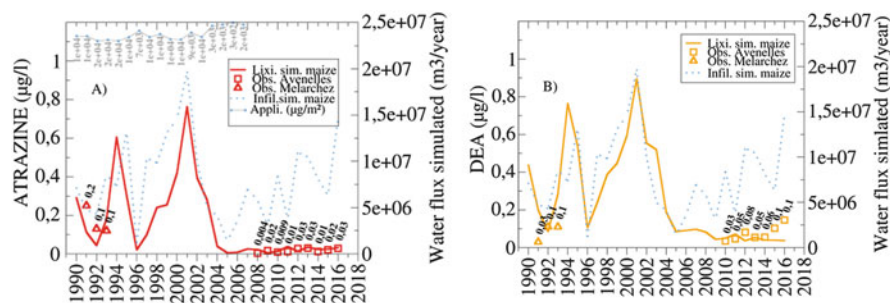
Fig. 5 Riverine observed (triangles and squares) and simulated (continuous line) annual concentration of atrazine (left) and its metabolite DEA (right) from 1990 to 2016 related to water transfer with annual outflow simulated (dotted blue line) and mean application dose of atrazine (solid blue line)

demonstrated by the 0.7 correlation coefficient, showing the ability of the model to simulate the background of atrazine 13 years after the end of the herbicide application. The observed evolution of DEA was rather similar to that of atrazine, with a lower discrepancy between the periods prior to and after its ban (Fig. 5, right). The simulated DEA concentrations were strongly related to the water discharge during the period of atrazine use. After its ban, the model tended to underestimate the DEA transfer for the last 2 years of the period. This might be due to the fact that in the model, the concentration was computed based only on the soil source of DEA, while the observation can include the source of DEA from the groundwater. In addition to water circulation in soils, integrating groundwater transfer in larger simulated basins is a step further, developed below.

5 The Spatial Approach in the Vesle Catchment

A spatial distribution of the STICS-Pest crop model was developed to take into account the inherent spatial heterogeneity associated with parameters dictating changes in water and pollutant inputs in an agro-pedo-hydrosystem, such as climate, crop rotations and management, pesticide inputs and soil properties.

This type of approach requires (1) an explicit structural description of all compartments of the hydrosystem (surface domain, vadose and saturated zones) as well as a reproduction of their respective hydrodynamic behaviours and (2) a fine spatial discretisation of transport processes throughout the entire system (spatial distribution on fine grid of water recharge, root zone concentrations in pesticides, etc.). Therefore, a coupling procedure with the spatially distributed MODCOU-NEWSAM hydrogeological model [51, 52] was developed.

The whole modelling platform was designed to simulate both pesticide fluxes coming from agricultural activity and their transport in soils as well as in

underground and surface water compartments over the Vesle basin. Again, we only focussed on atrazine and DEA. From a modelling standpoint, this watershed offers advantages such as relatively simple geological and hydrogeological configurations and spatial homogeneity in soil properties and agricultural practices.

To interface STICS and the MODCOU-NEWSAM hydrogeological model, the code was integrated into a computing structure [30, 51–53], allowing it to be used in a broad spatial manner according to a bottom-up approach [54]. Consequently, this procedure integrates the variability of inputs in space and time (soil types, climate, agro-system management).

It therefore requires three kinds of input: (1) climate data from the SAFRAN atmospheric analysis system [55, 56], (2) soil data at the 1:1000000 scale [57] for which parameters are estimated through the use of pedo-transfer functions [58–61] and (3) crop rotation and management [29, 62, 63] for which pesticide use was computed with crop rotation in the ARSEINE database [21] over a 45-year period (1970–2015) in Fig. 6.

MODCOU [64, 65] is a regional spatially distributed model which describes both surface and underground water flows at a daily time step. Mainly conditioned by land use, climate and parent soil material, surface water balance calculations are based on a conceptual reservoir-based approach [66]. Infiltration leaks through a vadose zone were implemented using a set of reservoirs introducing a delay between the infiltration and the aquifer recharge [67, 68]. The finite difference resolution scheme of the 2D diffusivity equation uses the recharge as well as water pumping to compute the dynamism of piezometric heads of the saturated zone. Computed discharges in each river cell of the hydrographic net result from both stream-aquifer exchange calculations, taking into account the coupling with piezometric heads and sub-surface run-off, which is routed across the drainage network [69].

Pesticide transfer within both the vadose and saturated zones is computed by the NEWSAM module in which the substance is assumed to be fully conservative since most of the pesticide-related transformation processes take place within the first few metres of the subsoil interface [70]. A resolution scheme of the convection-only
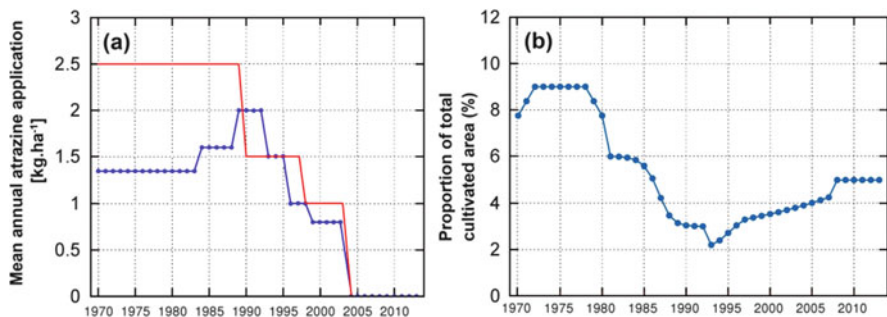
Fig. 6 Annual changes in atrazine application (in kg ha^{-1}) on maize (1971–2013 period) for one modelling unit (**a**), in red the approved dose and in blue the mean dose on the Vesle watershed and the ratio of maize (as a percentage of cultivated area) on the same modelling unit (**b**)

transport equation is run, with a 10-day time step, to compute the evolution of pesticide concentrations in each aquifer.

In this case, a regional application of the MODCOU-NEWSAM model [71] was developed, describing most of the Champagne area and covering the Vesle basin in its entirety (Fig. 1). The surface domain of the basin is discretised by over 5,000 cells within a progressive multi-scale grid of embedded square meshes. The groundwater domain is modelled by a multilayer structure of 5,900 cells. Both surface and aquifer grid cells vary from 250 m to 2 km in size. Two aquifer layers describe the main aquifers of the basin (Cenomanian Chalk aquifer and tertiary complex multilayered ensemble).

Prior to any pesticide-related simulations, hydro-dynamism was calibrated using measurements of seven hydrometric stations located on the river and four piezometers distributed along the watershed; nitrate concentration measurements from 14 boreholes were also used to calibrate solute transport.

For each cell of STICS-Pest, the spatialised model provides both water drainage and leached fluxes of atrazine and associated metabolites. Under agricultural lands only, leaching fluxes were diluted by the water drainage computed by STICS-Pest. Then computed concentrations were transmitted to the aquifer system through the unsaturated zone. Under urban and forest areas, the MODCOU water balance was used with associated pesticide concentrations set to 0. This value is justified by there being no treatment with atrazine in forests and by urban uses on impervious surfaces that directly transfer to rivers.

Figure 7 shows the location of each monitoring point used for the model calibration on the basin as well as a few sample results regarding piezometric heads (Fig. 7a), river flow (Fig. 7b) and nitrate concentration (Fig. 7c, d) at different stations and boreholes.

Good agreement was found for piezometric heads (Fig. 7a), river flow (Fig. 7b) and nitrate concentration (Fig. 7c, d) at different stations and boreholes.

The changes in atrazine at a borehole are accurately reproduced by the simulations during this period of available data (Fig. 7e). Maps of simulated concentrations for the Cenomanian aquifer layer at the end of December 2001 (deadline of authorised sale of atrazine) and in 2013 (final time step of the simulation), shown in Fig. 7, are also in agreement with observed concentrations.

A mass balance, at the scale of the entire area and over the simulation period (1971–2013), shows a 0.39% ratio between total simulated leached and applied masses of atrazine, which is close to the value previously determined, also using STICS-Pest, by [35] on the Orgeval catchment. More generally, this order of magnitude is similar in many studies reported in the literature [72–76].

6 Pesticides at the Seine River Basin Scale

At this stage of the modelling procedure, the results obtained on the Vesle basin show that it is possible to simulate the transfer of atrazine in a soil-groundwater-river system. However, considering the Seine River basin, various residence times in
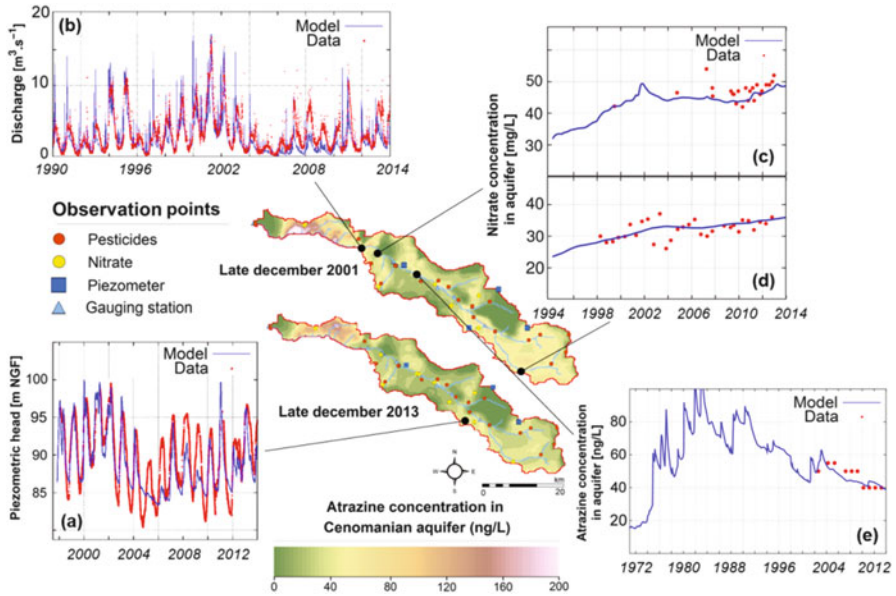
Fig. 7 Modelling results compared to measurements of groundwater levels in piezometers (**a**), river flow (**b**), nitrate (**c**, **d**) and atrazine concentrations (**e**). Maps of simulated atrazine concentrations in the Cenomanian aquifer layer (2001 and 2013). Observed data were extracted from the HYDRO and ADES databases [15, 77]

the vadose zone and aquifers make modelling more complex, and the mosaic of cropping systems must be associated with the diversity of soil types and the thickness of the unsaturated zone [21, 78].

In the first step, a prospective approach was implemented to understand pesticide contamination of groundwater in the Seine basin, again using the ADES database [15], in which pesticide contamination has been documented since 1997. As DEA is the most widely detected pesticide residue in water, it was possible to use this national monitoring database to understand the temporal evolution of the contamination. The mean concentrations of two different periods were compared: the first one from 1997 to 2003 corresponding to the use of atrazine (Fig. 8, left) and the second one from 2006 to 2014 (Fig. 8, right). Data between 2003 and 2005 were considered as a transition period when atrazine was still used by farmers (finishing stocks).

DEA was analysed on 1,436 piezometers, but many wells presented values below the limit of quantification. A value reported as below the limit of quantification was assigned a value of one-half of the limit of quantification. As this limit decreases over time from 0.1 to 0.005 μg L^{-1}, then the mean values can decrease over time due to the limit of quantification even if DEA was never detected. To better represent the evolution of DEA contamination, only mean values over 0.11 μg L^{-1} were considered (Fig. 8). This approach allowed us to focus on contaminated wells. Mean
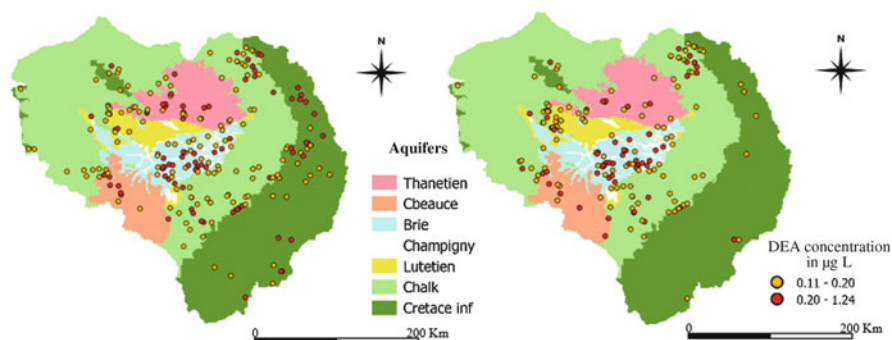
Fig. 8 Mean concentration of DEA above 0.11 µg L^{-1} in boreholes of the Seine aquifers (from ADES database), in the 1997–2003 period (left) and 2006–2014 (right)

concentrations over 0.2 µg L^{-1} are mostly observed in the Brie, Beauce and Champigny aquifers (see locations in Fig. 8) where maximum values were measured before 2003 (0.91, 1.8 and 1.42 µg L^{-1}, respectively). Some wells also show increasing concentrations of DEA over time in the Chalk and Champigny aquifers (i.e. from 0.14 to 0.18 and from 0.20 to 0.26 µg L^{-1}, respectively), whereas the Cretace aquifer shows more decreasing concentrations (from 0.21 to 0.12 µg L^{-1}). However, this cannot be directly extrapolated for the entire aquifer, because the wells did not show the same trend. For the 2006–2014 period, the mean DEA concentrations were 0.123 µg L^{-1}, 0.107 µg L^{-1} and 0.067 µg L^{-1} for the Champigny, Brie and Chalk aquifers, respectively.

A statistical approach was tested to determine the global trend of DEA contamination in each aquifer and the mean concentration in 2030 [79]. The mean values of 270 piezometers that compiled at least ten measurements throughout the period were identified. The linear tendency for each of them was calculated, and uncertainties were estimated successively using a Mann-Kendall test and a bootstrap method [38, 80]. In 2030, the estimated mean concentrations of DEA would be about 0.10 µg L^{-1}and 0.09 µg L^{-1} for the Brie and Champigny aquifers, respectively (Orgeval catchment), and about 0.01 µg L^{-1} for the Chalk aquifer (Vesle catchment). This slow decreasing concentration in the Brie and Champigny aquifers is due to a small number of boreholes (18 and 83, respectively) and occurrence of increasing contamination. In the Chalk aquifer (562 piezometers), the mean concentration would be below the limit of quantification in 2030, but this average does not reflect what could be observed locally.

This prospective method is advantageous because it presents a statistical trend of contamination. However, it is not relevant for other pesticides because data are limited in time and too scarce, even at the Seine basin scale. Therefore, the limit of quantification would have a considerable impact on mean concentrations, and this statistical approach could not be validated.

The next step for evaluating the contamination of surface and groundwaters at the Seine River basin scale will be based on mechanistic modelling, as already implemented on the Vesle basin.

7 Conclusion

Depending on the size of the watershed under study, pesticide use and database monitoring differ.

- At the plot scale, crop rotations and phytosanitary use and application conditions are known and can be combined for precise and adapted monitoring.
- In a catchment area such as Orgeval (100 km^2), the agricultural landscape is more complex. The observed contamination corresponds to major pesticide use. However, homogeneity is still observed due to a similar pedoclimatic context. The response time of the soil-groundwater-river system is fast, and contamination appears quickly and abruptly at the outlet because of drains. Major pesticide inputs can be identified using farmers' logbooks.
- In the Vesle basin (1,000 km^2), the water transfer time from groundwater to the river is longer. The landscape is contrasted, resulting in heterogeneous crops in the basin (alfalfa, annual crops and vineyards). Spatialisation of uses will be of particular importance in this context, and we need to combine agricultural practices (e.g. pesticide treatment) and soil characteristics. In this case, the random distribution of crops considered in our modelling approach of basins may have a considerable impact on the model's outputs. Vineyards receive specific treatments and are well identified in the Corine land cover database; its pesticide applications were therefore correctly located. Modelling also required estimating inputs over at least 30 years, to include the transfer time to the outlet. This retrospective raised the question of the initialisation of the model, which takes a considerable part in the uncertainty of the simulation results. Nevertheless, focusing on specific weeding practices in vineyards and field crops allowed us to estimate the uses of atrazine and to model its transfer. However, working at the sub-annual level would not be realistic at this time.
- At the scale of the Seine basin (75,000 km^2), the hydrogeological context is complex, with several superimposed aquifers, different response times and a patchwork of cropping systems. Monitoring databases are those assembled by the national authority for European framework directive monitoring [15, 81], and they allow only scarce and discontinuous monitoring of pesticide contamination. However, considering only the residues of atrazine, which has been widely used throughout the basin and frequently detected, it is possible to show that some aquifers still have an increasing contamination of atrazine residues despite its prohibition in 2003. Particularly vulnerable groundwaters such as the Champigny aquifer still show an increase in DEA levels, and other studies have shown

that concentrations of the percolating flow to the Chalk aquifer can reach 10 µg L^{-1} [39].

8 Perspectives

The reduction of the water resource contamination by pesticides remains a major issue. The strategy of banning molecules has only shifted the problem to new and unknown substances for which we have not yet identified the environmental effects. Improving water quality and reducing impacts are new challenges involving limiting and banning the use of these new substances. This requires a deep change in agricultural practices and systems. Organic agriculture is a typical agriculture system which bans chemical molecules of pesticides as well as mineral fertilisation. However, this agriculture accounts for only 2% of the agricultural land use in the Paris basin [82].

Even if this solution would be preferable for the environment and human health, buffer zones and grass strips can be used over the short term to reduce pesticide transfer [83–85]. In the case of the Seine catchment, about 20% of arable soils are drained, depending on soil waterlogging characteristics. Sub-surface drained areas are mainly covered with redoxic or reductic degraded luvisol. In this context, the management of sub-surface drained water is important to reducing the impact of agriculture's activities on water quality. An experiment conducted since 2012 near the Orgeval basin led to co-constructing, with local stakeholders, a set of four artificial wetlands implemented between the outlet of sub-surface buried pipes and the receiving waterbody. The ratio between the area of what the farmers accepted to convert into artificial wetland and the total cultivated areas (355 ha) was established at 0.20%. A 3-year evaluation of the removal rate of pesticides from surface water showed a reduction of about 30% of pesticides from agricultural plots and surface waterbodies by artificial wetlands, with, however, a high variability depending on (1) the pesticides' properties, (2) temperature dependency and (3) the hydraulic residence time. By extension of this in situ monitoring, the recommended ratio to adequately design artificial wetlands was evaluated at 1% for an objective of 70% pesticide removal from drained water. However, even if artificial wetlands are constructed at the recommended ratio on the Seine basin, it would not be able to solve pesticide contamination, because a large proportion of pesticides are directly transferred from fields to groundwater.

A mechanic modelling approach would help assess the risk of pesticide transfer in a watershed and explore scenarios of changing agriculture. However, several difficulties have been noted: (1) correctly representing past uses, (2) documenting the long-term behaviour of an active ingredient in a large watershed and (3) identifying the effect of changes in agricultural practices on pesticide transfer.

In that case, other parameters must be taken into account such as trajectories of pesticide uses and landscape changes regarding agricultural activities. The new national BNV-D database indicating sales of pesticides, available since 2008

(identification of substances, annual quantities at the distributor scale), could also help characterise and spatialise pesticide inputs and these changes at the regional scale [21]. This new database provides valuable perspectives for the characterisation of future uses. On the other hand, the characterisation of past practices, in particular those before the 1990s, remains difficult because of the absence of national databases and the disappearance of archival documents (re-structuring, destruction of old archives) and technical knowledge (retirement of advisors) on farms and advisory bodies.

Besides enlarging the modelling approach to the Seine River basin scale, another challenge is coupling pesticide transfer from soils and the groundwater model with the river transport model. Similar developments have been carried out for nitrate transfer in the PIREN-Seine programme (see [86]). Because specific processes for pesticide consideration were already integrated into the STICS agronomic model (especially sorption and degradation), it would also be possible to integrate them into the biogeochemical module in surface water. In any case, pesticide monitoring in rivers and groundwater is essential to compare simulated and observed data.

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