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Article

Transfer Pathways and Fluxes of Water-Soluble Pesticides in Various Compartments of the Agricultural Catchment of the Canche River (Northern France)

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Abstract: Five frequently used water-soluble pesticides (atrazine, diflufenican, metolachlor, pendimethalin, and ethofumesate) were monitored in surface water and groundwater of an agricultural catchment (Canche River) in Northern France for examining the edge-of-field pathways of substances and their characteristic time of transport. The study of surface water contamination was conducted in 2016 through two time scales: continuously over one year at a single location of the catchment and punctually during four seasons at 15 sampling locations along a longitudinal river profile. In addition, groundwater in winter and summer shows a generally low and relatively constant contamination level. Nevertheless, the outflow of pesticides from groundwater results in a background contamination of surface water. In addition to this, a contamination peak above the baseline level is observed in surface water subsequently to the period of substance application on the fields. Our results show that pesticides were essentially transported into the surface water by fast flow components (runoff water). Loss of pesticides during the contamination peak period and long-term monitoring were compared showing that the transport of substances within weeks after pesticides spreading dominates the annual flux of pesticides, except for atrazine which shows a constant background contamination pattern. Low frequency monitoring schemes provide only a partial picture of the contamination state and do not enable to evaluate the true contamination state of such rivers with regard to the fact that 3/4 of the annual load of pesticides are transported in the stream during only 2–3 months.

Keywords: water-soluble pesticides; transfer pathways; Canche River watershed; agricultural catchment; runoff; surface water; groundwater; flux rate

1. Introduction

The exposure of humans to pesticides is related, at least in part, to pesticides' fate and distribution between all compartments of the environment (i.e., atmosphere, soil, surface water, and groundwater). Therefore, understanding the pathways, the persistence, and the distribution of pesticides is of major interest in terms of risk management and for establishing contaminant budgets in the environment. Several edge-of-field runoff studies have demonstrated that significant amounts of pesticides are transported from the agricultural fields to rivers and into groundwater, e.g., [1–6]. Many factors control the transport of pesticides to the surface water such as the nature of the soil, topography, weather conditions such as precipitation, etc., specific pesticide properties, and agricultural management practices,

e.g., [7–10]. In this context, the polar and water-soluble pesticides raise a specific concern because they lead to rapid transfer into the surface water during periods of high runoff and thus to sudden changes in water contamination which may reach unexpectedly alarming levels. By comparison, hydrophobic substances are less problematic than water-soluble pesticides because they are subjected to various retardation processes during their transport in soil that result in a lower contamination of surface water [3].

The aim of this study is to gain a better understanding of the transport pathways from soil to surface water focused on five selected water-soluble pesticides ($\log S > -5.1 \text{ mol L}^{-1}$) that are present in the Canche watershed (France): Four herbicides (atrazine, diflufenican, metolachlor, and pendimethalin) and one fungicide (ethofumesate). There are various processes through which these pesticides can dissipate from an application area into the environment and thus the surface water. Previous work reported significant stream contamination by 29 antibiotics and drug residues [11]. However, to our knowledge, no study reports on the contamination state related to pesticide use although the catchment hosts an aquifer that supplies 97% of the water consumed in the Artois-Picardie Basin [12].

In the present study, the following two main transport processes are considered: (a) the transport from the agricultural field to the surface water mediated by the surface runoff with a travel time in the order of some meters per minute [7], and (b) the transport after leaching in groundwater by seepage through the unsaturated zone. We attempt to analyze the contribution of each flow component to the transport of pesticides. For this purpose, monitoring of pesticide concentrations was conducted in 2016 on two different time scales: (1) continuously over a one year period at a single location of the river, and (2) during four seasonal campaigns at 15 locations along the Canche River. Groundwater contamination was examined during summer and winter in 14 piezometers in the watershed. Finally, the calculated annual fluxes of contaminants in the Canche River were compared to the suspected amount of substances spread on the agricultural fields. This study provides valuable data for elucidating the dynamics of water-soluble pesticides at the catchment scale and raises some recommendations for improving the future monitoring schemes of pesticides.

2. Material and Methods

2.1. Sampling Sites and Strategy

The Canche River is located in Northern France. It is 96 km long and collects the water of a catchment of 1274 km². It presents seven main tributaries from upstream to downstream: Ternoise, Planquette, Créquoise, Bras de Bronne, Course, Dordogne, and Huîtrepin that are all located on the right bank of the main stream (Figure 1). The mean annual rainfall comprises $1000 \pm 150 \text{ mm}$ and the mean annual temperature is 11 °C. Altitudes ranges from 0 to 207 m and catchment slopes are in the range 2–3%. The catchment is mainly dominated by agricultural land use (80%) and affected by water erosion leading to highly variable specific sediment yield (29 to 185 kt year⁻¹ between 1999 and 2016) at the outlet of the Canche River [13].

The pesticide occurrence in the catchment was examined during one hydrological year by analyzing the pesticides content of the surface water and the suspended particulate matter collected during four seasonal campaigns (February, May, July, and November 2016) at eight locations along the river (*Canche sites 0–7*) and at seven sites situated in the major tributaries near their confluences (sampling points labeled with the name of the tributaries; Figure 1, Table S1). In addition, from February 2016 to April 2017, the dissolved concentration of pesticides was monitored at a selected location of the watershed (*Canche 5*) through 40 water grab samples with at least three sample collections per month. At the *Canche 5* sampling site the water contamination level was also continuously monitored between April 2016 to March 2017 by a successive exposure of 24 triplicates of passive samplers exposed to the water column for periods ranging between 15 and 30 days. The passive sampler devices were developed for the quantitative sampling of mid-polar compounds ($2 < \log P < 5$; for further reading please see [14]). In the field, sampling devices were exposed at 3 m of the river banks and 50 cm depth. In addition, the contamination of groundwater was measured at 15 monitoring wells of the catchment

investigating the shallow aquifer (during low water level in July and August 2016 and high water level in February and March 2017). In surface water and piezometers, water sampling collection consisted of a 2.5 L grab sample in amber glass bottles expressly brought to the laboratory for extraction and analysis (see Section 2.5). The suspended particulate matter (SPM) analysis was conducted on the same collected water sample after separation by filtration through GF/F filters (pore size 0.45 μm). Passive samplers and water samples were always analyzed within 24 h after collection.

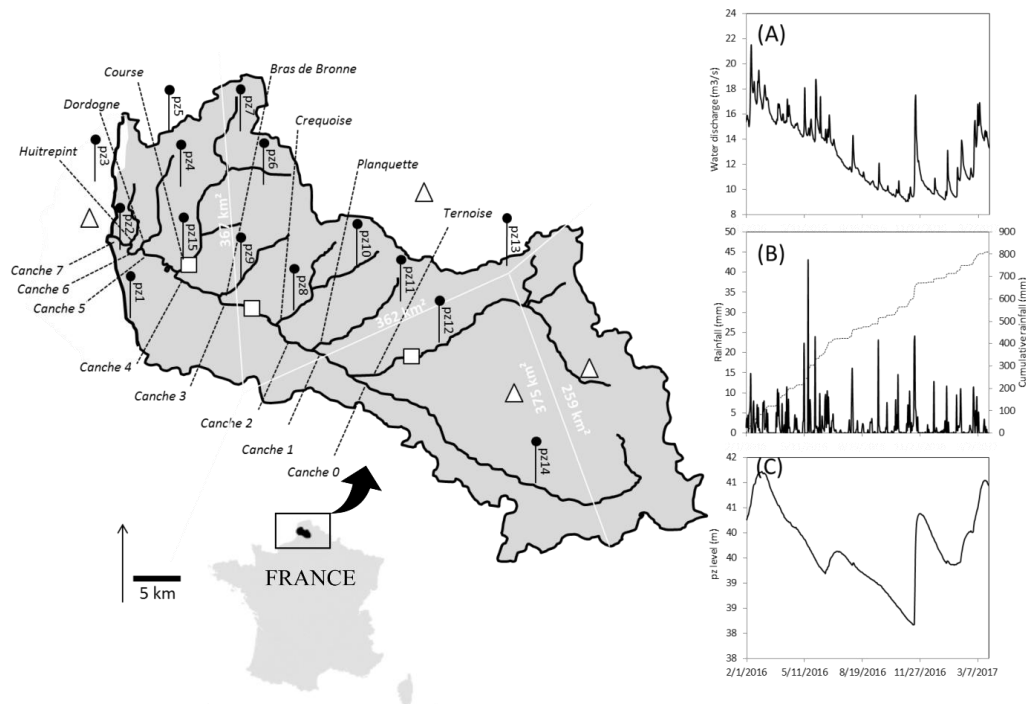


Figure 1. Map of the study area with the Canche River and its main tributaries. Dashed lines point to surface water sampling locations and filled black circles denote ground water sampling locations. The positions of rainfall gauges and discharge gauges are shown as triangle and square markers, respectively. White lines refer to the boundaries between Thiessen polygons used to determine the average rainfall on the catchment. (A) Time series of the water discharge ($\text{m}^3 \text{s}^{-1}$) at the gauging station on the main stream (data from Water Agency Artois-Picardie); (B) average rainfall (mm) on the catchment (data from Météo France); and (C) piezometric level (m) at pz 10 (data from Water Agency Artois-Picardie).

2.2. Hydrology of the Study Area

2.2.1. The Canche River Catchment

The 54 year-long average water discharge at the estuary of the Canche River is ca. $21 \text{ m}^3 \text{ s}^{-1}$ [15]. For the needs of this study, water discharge at each sampling location was calculated on the basis of measurements of water discharge at three gauging stations located along the river course. The gauging stations are located as follows: near Canche 3 (on the main stream) and on Ternoise and Course tributaries (Figure 1; data from Water Agency Artois-Picardie).

Flow discharge for the ungauged catchments Q_{ungauged} was calculated assuming similar hydro-climatological regimes in the entire Canche River catchment. Values were extrapolated from the closest monitoring station by multiplying the value Q_{gauged} with the appropriate fraction related to the ratio between the closest catchment area (A_{ungauged}) and the catchment area at the monitoring station A_{gauged} :

$$Q_{\text{ungauged}} = Q_{\text{gauged}} \times \frac{A_{\text{ungauged}}}{A_{\text{gauged}}} \quad (1)$$

with Q representing the discharge in $\text{m}^3 \text{s}^{-1}$ and A as the area of the catchments in km^2 .

According to [16], this method provides robust results for ungauged catchments (Table 1). Cross-validation with the high-frequency monitoring station on the Canche River catchment evaluated a 17% associated error (Figure S1; for further detail see also [17]).

The cumulative annual rainfall at the city of Croisette—in the center part of the study area—was 781 mm in 2016. The daily average rainfall on the catchment was calculated from the measured values at three locations in the catchment (Croisette, Saint-Michel-sur-Ternoise, Le Touquet) and one location 5 km to the northeast of the catchment (Radinghem; data Météo France). The average rainfall within the catchment was estimated by a weighted arithmetic mean where weights were the Thiessen polygons area of each respective gauge (Figure 1).

The study area is characterized by two aquifer units separated by an impervious layer of Marl facies from the Middle Turonian (Figure 2). The first shallow aquifer unit is about 5–50 m deep according to seasonality and topography [18], and is composed of white chalk with flints of the Upper Turonian-Senonian. The second deeper aquifer unit is composed of Cenomanian chalk without flint [19]. In the present study, only the upper shallow aquifer unit is investigated, due to its dominating role in water supply for the Artois-Picardie Basin. It constitutes a complex media with a double porosity due to the presence of fractures [20]. The transmissivity for this shallow aquifer unit is about $7 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ [19], and the storage coefficient lies between 5% and 7% [21].

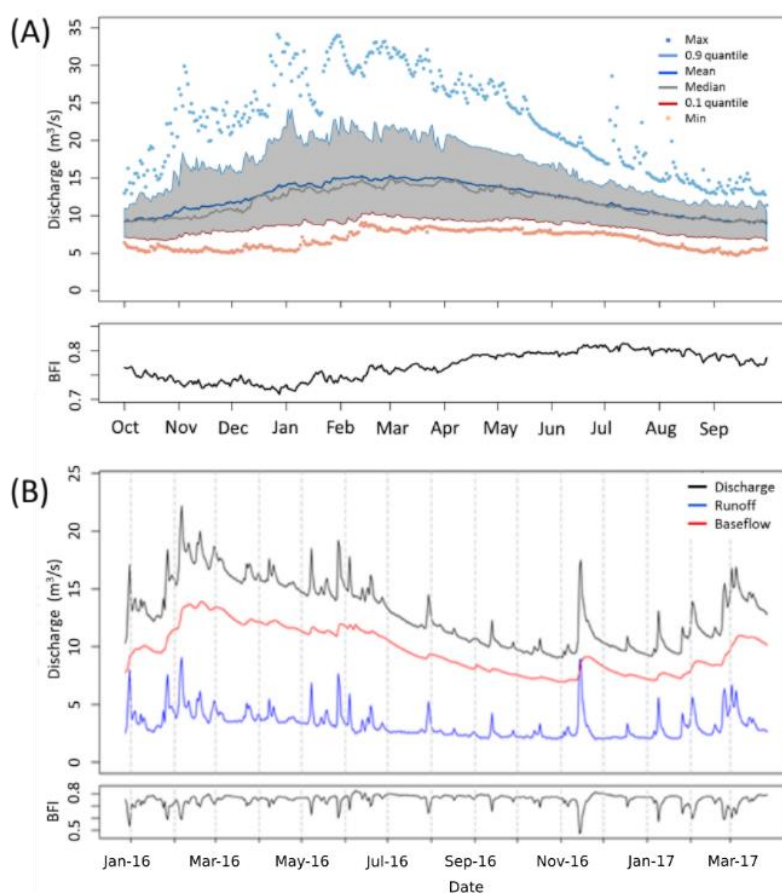


Figure 2. (A) Average flow regime of the Canche River and BFI over 44 years, (B) and the results of hydrograph separation over the study period.

Table 1. Hydrological parameters and land use of the Canche watershed for the studied period. All sampling sites named as “Canche x” refer to sampling points on the main stream of the river.

	Distance from the English Channel	Catchment Area at the Sampling Location	Cultivated Area	Repartition of the 3 Main Crops (Weat/Maize/Barley)	Distance from the Sources	Water Discharge * (Feb./May/July/Nov.)	Average Particulate Matter Content
	km	km ²	km ²	%	km	m ³ s ⁻¹	mg L ⁻¹
<i>Canche 0</i>	43.5	330	187	27/15/27	-	9/7/5/5 ^a	25 ± 13
<i>Ternoise</i>	45.5	318	109	28/21/17	41	7/5/5/4 ^b	34 ± 28
<i>Canche 1</i>	42	658	301	27/17/23	-	16/13/10/8 ^a	28 ± 12
<i>Planquette</i>	39.2	65	31	56/24/7	12	1/1/1/1 ^b	18 ± 10
<i>Canche 2</i>	35.7	750	344	30/18/21	-	17/13/11/9 ^a	34 ± 30
<i>Créquoise</i>	32.8	83	15	12/45/12	15	2/1/1/1 ^b	20 ± 16
<i>Canche 3</i>	31.5	846	364	29/19/21	-	19/15/12/10 ^a	28 ± 19
<i>Bras de Bronne</i>	25.4	45	25	44/26/6	11	2/1/1/1 ^c	34 ± 32
<i>Canche 4</i>	23.2	910	412	30/20/20	-	20/16/13/11 ^a	30 ± 14
<i>Course</i>	19.5	180	69	30/30/23	24	6/4/3/2 ^c	26 ± 20
<i>Canche 5</i>	18.2	1110	500	30/21/20	-	26/20/16/13 ^a	18 ± 21
<i>Dordogne</i>	11.9	39	23	51/16/7	10	2/1/1/1 ^c	33 ± 44
<i>Canche 6</i>	9.7	1170	534	31/21/20	-	28/21/17/14 ^a	43 ± 42
<i>Huitrepin</i>	9.1	24	12	56/11/13	8	2/1/1/1 ^c	36 ± 25
<i>Canche 7</i>	7.5	1200	549	32/21/20	-	29/22/18/14 ^a	42 ± 39

* Water discharges were extrapolated from the measured discharge at: ^a *Canche 3*, ^b *Ternoise*, ^c *Course*.

2.2.2. Hydrograph Separation

The stream flow is considered to be composed of (1) the runoff that travels quickly to the stream after rain events, and (2) the base flow which comes from the aquifer unit (Figure 2). The base flow is traditionally estimated through the analysis of stream flow time-series (i.e., hydrographs), separating stream flow into runoff and base flow based on various automated methods [22–25]. While the field data of baseflow and runoff are unknown, the recursive digital filter method is a stable, reproducible, and objective method of base flow separation when compared to smoothed minima methods [26,27] compared several methods for estimating base flow and reported that the Eckhardt two parameters digital filter method yielded base flow index (BFI) estimates comparable to those obtained using tracers. This filter assumes a linear relationship between base flow and aquifer storage during the recession period when the high frequency component ceases [24]. This assumption leads to the model of an exponential baseflow recession when there is no groundwater recharge [24]:

$$b_k = y_0 e^{-k/\tau} = \alpha y_0 \quad (2)$$

where b_k and y_0 are, respectively, the baseflow at time step k and the peak streamflow at the beginning of the recession period, k is the time step length, τ is the characteristic time constant and the α is a recession constant parameter. It describes the rate at which the streamflow decreases over the time following a recharge event:

$$\alpha = e^{-\Delta t/\tau} \quad (3)$$

Eckhardt's filter is given by:

$$b_k = \frac{(1 - \text{BFI}_{\max}) \times \alpha \times b_{k-1} + (1 - \alpha) \times \text{BFI}_{\max} \times y_k}{1 - \alpha \times \text{BFI}_{\max}} \quad (4)$$

where y_k and b_k are, respectively, the total streamflow and the estimated baseflow at time step k , and BFI_{\max} is the maximum base flow index which represents the ratio of total baseflow to total streamflow. This parameter is normally given according to the properties of the stream and its aquifers, and it is suggested that BFI_{\max} is equal to 0.8 for a perennial stream with porous aquifers, such as the Canche River [24]. For the present work, the hydrograph separation was only calculated at *Canche 5* because it is the reference location where the contamination was continuously monitored during the study period. The α parameter was determined by the recession curves over the period from 1963 to 2017. The minimum number of days required to detect a recession period was set to 5. Following this procedure, an α value of 0.97 was estimated (Figure S2).

The baseflow separation was then performed, starting from May 1973 because it was the driest identified period, thus at this date the baseflow represented the entire discharge. The long term streamflow pattern at *Canche 5* was examined for the period between 1973 and 2017 (Figure 2A). The annual mean discharge for this period was $12 \text{ m}^3 \text{ s}^{-1}$ and it was higher from January to May. Baseflow examination of the 44 years of daily discharge produced an average baseflow index BFI_{mean} of 0.77 (consistent with perennial stream with porous aquifer). By difference, the runoff fraction was 0.23. The BFI showed an obvious seasonal variation: The lowest BFI typically occurred in December (0.71), and increased gradually until July (0.81) when the maximum was reached. A similar BFI was observed during the study period in 2016 with an average runoff fraction of 0.24 (Figure 2B).

2.3. Land Cover and Agricultural Practices

The agricultural crops and the crop acreage are both key parameters driving the occurrence of pesticides in the catchment. They were primarily estimated from a 2011–2013 survey of the French government based on SPOT 5 images and an annual survey carried out on farmers (European Council Regulation No. 1593/2000). About 80% of the catchment area is used for the agricultural activity (excluding grassland), with an intensive production of soft wheat, durum wheat, barley, rapeseed,

sugar beet, maize, and potatoes [28]. The dominant soil type in the watershed is neoluvisoil or rendosol on the plateau and rendosol or calcosol on the slopes [29], the soil moisture regime is udic. In Table 2, the distribution of the three dominating agricultural crops in each sub-basin is given as a percentage of the cultivated area (excluding grassland). On average, the main agricultural crops are wheat ($34 \pm 10\%$), maize ($22 \pm 6\%$), and barley ($17 \pm 7\%$).

Table 2. Pesticides investigated in the present study and the suspected used in the study area, with a summary of the average dissolved concentration in surface and ground water.

	Atrazine	Diiflufenican	Ethofumesathe	Metolachlor	Pendimethalin
Targeted crop	Banned	Wheat/Barley	Sugar beet	Maize	Wheat/Barley
Spreading period	Banned	Nov.; April	April; May	April; May	Nov.; April
Application rate (kg/km ²)	Banned	12	250	216	90
Crop acreage (km ²)	Banned	283	24	114	283
Estimated annual spreading (T)	Banned	3	6	25	25
Log S (mol/L) * (SPM)/(water)	-3.9	-5.1	-3.1	-3.4	-3.9
Ground water contamination (min–median–max) ng/L	2–13–49	<1–0.1–1	<1–0–0.9	<1–0.3–3.6	<1–0–1.9
Surface water concentration during seasonal campaigns (min–median–max) ng/L	7–11–21	<1–3–52	<1–1–37	<1–2–352	<1–0–101
Surface water concentration at <i>Canche 5</i> (min–median–max) ng/L	8–11–16	<1–2–13	<1–0.4–61	<1–2–148	<1–1–10

* Data from VCCLAB, Virtual Computational Chemistry Laboratory, <http://www.vcclab.org>, 2005 [30].

2.4. Selection of Targeted Substances

According to the dominant crops, the recommended plant protection programs, and the results of the screening conducted from samples collected at *Canche 5* sampling point during the year 2015 (for further details see [14]), five pesticides were selected as representative compounds for this study. The shortlisted pesticides include four herbicides (atrazine, diflufenican, metolachlor, and pendimethalin) and one fungicide (ethofumesate). Since the study focuses on the fast transfer of compounds from the agricultural land to the surface water, only hydro-soluble compounds were chosen. It is noteworthy that the conclusions of this study highly depend on the compound properties and that hydrophobic compounds may have different transport pathways [3] than those of the selected hydrophilic compounds. Assigning each substance to a given agricultural crop is difficult because the same active substance can be applied to different crops (e.g., diflufenican and pendimethalin are used for wheat as well as for barley). However, for the majority of the substances, the dominant period of use, the corresponding crop, and the application rate can be identified, as an initial approximation, from the plant protection programs recommended by the manufacturers (Table 2).

2.5. Sample Preparation and Geochemical Analyses

After the water sample collection, 1 L was filtered through GF/F filters (Fischer Scientific, Illkirch Cedex, France) pre-cleaned by calcination at 400 °C during 12 h. The extraction of the dissolved pesticides consisted in spiking the filtered water with an internal standard solution (atrazine-d5, diflufenican-d3, metolachlor-d6, and pendimethalin-d5, in methanol) and passing the sample through a solid phase extraction cartridge (HyperSep™ Retain PEP; Fischer Scientific, Illkirch Cedex, France) successively preconditioned with 10 mL of dichloromethane (DCM), 10 mL of methanol (MeOH), and 10 mL of ultrapure water. Once the water sample was entirely percolated, the cartridges were

dried under vacuum for 15 min and analytes were recovered by eluting compounds successively with 10 mL of MeOH and 10 mL of DCM. The final extracts were subsequently reduced in volume and the solvent was changed to 100 μ L of ethyl acetate prior to gas chromatography analyses. All solvents were supplied by Fischer Scientific.

The collected particulate matter (SPM) on the GF/F filter was extracted after freeze-drying by immersion in 30 mL of DCM supplemented with the internal standard mixture. After a first extraction period of 24 h, the DCM extracts were collected and replaced by 30 mL of fresh solvent. After a second extraction period of 24 h, both extracts were homogenized, reduced in volume and the solvent was changed to 100 μ L of ethyl acetate prior to gas chromatography analyses.

Similarly, the extraction of passive samplers was conducted after recovery of the binding gel following the same procedure as for the particulate matter extraction (the detailed procedure is provided in [14]).

All extracts were analyzed by gas chromatography coupled to a mass spectrometer (GC-MS; Agilent Technology 7890B series coupled to 5977A mass spectrometer). One microliter of extract was injected at 250 °C in a split less mode on a 30 m column (HP5MS-UI 30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness,) using helium as a carrier gas at 1.3 mL min⁻¹ (constant flow rate). The initial oven temperature program was 55 °C for 0.5 min and was then increased at 10 °C min⁻¹ increments up to the maximum temperature of 300 °C which was held for 10 min. The GC-MS transfer line temperature was set at 300 °C. The source temperature and the quadrupole temperature of the MS were set to 270 °C and 150 °C, respectively. The mass spectrometer was operated in single ion monitoring mode for the selective detection of contaminants: atrazine (m/z = 200, 215), diflufenican (m/z = 394, 266), ethofumesate (m/z = 286, 207), metolachlor (m/z = 238, 162), and pendimethalin (m/z = 252, 281), and as for the internal standards: atrazine-d5 (m/z = 205, 220), diflufenican-d3 (m/z = 269, 397), metolachlor-d6 (m/z = 166, 242), and pendimethalin-d5 (m/z = 255, 286; note that here m is the mass of the molecule and z is the charge). The dwell time was set at 50 ms and a maximum number of six ions were simultaneously monitored to improve the detection limit of the method. For each compound the identification and quantification in the samples were ensured by comparison with a standard certified solution of the: (1) retention time of the signal, (2) presence of both characteristic masses, and (3) abundance ratio between signals of both masses.

2.6. QA/QC and Detection Limits

For all sample types, the detection limit was defined as 10 times the blank level measured for each sample analysis series. If the substance was not detected in the blank, the detection limit was set on the level required for a signal to noise ratio of three. On the basis of these criteria, the typical detection limit was below 1 ng L⁻¹ for water samples and passive samplers and was below 10 ng g⁻¹ for SPM samples.

Precision and accuracy of water sample analysis were evaluated by analyzing river water spiked with the targeted pesticide at low (0.1 ng L⁻¹) and high (1.0 ng L⁻¹) concentrations. For all substances, the relative standard deviation of five replicated analyses was less than 19% at both concentration levels. For the pesticides with dedicated internal standard (atrazine, diflufenican, metolachlor, and pendimethalin) the relative standard deviation dropped to 12% or below.

Spiking of particulate matter or binding gel of passive samplers for evaluating the recovery rate was critical because it did not ensure that the solid matrix was homogeneously contaminated as expected for a fluid sample. Therefore, variability of analysis method was performed by examining the relative standard deviation of six different samples simultaneously collected and separately extracted and analyzed. The variability was evaluated to 34% for particulate matter and to 22% for passive sampler analysis respectively.

2.7. Laboratory Determination of the Transfer Kinetics between Suspended Particulate Matter and Water Samples

Analyses of SPM and water samples during the seasonal campaigns were used to evaluate whether the pesticides were predominantly transported in the dissolved or solid phase. Evaluating pesticide distribution ratio between the SPM and the dissolved phase for examining if dissolved transport prevails on the SPM-mediated transport is a suitable approach only if the equilibrium of pesticides between both phases is at any time complete. However, during storms and high water discharge, heavily-contaminated soil particles may be eroded and subsequently transported in the water column [2]. If contaminants remain bounded to the particulate matter, in case of slow equilibration kinetics, the contaminant flux mediated by the SPM may dominate the flux of dissolved contaminants.

In order to evaluate the kinetics of the equilibration and to what extent the SPM mediated transport are significant, the required time for contaminants to desorb from SPM to the surrounding water was determined by a laboratory experiment: 80 g of wet SPM collected at *Canche 5* sampling site were mixed during one week in 3 L of water spiked with 800 µg of each of the selected pesticides. After this period, SPM was decanted and the overlaying mirror water was discarded. The SPM were then expressly immersed in a second tank containing 80 L of fresh water. During the following 295 h, the water contamination was regularly measured to evaluate the transfer kinetics of contaminants from the sorbed state to the dissolved phase.

3. Results and Discussion

3.1. Distribution of Pesticides between the SPM and the Dissolved Phase

The contamination ratio between the SPM and the dissolved fraction was determined from the four seasonal campaigns at each of the 29 sampling sites. On average, the concentration ratio reached $4442 \pm 14\%$ for atrazine and $6908 \pm 22\%$ for diflufenican (on a mass basis). The distribution ratios for the other investigated compounds are not reported here because they were below the detection limit level in the SPM samples. Scaled to the average load of SPM suspended in the water column ($32 \pm 20 \text{ mg L}^{-1}$), only 8% of the total atrazine contained in a given volume of raw water is sorbed to the SPM and travels with it. Comparable behavior is observed for diflufenican, the most hydrophobic compounds, with a value of 18% of sorption on the SPM. The distribution ratio of the compound depicts that the dissolved transport still dominates, published studies show that these are compounds showing partition coefficients with organic carbon below 1000 which are not predominantly sorbed to SPM [1,31]. It might be possible to some extent, that some hydrophobic substances could have been omitted by the screening mentioned in Section 2.4. Therefore, a more detailed analysis of the SPM samples would give more insight on the presence of substances that might be missing in the dissolved fraction.

Another aspect to consider is the equilibration kinetics of the substances between the dissolved fraction and the SPM-sorbed fraction to ensure that the concentration ratios mentioned above are valid throughout the entire catchment. In case of slow equilibration kinetics, an increase/decrease of the transport of pesticides mediated by the SPM may occur at some locations of the river. On the contrary, if equilibration kinetics is by far faster than the SPM travelling time in the river, the concentration ratio measured from the collected natural water should be considered as realistic along the river. The laboratory experiment of kinetics exchange of substances between the SPM and the liquid phase shows that the doubling time required for equilibration is in the order of a few minutes for all compounds (Figure S3). Based on the estimated water velocity at *Canche 5* (water discharge/river cross-sectional area), one min travelling time is equivalent to 27 m of river length, which corresponds to 0.03% of the total river length. Thus, the equilibrium of contaminants between the water and SPM can reasonably be assumed in the river since it is reached after a period much shorter than the typical residence time of particles in the river. In conclusion, because the selected set of compounds appears to be relatively hydro-soluble, and because equilibrium of the substances between water and SPM is

achieved all over the Canche River, only the dissolved transport of substances is considered in the further discussion. When it is required, the flux mediated by the SPM could be easily estimated by using the appropriate ratio of pesticide partitioning and the average SPM content.

3.2. Mass Balance of Pesticides from Seasonal Campaigns

The flux of a specific pesticide corresponds to the mass of the substance that is transported through a given section of the river during a specified time period. The daily dissolved flux of each pesticide at each sampling point of the seasonal campaigns was calculated as the product of the water discharge (Table 1) and the measured dissolved concentration in the water samples (Table S3). According to this calculation, all dissolved pesticide concentrations below the detection limit (1 ng L^{-1}) were set to zero. The calculated fluxes differ significantly depending on the substance, the tributaries and the season of the campaign. For instance, at the same sampling location (*Canche 5*) the seasonal fluxes are in the range of $11\text{--}27 \text{ g day}^{-1}$ for atrazine, $1\text{--}5 \text{ g day}^{-1}$ for diflufenican, $<0.8\text{--}14 \text{ g day}^{-1}$ for ethofumesate, $1\text{--}37 \text{ g day}^{-1}$ for metolachlor, and $<0.8\text{--}10 \text{ g day}^{-1}$ for pendimethalin (Table S3). Regarding the spatial variations, during the campaign of May 2016, fluxes are in the range $1\text{--}21 \text{ g day}^{-1}$ for atrazine, $0.1\text{--}6 \text{ g day}^{-1}$ for diflufenican, $0.3\text{--}23 \text{ g day}^{-1}$ for ethofumesate, $0.2\text{--}50 \text{ g day}^{-1}$ for metolachlor, and $<0.8\text{--}3 \text{ g day}^{-1}$ for pendimethalin depending on the respective sampling site (Figure 3; Table S3). This significant variability results from the large difference in water discharge between sampling locations albeit in some cases similar water concentrations are observed (e.g., atrazine).

The discrepancy between the summation of fluxes of two tributaries and the flux at the closest effluent point is indicative of the mass balance of the compounds. For all compounds, the analysis of the mass balance indicates that they can be considered conservative under the conditions and on the time scale of substance transport and that no significant input or loss occurs between the different sampling locations (Figure 3; Table S4). This observation is at least in part attributable to our sampling scheme that investigated all main tributaries of the catchment. However, it should be noted that experimental errors and uncertainties on fluxes (32%) may hide small additional input or loss of substances.

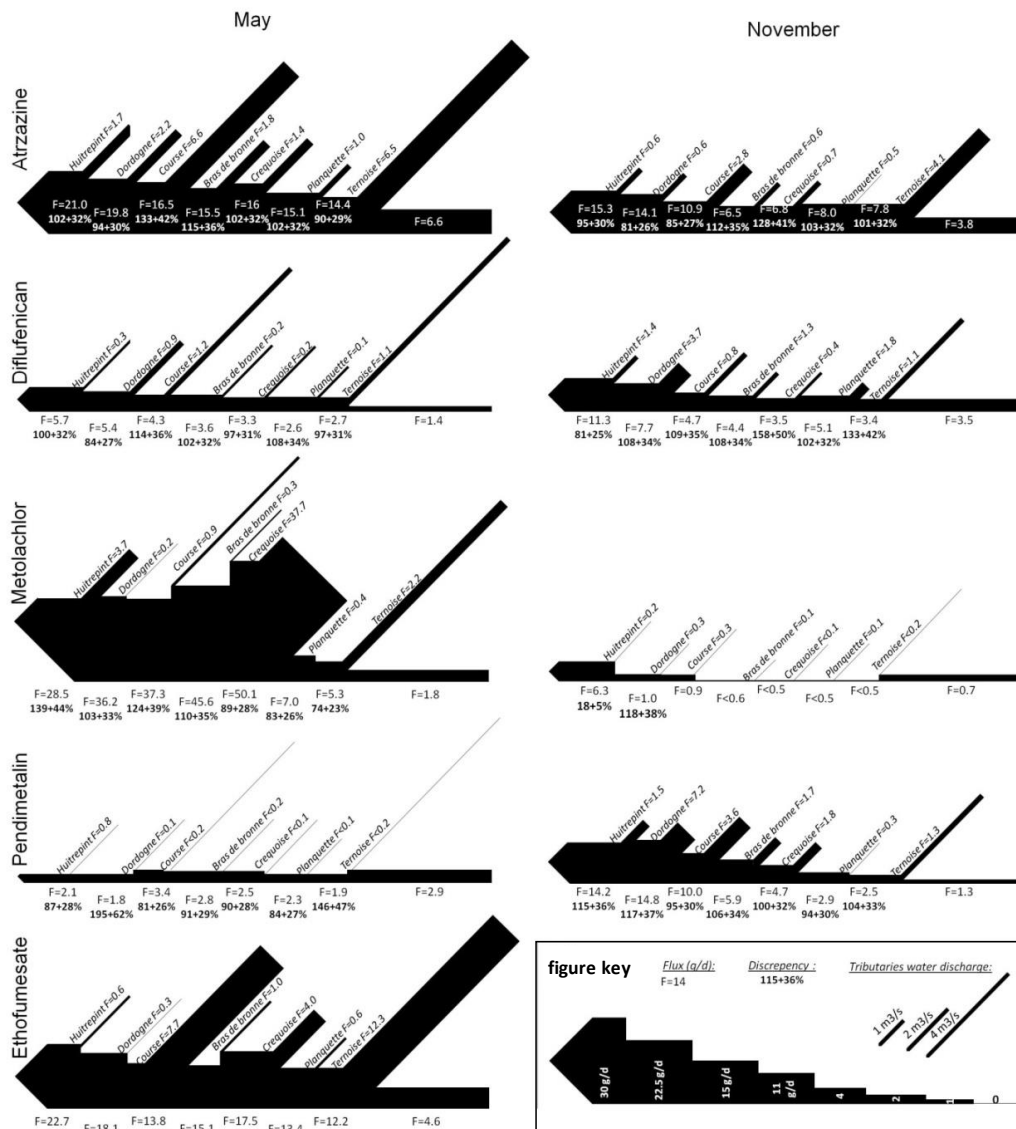


Figure 3. Sketches of cumulative mass balance analysis for May and November 2016 seasonal campaigns along the Canche River transect. For clarity, sketches of February and July 2016 investigated periods are not shown here. In addition, during February and July 2016 diflufenican and pendimethalin were not detected or at too low level for reliable mass balance analysis. Data of the missing campaigns is provided in Tables S3 and S4. For figure reading, please note that the widths of arrows are proportional to the flux of the respective compound and lengths of arrows are proportional to the water discharge (compare also to the example given in the “figure key” in the right lower window). Therefore, wide and short arrows refer to the highest concentrations of dissolved substances for which the toxicological effect is expected to be the most important. The bold numbers indicated the discrepancy between the sum of tributaries and the flux at the closest effluent point (expressed in percentage).

3.3. Temporal Trends of the Pesticides Fluxes

The specific flux is the pesticide flux in the water sample divided by the agricultural surface of the corresponding catchment, and indicates the most impacted locations for each substance. During May 2016 the Créquoise tributary shows a higher specific flux of ethofumesate and metolachlor than during the other seasonal campaigns. This could be assigned to the spreading of the substances on sugar beet and maize in the corresponding area at that time of the year (Table 2). In the same way, diflufenican and pendimethalin, both recommended for plant protection programs of wheat

and barley in autumn/winter, show hot-spot contamination in the Huîtrepin tributary in November 2016 (Figure 4). For the four seasonal campaigns, the observed contamination state corresponds to a snapshot measurement. It probably differs greatly from the contamination state a few days before or after the sample collection. Most probably, a similar high contamination peak occurs in another tributaries a few days before or after the sampling campaigns due to differences in spreading days. This is even more evident if one considers that the Huîtrepin and Créquoise do not have large areas planted with crops compared to the other tributaries.

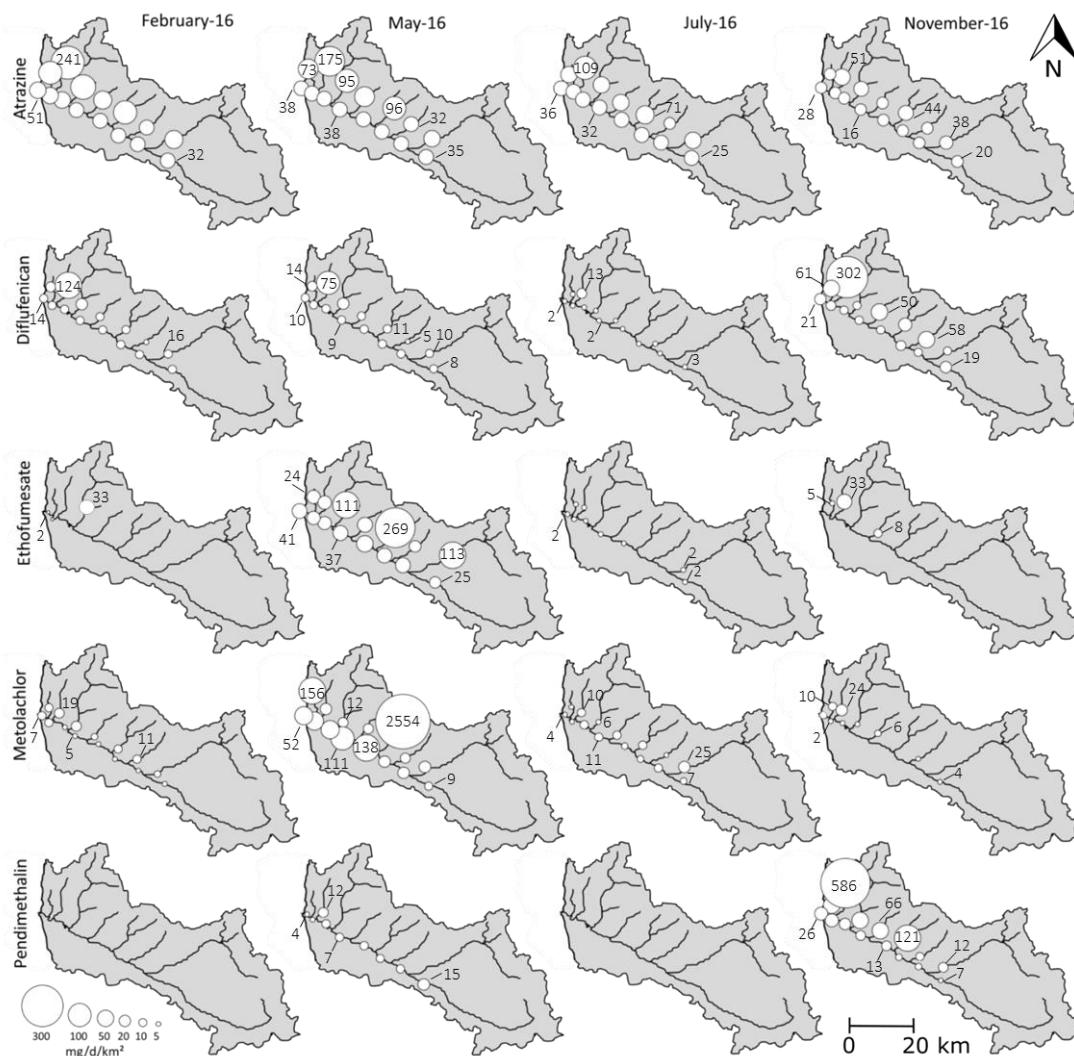


Figure 4. Map of the specific flux during seasonal campaigns ($\text{mg day}^{-1} \text{ km}^{-2}$; see also Table S2).

Regarding atrazine, which was extensively used during the 1990s and has been banned in Europe since 2004, is still detected in surface and ground water samples and shows quite constant concentration levels throughout the entire catchment and over the year. Consequently, the specific flux of atrazine is similar for all sampling locations and campaigns indicating that the contamination has reached a background level (diffuse contamination) in contrast to the other investigated pesticides (Figure 4; Table S5). This suggests that pesticide detection in a river is not only controlled by the chemical properties and the environmental conditions but is also highly influenced by the application practices and their subsequent environmental inheritance. This highlights that using punctual seasonal campaigns for establishing a general diagnostic of the chemical state of a river can be considered only to a limited extent, e.g., [32], and might lead to uncertainties about the assessment of water contamination.

On the contrary, a sampling point close to the river mouth, such as our study site *Canche 5*, provides a more representative evaluation of the overall contamination because it focuses on a large fraction of the catchment (92% of the full catchment area) and is less subjected to rapid changes due to the integrating effects of numerous tributaries. Coupling the discrete grab samples with the integrative passive sampling technique was assumed to allow the continuous monitoring of substance fluxes at *Canche 5* along the studied period. A detailed comparison of the measured concentration levels by passive samplers and grab samples is provided in supplementary material (Figure S3).

For the determination of pesticide fluxes over an extended period, the passive sampler approach is an improvement over the conventional discrete sampling method as it allows, without interruption, the determination of the averaged water contamination [6]. Combined with the estimated water discharge at *Canche 5*, the cumulated flux of the substances was calculated for the studied period from April 2016 to March 2017 (Figure 5). The maximal fluxes were observed during the pesticides spreading period (i.e., spring for metolachlor and ethofumesate and spring and fall for diflufenican and pendimethalin). Consistently with the observed almost constant dissolved concentration of atrazine, its flux remains almost constant throughout the year. A small increase is observed during the high-water period due to the water discharge increase by a factor of 1.6 in comparison to the low-water period. In contrary to the other pesticides, no contamination peaks were observed for atrazine.

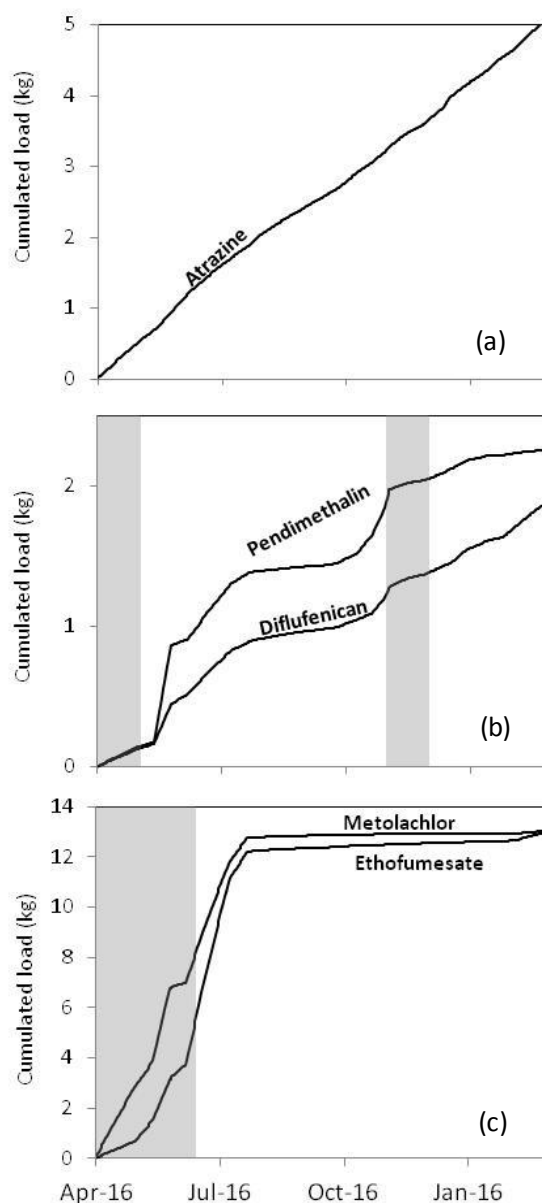


Figure 5. Cumulated fluxes for (a) atrazine, (b) pendimethalin and diflufenican and (c) metolachlor and ethofumesate at *Canche 5*, from continuous monitoring by passive samplers. Values were normalized to May 2016 baseline. Grey areas refer to the estimated application period of the corresponding substances.

The annual cumulated flux of pesticides can be ranked as follows: metolachlor > ethofumesate > atrazine > pendimethalin > diflufenican. During the study period, a total of 35 kg of these pesticides were discharged to the English Channel. Metolachlor, ethofumesate, and atrazine account for more than 88% of the total discharge. Finally, for nearly all detected pesticides (with the exception of atrazine), more than 3/4 of the total annual flux occurs during the contamination peaks even though it encompasses only 2–3 months of the investigated year (Figure 6).

Assuming that metolachlor was only spread on maize and ethofumesate on sugar beet, the specific flux of metolachlor would be about 122 kg km^{-2} of cultivated maize whereas the specific flux of ethofumesate would correspond to 621 kg km^{-2} of cultivated sugar beet. On the basis of the recommended application rate and the acreage for each crop, the annual amount of metolachlor and ethofumesate spread within the basin taken at *Canche 5* is estimated to be 23 t and 5 t, respectively. These values indicate that only between 0.06 and 0.25% of the active substance is found in surface water. This range of values is in agreement with earlier studies on the presence of these pesticides in

runoff water from the edges of agricultural fields, and in surface waters draining small agricultural watersheds e.g., [1]). For diflufenican and pendimethalin, it is more difficult to assign substances to a specific crop and agricultural surface (both are used for wheat and barley crops), therefore, similar comparisons were not made.

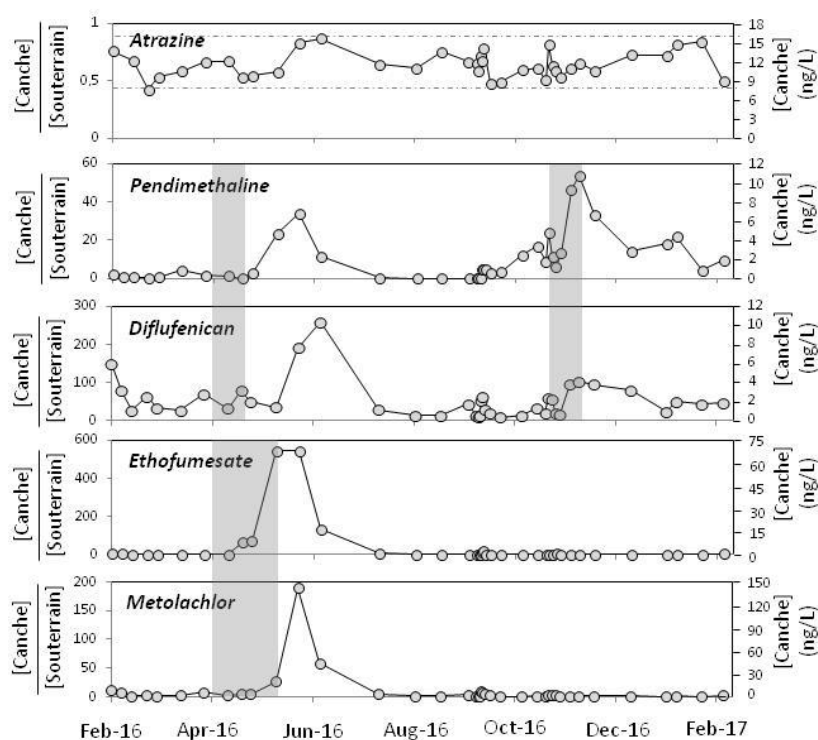


Figure 6. Surface (“Canche”) water to groundwater (“Souterrain”) concentration ratio for pesticides at Canche 5 (left y-axis). Additionally, as shown, the corresponding dissolved concentration (right y-axis). Grey areas refer to the suspected spreading period.

Any change in crop acreage, pesticides used on particular crops, or in application rates between the time the information on practices was collected (2011–2013) and the study period (2016) can be suspected to affect the accuracy of our interpretation. However, the background contamination probably results from pesticides that have been spread out several years before this study. Therefore, the background contamination reflects the historical substance usage rather than the practice of the current year and no direct link is expected with the recent practices in 2016. On the contrary, the contamination pulses in the river in 2016, which likely result from the pesticide spreading of the current year, will be subjected to the differences with the 2011–2013 survey. However, because the study focuses on the watershed scale, it is unlikely that this uncertainty significantly affects the results and the presented conclusions. Locally, crop rotation could induce differences in pesticide runoff losses between years, while no significant difference is expected between years in large watersheds, where changes in agricultural crop are smoothed due to the integrating effects of the different tributaries.

3.4. Ground Water Contamination in the Canche Catchment

Contamination of ground water was measured throughout the catchment during summer and winter periods. The most abundant pesticides detected in groundwater were atrazine ($14 \pm 11 \text{ ng L}^{-1}$) and metolachlor ($0.7 \pm 0.7 \text{ ng L}^{-1}$). Statistics of groundwater contamination are provided in Table 2. For atrazine there was an apparent local increase of contamination in groundwater sample sites (piezometer) pz6 and pz7. Higher sorption capability of soil, lower degradation rate, and higher historical use of the substances in this area are three possible explanations. Contrarily to the surface water, there is no strong annual variability of the groundwater contamination. This observation is

also supported by the temporal evolution of atrazine concentration at pz7 sampling well that shows a relative constant contamination level of the aquifer unit since 1993 (monitoring mandated by the French government; [18]; Figure S4). Several studies report consistent observations indicating slow contaminant transport in soil and shallow aquifers. For instance, [13] estimate the contamination for the Canche basin using a hydrodispersive modeling approach: a nonreactive solute that was applied on 1 km² of soil surface is spread on about 34–62 km² after 1.5 years following the considered models. Other studies indicate that groundwater travels in the order of cm per day [3]. Additionally, the targeted compounds are subjected to retardation processes due to the sorption onto the stationary soil particulates (reactive transport) that lead to further reduction by several orders of magnitude of the transport of substances in the shallow aquifer [33].

3.5. Transport Pathways of Substances in the Canche River Catchment

Previous studies [3,5,34] state that once pesticides are drained from agricultural fields, a fraction of the substances are directly transported into the river, inducing a contamination peak, while a second fraction percolates to the groundwater before potentially reaching the surface water through subsurface pathways. Due to the characteristic travel time/residence time of transport in soil and ground water, substances that were spread several years ago may still contribute to a significant amount of the surface water contamination (e.g., [35]). Ultimately, substances such as atrazine which was banned in France in 2003 are still observed in the Canche River in 2017 (Figures 6 and 7). As a result, the presence of pesticides in surface water does not necessarily indicate that substances were used during the corresponding period because multiple zones of compound accumulation (soil, ground water, captive ground water) are likely to induce a delay between the use of the substance and its occurrence in surface water.

From this dual mode of contaminant transport, we can suspect two distinct regimes of contamination in surface water that may occur separately or combined: (1) the first regime of background contamination (baseline) is almost constant over time and results from the seepage of the contaminated groundwater into the river; (2) the second regime is related to the rapid runoff transport of the spread substances directly into the surface water resulting in a pulse of contamination. Surface water contamination is, thus, a mix result of mixing of these two contamination sources.

Atrazine is a suitable proxy to track the background contamination as it was not used since more than 10 years, and thus can be assumed to come only from groundwater input, while being absent in surface runoff. Atrazine concentration in the river ($[atra]_{riv}$) can thus be calculated by:

$$[atra]_{riv} = \frac{[atra]_{gw} \times Q_{bf}}{Q_{tot}} \quad (5)$$

where $[atra]_{gw}$ is the average atrazine concentration measured in groundwater, Q_{bf} (resp. Q_{tot}) is the calculated base flow (resp. measured total flow) in the Canche River. Equation (5) allows calculating the temporal evolution of atrazine concentration in the river from the average contamination of the groundwater, assuming dilution by atrazine-uncontaminated runoff. The calculated atrazine concentrations in the river are consistent with the measured values, which confirm the hydrograph separation and the corresponding base flow index (Figure 7). Indeed, under this assumption, the surface to groundwater concentration ratio of atrazine that reaches an average value of 0.76 is in direct relation with the calculated BFI index from the Eckhardt filter (BFI = 0.76).

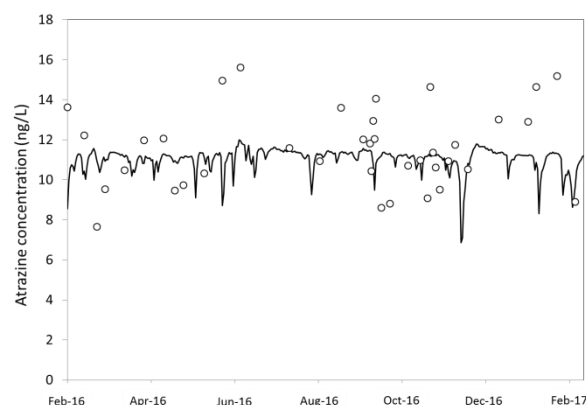


Figure 7. Atrazine concentration in the surface water at *Canche 5*. Markers indicate the experimentally-measured concentrations and the line refers to the calculated concentration assuming that atrazine in the surface water was exclusively supplied by the ground water seepage (Equation (3)).

By extension, the comparison between the dissolved contamination of surface water and the groundwater contamination is indicative of the state of equilibrium for a given contaminant (Figure 6). The ratio of the contamination level in the order of $BFI \approx 0.75$ is typical for a background contamination regime where pollutants are released into the river by the mean of groundwater input. On the contrary, the contamination ratio that differs from BFI indicates for example a dilution by rainfall (contamination is much lower than in the groundwater) or indicates pollutant input by runoff or atmospheric deposition (contamination level is higher than in the groundwater). In such a case, pesticide transport in surface runoff water results in a contamination peak of the river followed by the establishment of a new equilibrium state with the groundwater. Usually, contamination pulses occur during short time lapse and could reach a level one order of magnitude higher than the contamination baseline [3]. For ethofumesate, diflufenican, metolachlore, and pendimethalin this was observed from May to June 2016, immediately after pesticide spreading, when spring rain was intense enough to transport substances into the river (Figure 6). During fall, pendimethalin and diflufenican showed a second period when the disequilibrium between the surface water and the groundwater was significant. This may be assigned to a second spreading of these herbicides, notably on winter wheat and barley. These observations indicate that, during spring and fall, the contamination of the river results from precipitations that leach pesticides directly into the river while contamination flux during winter results from pesticide transport “stocked” in the groundwater that seep into the river bed (Figure 8).

The measured concentrations of pesticides in the Canche River and in the groundwater of the watershed are combined with the time series of the base flow and runoff obtained from the Eckhardt’s filter separation, to estimate an average concentration in the runoff following:

$$[pest]_{runoff} = \frac{[pest]_{riv} \times Q_{tot} - [pest]_{gw} \times Q_{bf}}{Q_{runoff}} \quad (6)$$

where $[pest]_{gw}$ (resp. $[pest]_{riv}$) is the measured concentration in the groundwater (resp. in the Canche River), and Q_{runoff} is the calculated runoff in the Canche River. Average pesticide concentrations in the groundwater were calculated as the mean of all measured values in the 15 piezometers, both in summer 2016 and winter 2017. Note that diflufenican, metolachlor, pendimethalin, and ethofumesate are almost absent in the groundwater and thus all drained substances should be assigned to the transport mediated by runoff. Concentrations calculated in runoff are on average 3.5 times higher than those in surface water (Figure 8). A seasonal trend can be clearly distinguished, with higher contamination of runoff during spring 2016 (and fall 2016 for pendimethalin and diflufenican) at first order, consistent with periods of pesticide applications.

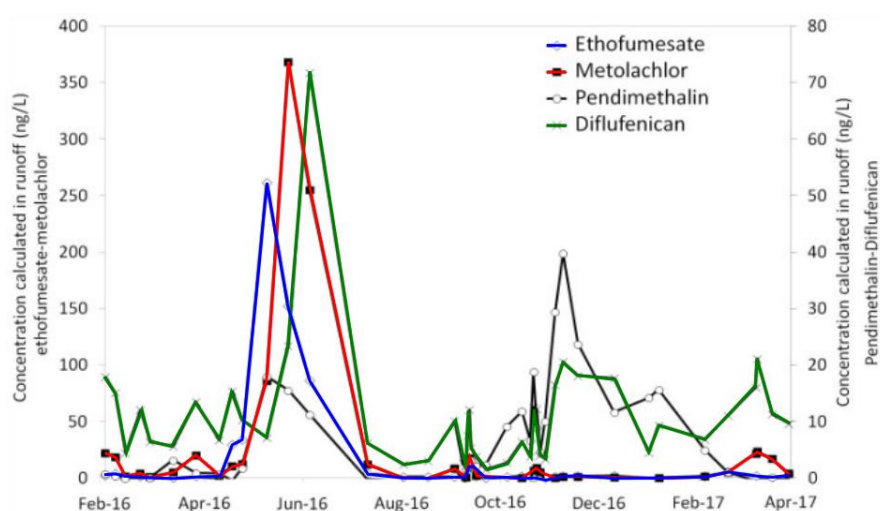


Figure 8. Reconstructed concentrations at *Canche 5* of diflufenican, ethofumesate, metolachlor, and pendimethalin in surface runoff water.

3.6. Transport Processes Apportionment

In the present study we assume that pesticides reach the river through two main pathways: seepage of contaminated groundwater and via surface runoff. Other processes such as atmospheric deposition and input of artificial effluents are not considered. The portion of pesticide fluxes into the river that originates from the shallow aquifer was estimated as the product between the average groundwater contamination and the baseflow estimated using the Eckhardt filter (see Section 2.2). Note that this approach assumes non-reactive transport of substances between both compartments. The difference between the contaminant flux assigned to the shallow aquifer input and the total flux of pesticide transported through the river is assumed to be the contaminant flow mediated by runoff and the near surface transport processes.

Comparison between the annual flux of substances in the catchment by groundwater seepage and runoff at the mouth of the Canche River are given in Figure 9 for each targeted pesticide. An estimation of the amount of pesticide spread per annum is also given. Except for atrazine, the amount of spread pesticides exceeds, by several orders of magnitude, the amount of substance released into the English Channel. The amount of pesticide transported by runoff processes is on average one order of magnitude higher than the amount released into the river by the groundwater seepage. For atrazine a different pattern than for the other targeted compounds is observed because of its residual status. In this case, input into the river by groundwater outflowing equalizes the total flux in the surface water that is indicative for the persistent chronic atrazine contamination of the catchment.

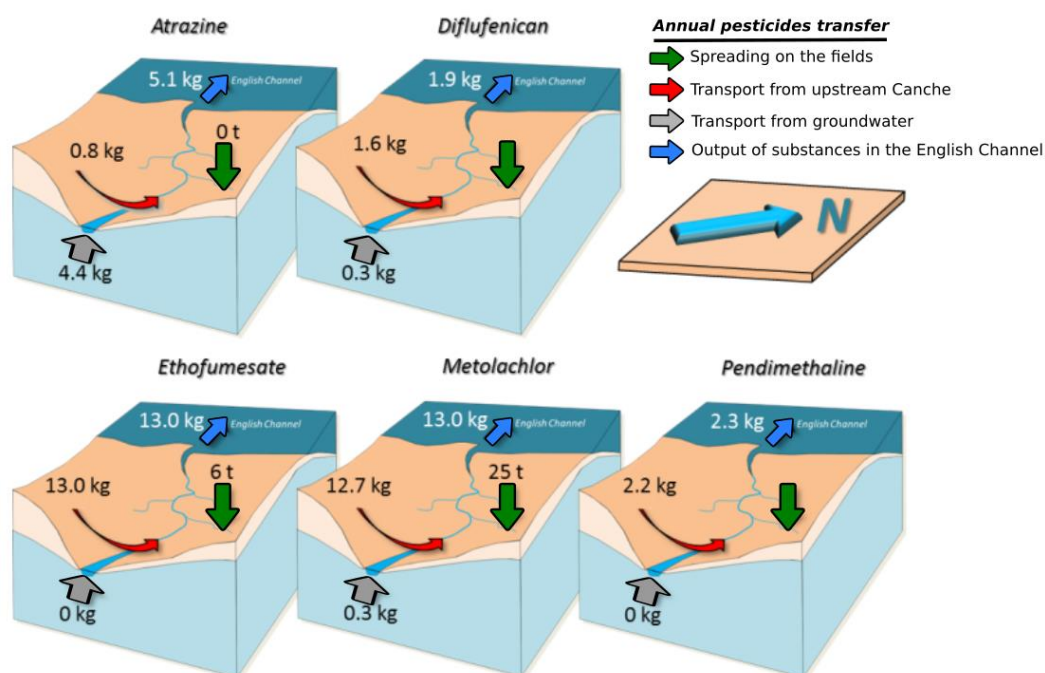


Figure 9. Mass balance of pesticides transfer in the Canche River. Arrows present the annual inputs from (1) spreading on the fields, (2) transport from upstream part of the river, and (3) from groundwater and output of substances in the English Channel (expressed in kg). Values are given for the catchment related to *Canche 5* (corresponding to 92% of the total catchment acreage, compare Tables S6–S8).

4. Conclusions

A general conceptual model for the dissolved pesticides transfer in the Canche River catchment is shown in Figure 10. The dominant input source of dissolved hydrophilic pesticides is triggered by rainfall events that cause important water runoff to the river system. Since runoff events are limited in time and area, the contamination peak in the river is characterized by a relatively high but narrow peak and depends strongly on the position of observation. The spring rainfall season after pesticide spreading was by far the most probable process explaining the pesticide contamination in the surface water of the Canche River (except for atrazine). The detected substances and their exact chronology strongly depend on the agricultural land use that, in turn, depend on the actual cultivation and their peculiarities (time of seeding, different treatments needed, etc.). Thus, as this study has clearly shown, using solely punctual measurement campaigns would lead to considerable uncertainties about the diagnosis of river contamination.

Outflow of contaminated groundwater is the second major source for dissolved pesticide concentration in surface water. This contamination is present as a relatively stable background value, whatever the sampling interval or position. This is mainly due to the persistence of atrazine in the groundwater (and relatively negligible for the other investigated pesticides).

Ultimately, the main fraction of annual pesticides flow occurs during the contamination peak period. In surface water, pesticide contamination is highly variable and its release depends of multiple and poorly known factors such as the spreading period. An important side-effect, however, is that the usual monitoring schemes should be adapted to efficiently track contamination pulses in order to improve our knowledge of the real contamination state of a given site/catchment. This forms a main difficulty for implementing effective monitoring programs such as those related to the Water Framework Directive. Therefore, the agarose gel based passive samplers used in the present study were of great help for determining realistic annual pesticide fluxes without expensive and laborious monitoring program. With a minimum effort they do provide a representative description of the contamination state of the site/catchment despite the highly variable water contamination level.

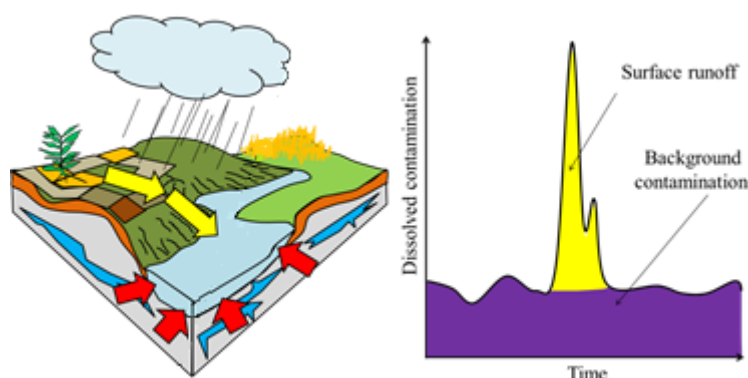


Figure 10. Abstract of the principal findings of this study; the sketch on the left side pictures the sources mixture of dissolved pesticides in the Canche River surface water, runoff originating from agricultural fields during rain events (yellow arrows) and input of groundwater (red arrows). The right panel shows a schematic view on contaminant concentrations in the river, highlighting the temporal character of the two main input sources, relatively constant for the groundwater “background contamination” and important punctual peaks for surface runoff contamination.

Thus, to have a good idea of the total flux of dissolved pesticides in a given catchment, the monitoring station has to be at the outlet/exit of the catchment. For detailed information on the respective regional input of the different tributaries, in particular if the land use within a catchment is very heterogeneous (different type of cultivations or conventional vs. biological agricultural areas), a multitude of monitoring station is necessary, which is often a logistical limit of environmental studies.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/11/7/1428/s1>, Figure S1: Comparison between the measured water discharge at *Course* gauging station and the estimation method using as reference the gauging station on the main stream, Figure S2: Transport kinetics of diflufenican from the SPM-sorbed state to the dissolved phase, Figure S3: Dissolved concentration measured at *Canche 5* sampling site, Figure S4: Dissolved concentration of atrazine at pz7 sampling point (groundwater), Table S1: GPS coordinates of sampling sites, Table S2: Dissolved concentrations of pesticides during the seasonal campaign (ng L^{-1}), Table S3: Herbicides flux during the seasonal campaigns (g day^{-1}), Table S4: Mass balance analysis: discrepancy between the tributaries and the closest effluent point (%), Table S5: Specific fluxes during the seasonal campaigns ($\text{mg day}^{-1} \text{ km}^{-2}$), Table S6: Dissolved concentrations of pesticides at *Canche 5* sampling site (ng L^{-1}), Table S7: Average dissolved concentrations of pesticides at *Canche 5* sampling site (passive samplers; ng L^{-1}), Table S8: Dissolved concentrations of pesticides in ground water during summer and winter (ng L^{-1}).

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