Flood event impact on pesticide transfer in a small agricultural catchment (Moutousse at Aurade, south west France)

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In this paper, pesticide transfer dynamic is studied during two flood events in a small experimental catchment close to Toulouse (south west France). Thirteen pesticide molecules (herbicides, fungicides) have been analysed by multi-residue technique on filtered and unfiltered waters. The results show very high pesticide concentrations in the different fractions compared to low flow periods and to the data collected by the French institutional networks in charge of the pesticide river water pollution survey. Several molecules present concentration higher than $0.1\,\mu g\,L^{-1}$ and even higher than $1\,\mu g\,L^{-1}$ in the unfiltered waters. In the suspended matters the concentrations vary respectively between 0.1 and $30\,\mu g\,g^{-1}$ according to the molecules and can represent 40 to 90% of the total concentration for low soluble molecules. All the molecule concentrations and fluxes increase during the flood flows and have positive relationships with the stream discharge, but hysteresis between rising and falling periods can be observed for some molecules. Pesticide concentrations in unfiltered waters and partitioning between dissolved and particulate fractions ($K_d = [diss]/[part]$) are controlled by dissolved organic carbon and total suspended matter. A good negative relationship can be established between $\log K_d$ and $\log K_{ow}$ for 6 molecules.

Keywords: fungicide; herbicide; stream waters; filtered waters; unfiltered waters; suspended matters; dissolved organic carbon; hysteresis; partition coefficient

1. Introduction

Increase in the use of pesticides in the past decades has brought about a tremendous change in intensive farming and agriculture practices [1]. Today, pesticides are conclusively identified as the main source of surface water and groundwater contamination and have become a major environmental preoccupation in Western Europe [2–5]. France ranks third after the USA and Japan in the use of pesticides [6]. There are more than 6000 products

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and approximately 800 are considered as active substance (400 used in France) [7]. Herbicides such as s-triazines substituted ureas, and anilides have been the subject of a lot of environmental research because they account for 47% of the world's commercial pesticide consumption [8,9].

Reports recently came out in France demonstrated a direct link between water contamination and use of pesticides in agriculture (96% and 61% of sampling points in surface waters and groundwaters respectively) [10]. Sauret *et al.* [11] also pointed out, that 19 million hectares of crops are annually sprayed with pesticides and this represents 35% of the total surface area of France.

Currently pesticide transports from agricultural land to atmosphere, groundwaters and river waters have been the issue of scientific interest and investigated by a number of authors [12–20]. The studies performed by Richards *et al.* [21], Larson and Capel [22], indicate that transport of pesticides from cultivated land to surrounding surface water occurs through surface run-off and/or sub-surface flow. Rain and irrigation are the main inducers of pesticide transfers.

While it is widely acknowledged that surface and sub-surface run-off is the key process in pesticide shifting and hence, surface water contamination, only a few studies have addressed the contribution of the flood periods in the river transport of pesticides. Therefore we have to pay special attention to run-off during high flow for transport of pesticides and to study the role of different flows (surface run-off, sub-surface and groundwater flows) during the flood events.

Properties of pesticides play a major role in influencing their concentration in run-off. Pesticides can be adsorbed onto eroded particles and transported in the river water by the suspended matters (TSM) [23]. They can be also complexed by dissolved organic matter and transported in the solute fraction. Dissolved organic carbon (DOC) is regarded as the main sorbent for hydrophobic pesticides in soil/water system. This is why it is important to consider these parameters (TSM, DOC) when we want to evaluate pesticide concentration in river water [24] and to assess the role played by TSM and DOC in the fluvial transport of pesticides, particularly during flood events.

The main objectives of this study are:

- To determine the concentration of pesticides in different fractions (dissolved and suspended particulate) during the flood events in a small agricultural catchment in south west France.
- To investigate spatial variations of pesticide concentrations within the catchment according to different cultures and agricultural practices.
- To determine the temporal variations of concentrations and fluxes in different fractions during the flood event at the outlet of the catchment.
- To better understand the relationships between pesticide concentrations and stream discharge variations.
- To assess the role of the main controlling factors such as pH, Conductivity, DOC and TSM on pesticide partitioning between dissolved and particulate fractions (K_d).
- To determine if there is a relationship between the partition coefficient K_d estimated using field measurements and the octanol-water partition coefficient (K_{ow}) extracted from databases for different molecules.

2. Experimental

2.1 *Study area*

2.1.1 *Location and characteristics*

The experimental area, Montoussé catchment at Auradé, is located in the Midi–Pyrénées province (south west France), 35 km west of Toulouse. The study area is a hillside of the 'Coteaux de Gascogne' with an altitude of approximately 300 m. The geological substratum is a Miocene molassic deposit (called molasse) resulting from the erosion of the Pyrénées Mountains and the subsequent sediment deposition in the Gascogne fan at the end of the Tertiary Period. This molasse consists in a mixing of sands, clays, limestones and calcareous sediments. The study area is characterised by a fairly impermeable substratum due to its widely extended clay content. As the result of this geological substratum, river discharge is mostly supplied by surface and subsurface run-offs. Groundwater reservoirs are very limited and during the summer dry period the stream discharge is very low and sometimes the creek is dried. The land slopes to the north varying between 0% and 20% and are drained by a system of river flowing to the North into the main fluvial axis of south west France, the Garonne River.

The Montoussé creek at Auradé drains a catchment area of 328 hectares, of which 90% is devoted to agricultural activities on highly fertile land with calcareous (around pH = 8) and clayey (36%) soils. The main cultures are winter wheat (20%) and durum wheat (31%) in rotation with sunflower (47%). The main period for herbicide use is the end of April and beginning of May for triazine on sunflower and from the end of November to January for phenylurea on wheat. In this survey, 10 sampling stations were selected on the Montoussé creek and on its tributaries according to soil occupation.

2.1.2 *Climate and hydrology*

The climate of Auradé area is characterised as oceanic because the influence of the Atlantic Ocean plays an important role in regulating temperature variations and therefore determining climate conditions. The average annual precipitation is about 700 mm to 800 mm, mostly in the form of rain, which is the main hydrological source of supply for surface and subsurface run-offs in this area with the highest rate of discharge in February while the water flows more slowly from June to September. The bulk of annual rainfall occurs, in the form of thunderstorms, from November through December and April to May. The average water evapotranspiration from the soil/vegetation system is very high and stands, from west to east, at 500 mm to 600 mm.

The mean annual temperature of the area averages about 13°C. The average minimum January temperatures have been recorded at 5°C. The area receives the lowest amount of precipitation from June to August whereas October to May is considered as the wet period.

2.2 *Surface water sampling and pre-treatment of the samples*

Two storm events (March 2006 and May 2008) have been sampled in this catchment. During the first one [25], two water samples of 2.5 L each have been collected at the peak discharge in glass jams for each of the 10 stations, spatially distributed within the whole catchment (Figure 1). During the second storm [26], 12 samples of 0.8 to 2.5 L according to
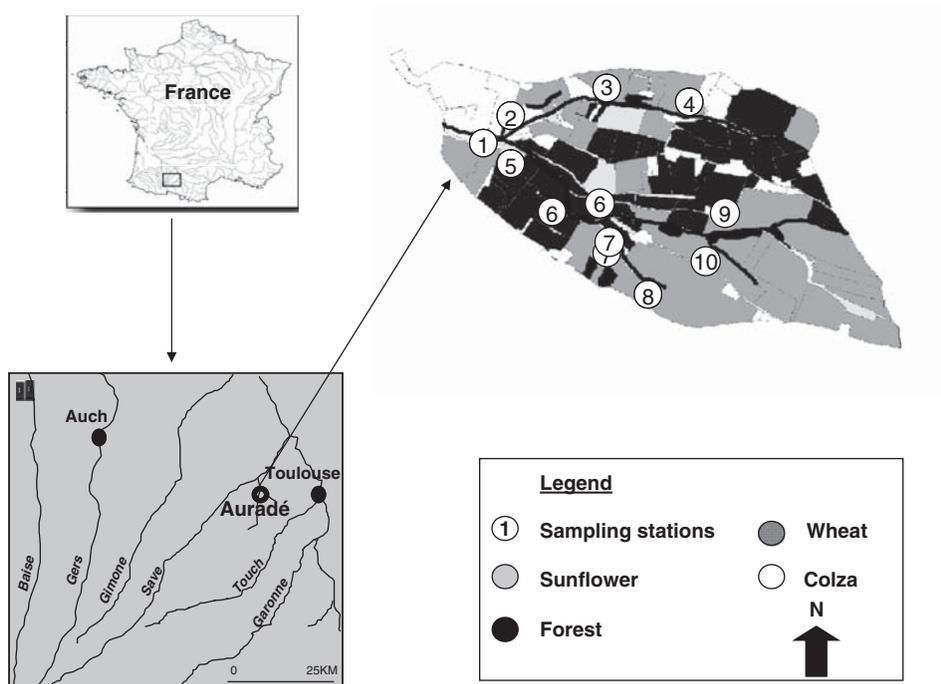
Figure 1. Geographical situation map of the Montoussé experimental catchment at Auradé (Gers, south west France) and location of the sampling stations (1 to 10).

discharge intensity were collected during the whole period of the event at the outlet of the catchment using an automatic sampler (Model: ORI® Abwassertechnik Gmbh & Co., Type MIC B). The automatic sampler is programmed for 30 min interval sampling.

For unfiltered water samples, dichloromethane (1 : 40;V/V) was added in the field to avoid bacterial activity [27], and the glass bottles with Teflon-lined lids were finally stored in the dark and cold conditions until extraction the next day.

2.3 *Method of analysis: multi-residue approach*

2.3.1 *Sample analysis*

2.3.1.1 *Chemicals and reagents*. Pesticide analyses were performed by solvents of analytical grade ('pestipure' by SDS, Solvent Documents Syntheses, Peypin, France). Anhydrous sodium sulphate from SDS was used for drying the organic phases. Pesticide Mix44 prepared by Dr Ehrenstorfer (purchased from Cluzeau Information Laboratory (CIL), Sainte-Foy-la-Grande, France) was used as reference material.

2.3.1.2 *Filtration and extraction of sample*. The water sample was filtered by applying vacuum. The filter used to filtration is a cellulose ester filter (Millipore, 0.45 μm) [28]. Each filter was rinsed with MilliQ water before filtration. Filter blanks were measured and pesticide concentrations were always under the detection limit (0.005 to 0.01 μg L^{-1} according to the molecules). To extract water samples, the liquid/liquid extraction

technique was applied [29], by using shaker flask (3–4 L with Teflon key) as a means and dichloromethane as a solvent for phase exchange. The total solvent/water ratio was noted as 1 : 6, V/V. Once the extraction performed, dichloromethane was dried on 50 g anhydrous sodium sulphate, and the remaining organic phase was evaporated under vacuum and the dry residue was recuperated with 2 ml of hexane.

2.3.1.3 *Chromatographic conditions*. GC separation was done on a column of Zebra ZB-5MS 30 m 0.25 mm i.d., 0.25 μm film from Phenomenex® (Torrance CA) with Thermo Fishers Scientific (Waltham, MA). Trace GC 2000 coupled with a DSQ II mass detector. One μL^{-1} of the extract in hexane was injected by a Tri Plus Thermo Fisher Scientific auto sampler of a 5 mm inlet with retraction in the splitless mode at 280°C for the injector and at 45°C hold 0.5 min in the oven under a surge pressure of 100 kPa. The first step had the temperature increase rate of 35°C min^{-1} up to 180°C followed by a second step at 6°C min^{-1} up to 240°C and plateau of 35 min for this final temperature. Carrier gas was high quality Helium Alpha gaz 2 from Air Liquid Company (France) and was set a constant flow rate of 1 mm min^{-1}. The temperature of the transfer line was 220°C and the ion source temperature was 200°C. The detector was used in the Specific Ions Monitoring mode (SIM) with a detector gain of 1633 V.

2.3.1.4 *Recovery and detection limits*. Extraction recoveries were done on spiked water samples with mixes of the different molecules analysed in this study by using Pesticide-Mix44 reference material and other different molecules separately (prepared by Dr Ehrenstorfer). The recovery values ranged from 92% to 102%) and were in agreement with our previous work [27]. The limit of detection based on a signal to noise ratio of 3 was estimated at 0.005 to 0.01 $\mu g\,L^{-1}$ according to the molecules.

3. Results and discussion

3.1 *Temporal variations during the flood of May 2008*

3.1.1 *DOC, TSM and water discharge fluctuations*

Due to Montoussé small catchment size, a direct response of the discharge to the rainfall was observed (Figure 2). The evolutions of DOC and TSM concentrations showed an increase during flood with increasing discharge, although there was a lag between the peak discharge and the maximum concentration of DOC and TSM. As Figure 3 suggests, TSM concentrations reach the maximum before the DOC content and after the peak discharge but declines more rapidly than the DOC content, which remains relatively high during the recession period. Hyer *et al.* [30] have also noted that a high suspended sediment concentration during the recession curve of the storm may indicate suspended sediment contribution by the soil water. The authors argue that it is equally likely that the contributions of soil water sustain the flow during recession periods and thereby sustain the energy for sediment transport.

Worrall and Burt [31], suggesting that increase in DOC concentration could result from change in hydrology, and Tranvik and Jansson [32], have mentioned a decrease in discharge could result in a change in concentration. However, Werrity [33] established that there is a positive relation between discharge and DOC concentration for UK rivers.
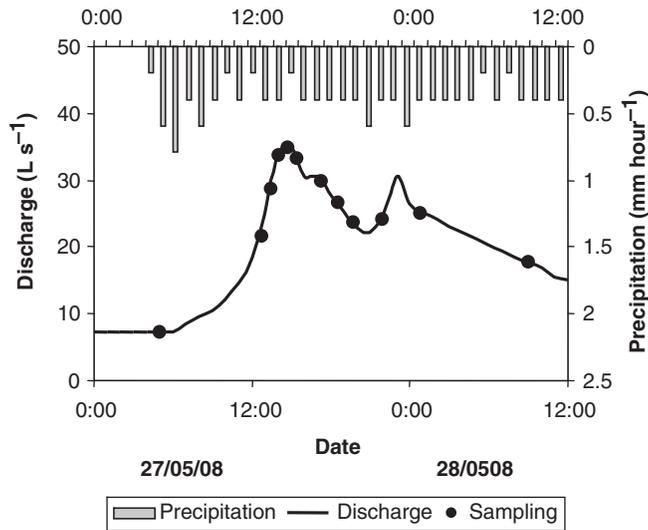
Figure 2. Daily precipitation and stream discharge measured at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008. Black circles on the hydrogragh represent the sampling periods.
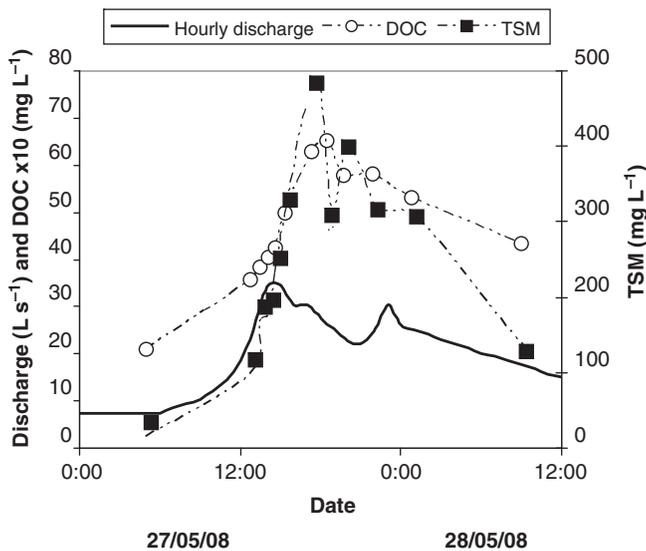

Figure 3. TSM and DOC concentration variations compared to stream discharge fluctuations at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008.

McDowell and Likens [34], Idir *et al*. [35], Ladouche *et al*. [36], indicated that generally DOC concentration increases with higher flows.

In this study we can observe that the concentrations and fluxes of TSM and DOC are higher during the recession phase of which the contribution to the total flood event represents 67% for DOC and 73% for TSM loads. Consequently, for a given discharge
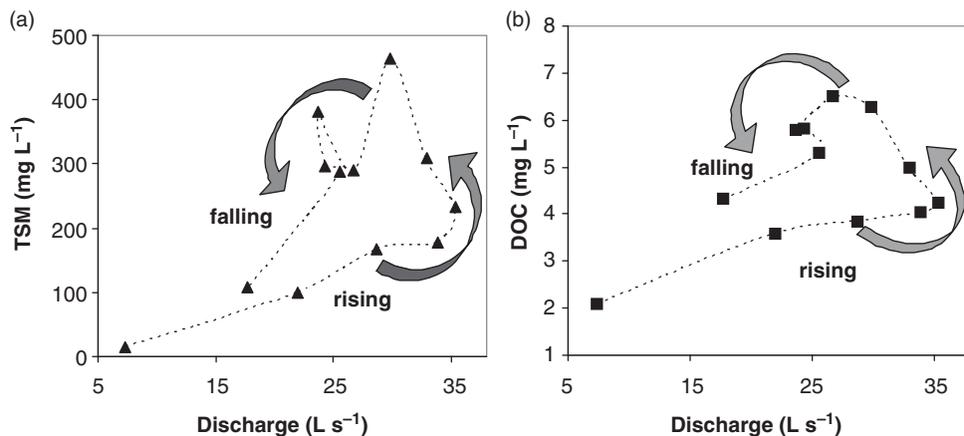
Figure 4. Relationships between TSM (a) or DOC (b) contents and stream discharge at the outlet of the Montoussé catchment during the flood event of May 2008, showing the hysteresis phenomenum between rising and falling limbs of the storm hydrograph.

value, TSM and DOC contents are higher during the falling limb of the hydrograph than during the rising period (Figure 4). As it is already shown by Probst [37] in the Garonne basin, nitrate also reaches its highest concentration after the peak discharge when the subsurface flow contribution is at its maximum rather than before or during the maximum discharge which generally corresponds to the highest surface run-off contribution.

There is no significant relationship between discharge and TSM (Pearson's correlation coefficient, $R^2 = 0.185$ and $p = 0.175$) or DOC ($R^2 = 0.293$ and $p = 0.063$). On the contrary a strong relationship between DOC and TSM was observed ($R^2 = 0.792$, $n = 12$, $p < 0.01$).

3.1.2 Variations of pesticide concentrations and fluxes

3.1.2.1 *Concentration in unfiltered waters*. Most of the pesticide concentrations increase during the flood event with increasing discharge although there were two magnitudes for pesticide concentration as shown in Figure 5a and b for unfiltered waters. The same general pattern of pesticide flushing during storm event (increasing pesticide concentration with increasing discharge) was also observed by Goolsby *et al.* [38] and Thurman *et al.* [39].

As seen for unfiltered waters, linuron, aclonifen, chlorotoluron, pendimethalin (Figure 5a) present the highest concentrations which are generally superior to $0.1\,\mu g\,L^{-1}$ and can even reach 1 to $1.5\,\mu g\,L^{-1}$. The concentrations of the other molecules (Figure 5b) are generally lower than $0.1\,\mu g\,L^{-1}$ but they present the same pattern with discharge variations. We observed a dilution for some of the molecules in the peak of discharge which could be interpreted by a dilution of the base flow 'old water' by fresh water supplied by the surface run-off and originating from the rain waters with lower pesticide contents.

As seen in Figure 5, pesticide concentrations in unfiltered waters are higher after the peak discharge during the recession period than during the rising discharge, showing a hysteresis between the two hydrological periods. That means most of the pesticides are mainly exported by the subsurface run-off. This hysteresis phenomenon is illustrated as an
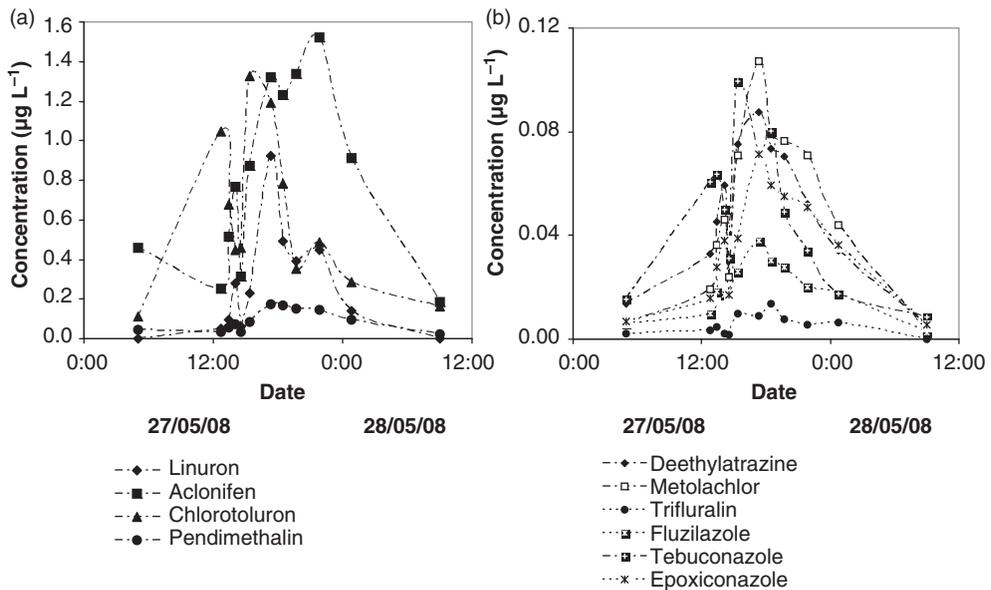
Figure 5. Variations of pesticide concentrations in unfiltered waters at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008. (a) high concentration molecules, (b) low concentration molecules.
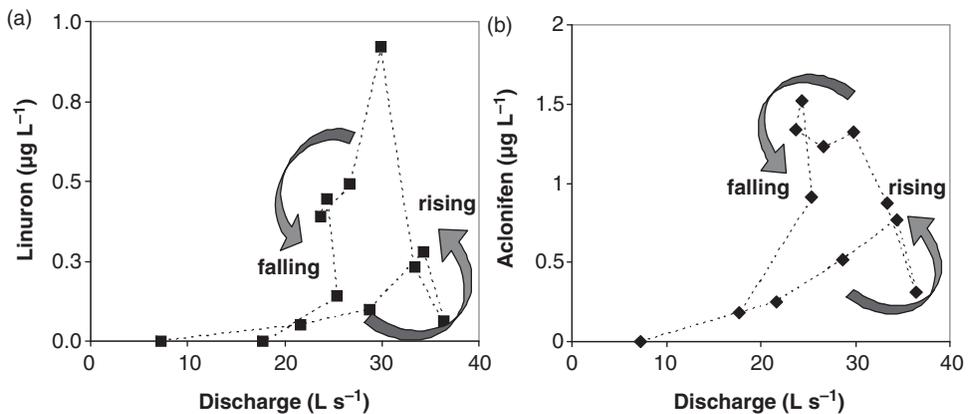

Figure 6. Relationships between linuron (a) or aclonifen (b) concentrations and stream discharge at the outlet of the Montoussé catchment during the flood event of May 2008, showing the hysteresis phenomenum between rising and falling limbs of the storm hydrograph.

example in Figure 6a and b, respectively for linuron and aclonifen which have the highest concentrations during the flood event. As already seen for TSM and DOC, there is a lag of concentration between the rising period and the falling limb of the hydrograph showing higher linuron and aclonifen concentrations during the recession period, when the subsurface run-off contribution reaches its maximum, than during the rising discharge.
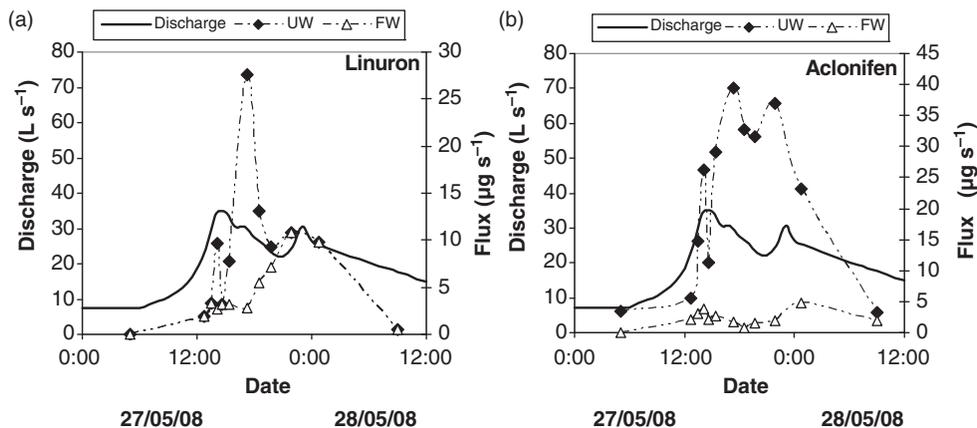
Figure 7. Discharge and variations of linuron (a) and aclonifen (b) fluxes measured in filtered (FW) and unfiltered (UW) waters during the flood flow of May 2008.

3.1.2.2 *Flux variations in filtered and unfiltered waters.* As for the concentrations, the fluxes of different pesticides increase during the flood event, in the unfiltered waters as well as in the filtered waters (see Figure 7a for linuron and Figure 7b for aclonifen). The difference between the two fluxes (unfiltered minus filtered) allows estimating the pesticide flux exported in the suspended matters. This difference varies according to the characteristics of the molecules, particularly to their water solubility (S_w in $mg\,L^{-1}$) and K_{ow} (see in the pesticide manual [40]). As an example, there are few differences for highly soluble molecules like metolachlor ($S_w = 488\,mg\,L^{-1}$ and $\log K_{ow} = 2.9$) for which the particulate fraction (unfiltered minus filtered) averages only 3.5% during the storm event of May 2008. On the contrary, there is a significant difference for molecules like chlorotoluron ($S_w = 74\,mg\,L^{-1}$ and $\log K_{ow} = 2.5$) and linuron ($S_w = 63.8\,mg\,L^{-1}$ and $\log K_{ow} = 3$), particularly during the discharge peak. For these molecules the contribution of the particulate fractions represents respectively 30% and 27% of the total fluxes (solute plus particulate fractions). Finally, for low soluble molecules like aclonifen ($S_w = 1.4\,mg\,L^{-1}$ and $\log K_{ow} = 4.37$) and pendimethalin ($S_w = 0.33\,mg\,L^{-1}$ and $\log K_{ow} = 5.2$), the difference is very important and it represents respectively 82% and 87% of the total fluxes.

3.2 *Spatial variation of the concentrations during the flood of March 2006*

The results obtained during the flood of March 2006 show that for the different stations, the pesticide concentrations are very high in different fractions (filtered water, unfiltered water and suspended matter) compared to low flow periods and also to the data collected by the French institutional networks in charge of the river water pesticide pollution survey.

In the filtered water, 6 molecules have concentrations higher than $0.1\,\mu g\,L^{-1}$, and even higher than $1\,\mu g\,L^{-1}$ for pendimethalin and chlorotoluron. It is very difficult to identify different patterns in the spatial distribution of the molecules within the catchment because the main cultures have been wheat and sunflower in rotation for several decades.

In the unfiltered water two molecules (aclonifen and DEA) have concentrations between 0.1 and $0.5\,\mu g\,L^{-1}$, and 5 molecules (metobromuron, isoproturon, chlorotoluron,
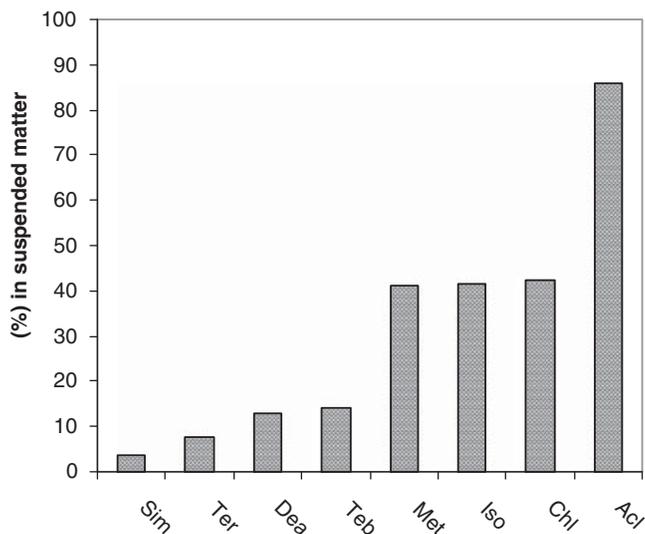
Figure 8. Percentage of particulate fractions (unfiltered minus filtered waters) to the total molecule measured in unfiltered waters during the flood event of March 2006. Average values for the 10 stations.

pendimethalin, terbuthylazin) have concentrations higher than $1\,\mu g\,L^{-1}$ (up to $8\,\mu g\,L^{-1}$ for pendimethalin at the outlet of the catchment, station 1). As for the filtered waters, it is difficult to exhibit a difference in the spatial distribution of the molecules. Fungicides (ex: tebuconazole) have lower concentrations than herbicides. Readman *et al.* [41] pointed out that surface water is not subject to contamination by fungicide probably due to their inadequate persistence.

In the suspended matters, the concentrations vary between 0.1 to $30\,\mu g\,g^{-1}$. The highest values (generally greater than $5\,\mu g\,g^{-1}$) are observed for pendimethalin and metobromuron. As seen in Figure 8, the percentage of each molecule in the suspended matter compared to the total molecules in the unfiltered water varies according to the molecule. The amount of percentage of 15% is rather insignificant for 4 molecules, but it is around 40% for metobromuron, isoproturon and chlorotoluron, and even close to 90% for aclonifen, that means for the last 4 molecules, an important amount of pesticide load (40% to 90%) is missed when only filtered waters are analysed.

3.3 *Relationships with the main controlling factors, TSM and DOC*

There is a relationship between the chemical properties of pesticides and their mobility. The mobility of pesticide can be expressed in term of their sorption on soil organic carbon (sorption coefficient, K_{oc}) and their persistence defined as field dissipation half life within the soil. Low volatility and hydrophobic characteristic of pesticides enhance their adsorption onto the surface of suspended particulate matter [42]. They are also easily adsorbed by humic and fluvic acids as soon as by lipids and proteins, forming dissolved organic matter (DOM). DOC and TSM are two very widely known parameters to control pesticide concentrations [43,44].
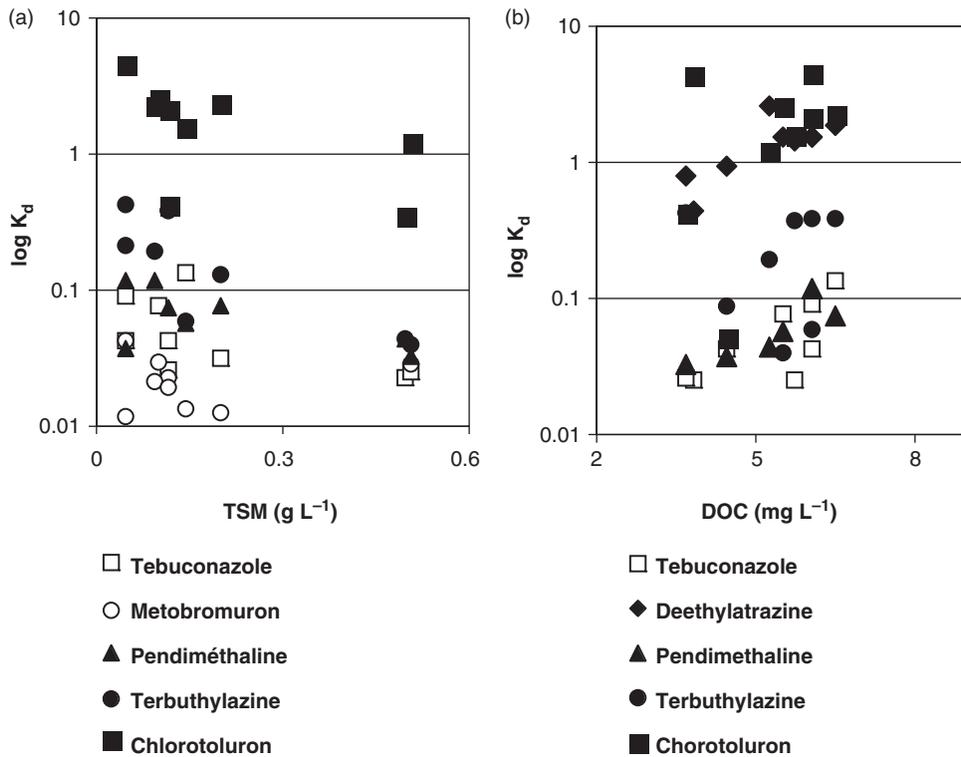
Figure 9. Relationships between the partition coefficient K_d of different pesticides and TSM (a) or DOC (b) concentrations at the outlet of the Montoussé catchment (station 1) during the flood event of March 2006.

According to each pesticide characteristic, particularly their solubility and partition coefficients (K_{ow} (octanol/water) and K_{oc} (organic carbon/water)), their partitioning into the different fractions (dissolved and particulate) varies.

For the flood event of March 2006, the partition coefficient (K_d in $g\,L^{-1}$) of each molecules was calculated as the concentration (C) ratio between dissolved ($\mu g\,L^{-1}$) and particulate ($\mu g\,g^{-1}$) fractions:

$$K_d(g\,L^{-1}) = C_{dissolved}(\mu g\,L^{-1})/C_{particulate}(\mu g\,g^{-1}) \qquad (1)$$

$C_{dissolved}$ is the pesticide concentration measured in filtered water. $C_{particulate}$ is the concentration difference between unfiltered and filtered waters, divided by the TSM concentration as follows:

$$C_{particulate}(\mu g\,g^{-1}) = \left[(C_{unfiltered}(\mu g\,L^{-1}) - C_{filtered}(\mu g\,L^{-1})\right]/TSM\ (g\,L^{-1}) \qquad (2)$$

There was a reverse relationship between K_d and TSM concentrations for tebuconazole, metobromuron, pendimethalin, terbuthylazin and chlorotoluron (Figure 9a) showing that the adsorption of these molecules onto particulate phases increases with increasing TSM concentrations. On the contrary, for tebuconazole, deethylatrazine, pendimethalin, terbuthylazin and chlorotoluron, K_d values increase with increasing DOC contents,
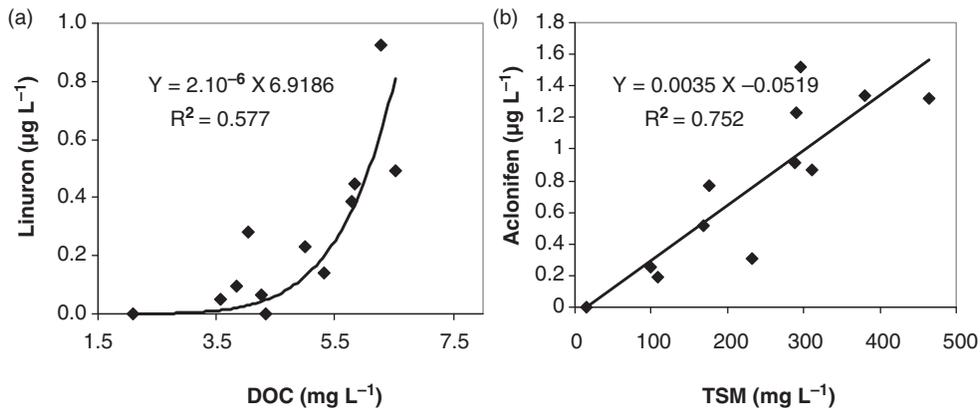
Figure 10. Linuron (unfiltered waters) *versus* DOC concentrations (a) and aclonifen (unfiltered waters) *versus* TSM content (b) at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008.

showing that these molecules are highly complexed by the DOC (Figure 9b). The presence of the above molecules depends on the quality of DOC and TSM in the water.

For the flood of May 2008, two molecules namely linuron and aclonifen, showing the highest concentrations were selected to illustrate their behaviour with DOC and TSM. It was observed that there were significant relationships between linuron (unfiltered waters, Figure 10a) or aclonifen concentrations and TSM. In the same way, linuron and aclonifen (unfiltered waters, Figure 10b) had very good correlation with DOC. The best model adjusted to the relationship between linuron and the two controlling factors (TSM and DOC) was log-log (see below, linuron *versus* DOC) while the relationships were linear for aclonifen (see below, aclonifen *versus* TSM):

$$[linuron] = 2.10^{-6} [DOC]^{6.9186}$$
$$R^2 = 0.577, \quad p < 0.01$$

(3)

$$[aclonifen] = 0.0035 [TSM] - 0.0519$$
$$R^2 = 0.752, \quad p < 0.01$$

(4)

with [linuron] and [aclonifen] in $\mu g\,L^{-1}$, and [TSM] and [DOC] in $mg\,L^{-1}$.

Some other molecules like pendimethalin, metolachlor and epoxiconazole significantly correlated both with DOC and TSM.

It is worth noting that adsorption/desorption of pesticides depends strongly on pH [45,46]. However, in this study, pH and conductivity seem to have no influence on the K_d values, probably because pH (7.9–8.3) and conductivity (500–800 $\mu S\,cm^{-1}$) were high and relatively constant in such a carbonate environment.

3.4 Relationship between K_d and K_{ow}

The octanol-water partition coefficient K_{ow} is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. K_{ow} values for pesticides are generally listed in databases (see, for example, in the pesticide manual [40]).
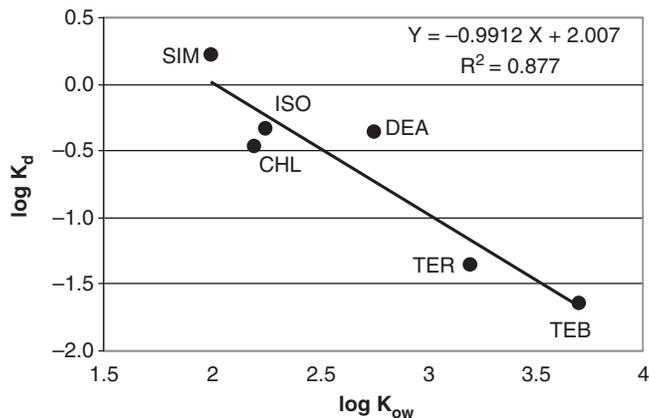
Figure 11. Relationship between $\log K_d$ and $\log K_{ow}$ during March 2006 flood event at the outlet of the Montoussé catchment (station 1). SIM: simazin, CHL: chlorotoluron, ISO: isoproturon, DEA: deethylatrazine, TER: terbuthylazin, TEB: tebuconazole.

K_{ow} can be estimated also from water solubility, except for low soluble molecules for which there is no relationship between K_{ow} and solubility (S_w in mg L^{-1}), as it is the case in this study for simazine ($\log K_{ow} = 2.1$ and $S_w = 6.2$), isoproturon ($\log K_{ow} = 2.5$ and $S_w = 65$), chlorotoluron ($\log K_{ow} = 2.5$ and $S_w = 74$), deethylatrazine ($\log K_{ow} = 2.75$ and $S_w = 6$), terbuthylazine ($\log K_{ow} = 3.21$ and $S_w = 8.5$) and tebuconazole ($\log K_{ow} = 3.7$ and $S_w = 36$).

It was interesting to check if there was a relationship between K_{ow} values extracted for each molecule from the literature and K_d calculated in this study for each molecule from field measurements. As seen in Figure 11, there was a reverse relationship between the K_d and K_{ow} values for the different pesticide molecules, except for Metobromuron for which K_d is very low in such a catchment.

The equation of this relationship is as follows:

$$\log K_d = -0.9912 \log K_{ow} + 2.007$$
$$R^2 = 0.877, \quad p < 0.01$$

(5)

The above equation is characteristic of such an environment with stream water dominated by calcium, magnesium and bicarbonates, high water pH (7.9 to 8.3), relatively high DOC content (up to 7 mg L^{-1}) and TSM concentration (up to 500 mg L^{-1}), SPM mainly composed of fine particles (2:1 clay minerals of montmorillonite and vermiculite group with high specific surface area and high exchange capacity) with low particulate organic carbon content (0.5% to 2%). This equation is probably not relevant for other environments with stream waters and suspended matters of different compositions but it could be used in other catchments with the same characteristics of the Montoussé to estimate the distribution of pesticides between the dissolved and particulate fractions using K_{ow} values from databases.

These results indicate that when analysing pesticides in surface waters, suspended matter should be separated, and both phases (filtered water and suspended particulate matter) should be analysed if we want to better understand the transfer dynamic of pesticides.

4. Conclusion

The flood flows play a major role in the transfer of pesticides because all the molecules measured during these events have high to very high concentrations in different fractions (dissolved and particulate), leading to very high fluxes exported at the outlet of the catchment. These hydrological periods are also very important to have a better understanding of the transfer dynamic of these molecules and particularly, to determine the main hydrological processes (run-off, subsurface run-off and groundwater flow) controlling their transfers from the soil to the stream water. The main results obtained in this study were:

- The contribution of the particulate fraction can represent between 40% and 90% of the total molecule measured in the unfiltered water for the low soluble molecule. That means an important amount of pesticide load is missed when only filtered waters are analysed.
- No spatial variation within the catchment can be observed for pesticide concentrations in the different fractions tested mainly because the main cultures are wheat and sunflower in rotation since several decades.
- The pesticide concentrations and fluxes increase with increasing discharge but there is a lag between the peak discharge and the concentration maximum which arrives later.
- The concentration-discharge relationship exhibits hysteresis phenomenon with higher concentration during the falling limb of the hydrograph than during the rising period, showing that the concentration increases due to increasing subsurface run-off contribution.
- The DOC and TSM are the two major physico-chemical parameters which are controlling the mobility of pesticides and their partitioning (K_d) between the dissolved and the particulate fractions during their fluvial transport.
- Some molecules like simazin, isoproturon, chlorotoluron, DEA, terbuthylazin and tebuconazole exhibit a good relationship between K_d and K_{ow}, showing that their partitioning (K_d) between dissolved and particulate fractions measured in the field during the flood event can be estimated from their K_{ow} value extracted from databases.

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