Trace Element and Pesticide Dynamics During a Flood Event in the Save Agricultural Watershed: Soil-River Transfer Pathways and Controlling Factors

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Abstract Agricultural practices are the main source of water contamination in rural areas. Rainfall events, and subsequently, soil leaching and storm runoff are mainly controlling the transfer of pollutants from diffuse sources in watersheds during floods. These periods are also very important to better understand their dynamics, particularly their different soil-river transfer pathways (surface runoff SR, subsurface runoff SSR, and groundwater flow GF). This study focuses on riverine transfers of both pesticides and trace elements. High-resolution monitoring of water discharge and water sampling were performed during a flood event that occured in May 2010 in an agricultural catchment of SW France. Chemical composition of major and trace elements, silica, alkalinity, pH and conductivity, DOC and POC, TSM, and commonly used pesticides were analyzed with a high sampling frequency. The different stream flow components (SR, SSR, and GF) were assessed using two independent hydrograph separation methods: a hydrological approach based on Maillet's formula (1905) for the recession period and a chemical approach based on physico-chemical tracers, TSM for SR and PO_4^{3-} for GF. Both methods exhibited important contributions of SR (33 %) and SSR (40 %) to the total riverine pollutant transfers. The contribution of different components was also visible using concentration-discharge relationships which exhibited hysteresis phenomenon between the rising and the falling limbs of the hydrograph. Higher concentrations during the rising period (clockwise hysteresis) were characteristic of pollutants mainly exported by SR (trifluralin, Cd). Anticlockwise hysteresis with higher concentration during the recession period showed pollutants mainly exported by SSR (metolachlor, Cu). Moreover, significant relationships were highlighted between the controlling factors (DOC, POC, and TSM) and SR, SSR, and GF contributions: DOC and the complexed pollutants were highly correlated to SSR while POC, TSM, and the adsorbed pollutants were linked to SR. During the flood, K_d of most pollutants increased, particularly at the beginning, and therefore, future studies should investigate their availability to living organisms and thus their toxicity. An additional characteristic equation between K_d and K_{ow} of the different pesticides was proposed to help future management, modelling, and estimation of pollutant transfers during floods.

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1 Introduction

Previous studies showed high concentrations of pesticides and trace elements in surface water worldwide

(Gaiero et al. 2003; Martin et al. 2003; Simeonov et al. 2003; Kar et al. 2007; Salpeteur and Angel 2010; El Azzi et al. 2013). Consequently, the transfer of pollutants in the environment has become a major concern.

Rainfall events lead to physical erosion, soil leaching, and storm runoff responsible for the export of high fluxes of pollutants to the outlet of agricultural watersheds (Shafer et al. 1997; Taghavi et al. 2011; Roussiez et al. 2013). These fluxes have significant impacts on biota and aquatic ecosystems. Therefore, rainfall events are very important to understand the transfer dynamics of pollutants. These transfers can occur along multiple pathways from soil to stream: surface runoff (SR), subsurface runoff (SSR), and groundwater flow (GF). Surface runoff erodes the superficial soil horizon by both rain splash and mechanical erosion (Deasy et al. 2009). Pollutants leaching through the pores of the soil are transported in the upper soil horizons by SSR (Kleinman et al. 2008) or reach the deep horizons into the groundwater. Properties of the soil and physico-chemical characteristics of the pollutants play a major role in influencing their concentration in stream flow components and their partitioning between dissolved and particulate fractions (Ahmad et al. 2006; Arias-Estévez et al. 2008; Boithias et al. 2014). In fact, pollutants can be either bind to eroded particles and transported in the river water adsorbed onto the suspended matter or be complexed by dissolved organic matter and transported in the dissolved fraction (Edwards and Withers 2008; Arias-Estévez et al. 2008; El Azzi et al. 2013). Hence, in order to assess the impact of storm events on water quality and aquatic ecosystems, it is necessary to better identify the factors controlling the transfer of pollutants such as the total suspended matter (TSM), the particulate (POC), and the dissolved organic carbon (DOC).

In this study, high resolution data during a flash flood event were collected in the Save agricultural catchment in the south-west of France. The flood event was studied because it was previously proven that pollutant concentrations in dissolved and particulate matter increased 1- to 17-fold during these events (Shafer et al. 1997; El Azzi et al. 2013). The main objectives were to (1) measure pollutant concentrations during a storm flow event in the Save agricultural catchment; (2) determine pollutants' distribution in the different fractions (dissolved phase, suspended matter) and their variation during the flood event; (3) evaluate the contribution of storm flow components (SR, SSR, and GF) to pollutant transfer; and (4) identify the main controlling factors of this transfer from the soil to the river.

2 Materials and Methods

2.1 The Save River Catchment

The Save River, located in the "Coteaux de Gascogne" region (south-west of France), originates from the piedmont of the Pyrénées Mountains. Of about 140 km length, it drains an agricultural catchment of 1110 km^2. Sampling was conducted at Larra station (43° 43′ 4″ N–01° 14′ 40″ E), ahead of the confluence of the Save River with the Garonne River (Fig. 1, from Macary et al. 2014).

Ninety percent of this catchment's area is used for agriculture (Boithias et al. 2011). The upstream part of the catchment is a hilly agricultural area mainly covered with pasture—a 5-year rotation including 1 year of corn and 4 years of grazed fescue—and sometimes forest. The lower part is devoted to intensive agriculture with mainly a 2-year crop rotation of sunflower and winter wheat. Fertilizers are generally applied from late winter to spring. The climate is oceanic with an average annual precipitation of about 750 mm, mostly occurring in the form of thunderstorms (Taghavi et al. 2011). The Save River hydrological regime is mainly pluvial with a mean annual discharge of maximum discharge 6.1 m^3 s^{-1} (Boithias et al. 2011). During the low water period, from June to September, river flow is sustained upstream by the Neste canal (1.3 m^3 s^{-1}).

The catchment lies on detrital calcareous and clayey sediments. Calcic soils represent over 90% of the whole catchment with a clay content ranging from 40 to 50%. Non-calcic silty soils represent less than 10% of the soil in this area (50–60% silt; Revel and Guiresse 1995).

Storm events in this watershed lead to significant surface runoff and erosion. In fact, average mechanical and chemical erosion in this area are estimated to 27 (with river suspended matter primarily composed of silica, aluminum, iron, and titanium) and 70 t km^{-2} year^{-1} (with total dissolved solids mainly composed of calcium, magnesium, sodium, and carbonates), respectively (Probst 1983; Probst and Bazerbachi 1986).

2.2 Field Sampling and Water Sample Pre-Treatment

This study concerns a flood event which occurred from the 4th till the 13th of May 2010 (Fig. 2). This period coincides with a period of pesticides' application in the watershed (Boithias et al. 2011). The most applied pesticides during this period are trifluralin and metolachlor,

Fig. 1 Location and land-use maps of the Save watershed with indication of the LARRA sampling station (*star*) at the outlet. The land-use map is extracted from Macary et al. (2014)
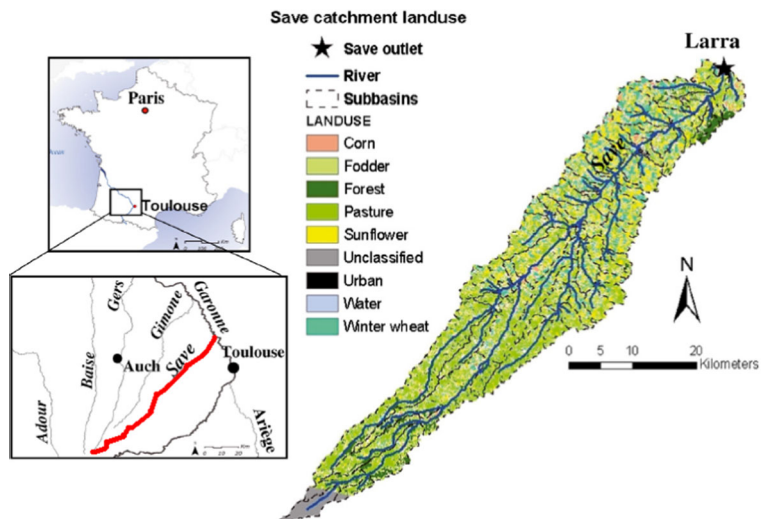
two herbicides on which this study focused the most. Each year, 23 tons of metolachlor, a highly soluble chemical ($S_w = 488$ mg L^{-1}, log $K_{ow} = 2.9$), and 18 tons of trifluralin, a poorly soluble chemical ($S_w = 0.22$ mg L^{-1}, log $K_{ow} = 4.83$), are applied on the catchment.

During the studied flood event, the instantaneous discharge increased from 3 m^3 s^{-1} to a peak storm flow of almost 50 m^3 s^{-1}. Twenty-two sampling points are represented on the storm hydrograph (Fig. 2). Two hours separated the samples during the rising limb of the hydrograph whereas longer time separated samples during the recession limb.

Water samples from the first meter depth of the river water column were manually collected by standing on a bridge at the outlet of the drainage basin at the Larra
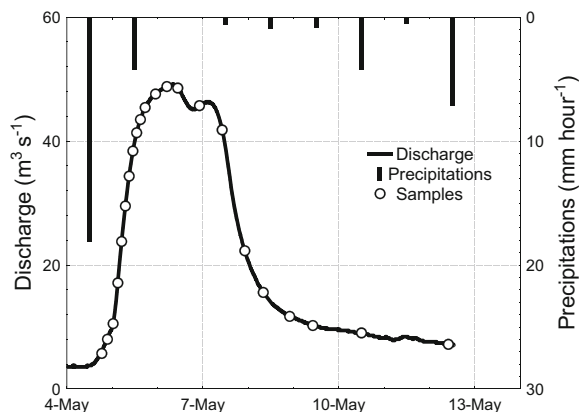

Fig. 2 Variations of Save river discharge and precipitations during the storm event of May 2010. Sampling points are represented with the *squares*. Source for discharge: CACG-France (www.cacg.fr)

station and using a 10 L bucket. After the sampling, the conditioning procedure differed for major elements, trace elements, and pesticides analysis, but all samples were kept in cold conditions.

For major and trace elements analysis, samples were filtered through a 0.22 μm pore diameter nitrocellulose filter previously rinsed with Ultrapure water (>18.2 MΩ.cm). The dissolved phase was then stabilized with ultrapure 15 M HNO$_3$ to drop down the pH of the solution at 1 before analysis. Then, all the samples were stored in a dark room at 4 °C.

For trace elements analysis, two water samples of 1 L each were stored at 4 °C. Prior to sampling, plastic materials were washed with 1 N HCl during 48 h, and then rinsed 3 times with Ultrapure water (>18.2 MΩ.cm) to limit the risks of contamination. Because trace elements, especially metals, are preferentially associated with the finest fractions presenting high specific surface areas (Gaiero et al. 2003; Zhao et al. 2011), a separation of the fine fractions was done to correct the grain-size effect (Förstner et al. 1979). Total suspended matter was separated by continuous-flow ultracentrifugation (Beckman; 700 mL/min; 17,000 RPM) at 0.22 μm. Contamination was avoided by rinsing three times with Ultrapure water (>18.2 MΩ cm). After separation, TSM samples were dried at room temperature, then stored in a cold room at 4 °C.

For pesticides analysis, two water samples of 2.5 L each were stored in glass bottles with Teflon-lined lids. Prior to sampling, glass material was cleaned with Decon® (a blend of amphoteric surface active agents, non-phosphate detergent builders, alkalis, and

sequestering agents in an aqueous base) and rinsed with Ultrapure (>18.2 MΩ cm) water. One of the two bottles was filtered with a cellulose ester filter (Millipore, 0.45 μm) by applying vacuum, then dichloromethane was added (1:40; *v/v*) to inhibit bacterial activity (Devault et al. 2007). Previously weighted filters were used to calculate TSM content at each sampling point. In the unfiltered samples, dichloromethane was directly added on the field (1:40; *v/v*). The glass bottles were then stored in dark and cold conditions until extraction few days later. Three filter blanks per sampling point were analyzed and their pesticide concentrations were always under the detection limit (1–3 ng L^{-1}).

2.3 Physico-Chemical Analysis

pH, temperature, and electrical conductivity were measured both on the field and in the laboratory. All the other physico-chemical parameters were only analyzed in the laboratory. Pesticides commonly detected in the Save River (acetochlor, aclonifen, atrazin, epoxiconazol, fenpropimorph, linuron, flusilazol, isoproturon, metolachlor, and trifluralin (Taghavi et al. 2011)) and six potentially harmful elements (Cd, Co, Cu, Ni, Pb, and Zn) were considered.

2.3.1 Dissolved and Particulate Organic Carbon (DOC and POC)

Pre-burned GF/F 0.7 μm pore diameter filters were used to filter 250 mL of each raw sample.

Bacterial development was prevented by addition of HgCl$_2$ 10^{-2} g L^{-1} to the samples destined for DOC analyses with a Shimadzu TOC 5000 Analyzer. Each value represents a mean of three to five measurements (limit of quantification 0.14 mg L^{-1} and uncertainty of 2%).

After filtration, the filters were dried and analyzed for POC using a Carlo Erba NA 2100 protein CHN analyzer (limit of quantification <0.02%).

2.3.2 Dissolved Major and Trace Elements

Water samples were analyzed for dissolved major and trace elements.

Major cation (Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+}) concentrations were analyzed by inductively coupled plasma-optic emission spectrometry (ICP-OES Thermo IRIS INTREPID II XDL). Typical limits of quantification

were between 0.5 and 0.3 mg L^{-1} for Na$^+$ and K$^+$ and between 0.07 and 0.03 mg L^{-1} for Ca^{2+} and Mg^{2+}.

Major anion (Cl$^-$, NO$_3^-$, PO$_4^{3-}$, and SO$_4^{2-}$) concentrations were measured by ion chromatography (HPLC, Dionex 4000I). Typical limit of quantification was 0.1 mg L^{-1}.

The international geostandard MISSISSIPPI-03 (Riverine Water Reference Material for major elements certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. A good agreement between the replicated measurements and the certified values was obtained (relative difference <10%).

Trace element concentrations were measured in 2% suprapure HNO$_3$ by inductively coupled plasma-quadrupole mass spectrometry (ICP-Q-MS Agilent 7500ce) equipped with a collision cell He. Typical detection limits are between 1 and 100 ng L^{-1} and the external precision is ±5%. An internal standard NIST 96 containing In and Re was used to correct the instrumental drift. For each element, the relative standard deviation (RSD) was lower than 5 %. The international geostandard SLRS-5 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was used to check the validity and reproducibility of each analysis. A good agreement between the replicated measurements and the certified values was obtained (relative difference <10%).

2.3.3 Particulate Trace Elements

Total digestion was performed in a clean room on the fine TSM fraction (>0.22 μm). Dry weight (0.1 g) was digested with 1 mL of double-distilled HNO$_3$ (68 %) and 1 mL of concentrated HF (47 to 51%). The dry residue was then attacked with 1.6 mL of double-distilled HNO$_3$ and 0.6 mL (three times) of H$_2$O$_2$ 35% to destroy the organic matter. Finally, the sample underwent a digestion in 2 mL of double-distilled HNO$_3$. This procedure was successfully tested by N'guessan et al. (2009) for total digestion of fluvial sediments and soils.

During the digestion procedure, blanks and certified reference materials (SRM-1646a—estuarine sediment, SUD-1—lake sediment, and WQB-1 and STSD-3—stream sediments) evaluated the potential external contamination and the efficiency of the chemical procedure. Average recovery rates of used standards were satisfactory: between 94 and 105% for SRM-1646a, SUD-1,

WQB-1, and STSD-3. The total digestion can, therefore, be considered reliable. Trace element concentrations were determined in 2% HNO_3 by ICP-Q-MS Agilent 7500ce equipped with a collision cell He.

2.3.4 Pesticide Analysis: Multi-Residue Approach

Pesticides' concentrations were analyzed in both filtered and unfiltered waters. Then the particulate fraction was estimated by difference between unfiltered and filtered water analyses, as already done successfully by Taghavi et al. (2010). Pesticide analysis was performed by solvents of analytical grade ("pestipure" by SDS, Solvent Documents Syntheses, Peypin, France). Anhydrous sodium sulfate from SDS was used to dry the organic phases.

To extract water samples, the liquid/liquid extraction technique was applied (Tan 1992) in shaker flasks (3–4 L with Teflon key). Each water sample corresponded to 1 L. Dichloromethane was used as a solvent for phase exchange with a solvent/water ratio of 1:6 (*v/v*). Once the extraction was performed, dichloromethane was dried on 50 g anhydrous sodium sulfate and the remaining organic phase was evaporated under vacuum. The dry residue was reconstituted with 2 mL of hexane.

The contaminants were identified on a gas chromatography column from Zebra ZB-5MS 30 m, 0.25 mm i.d., and 0.25 μm film from Phenomenex® (Torrance CA) with Thermo Fisher Scientific (Waltham.MA) Trace GC 2000 coupled with a DSQ II mass detector. The chromatographic conditions are described by Taghavi et al. (2011).

The detection limit, based on a signal-to-noise ratio of 3, was estimated to 1 to 3 ng L^{-1} depending on the molecule. Pesticide Mix44 prepared by Dr. Ehrenstorfer (purchased from Cluzeau Information Laboratory (CIL), Sainte-Foy-la-Grande, France) was used as standard solution. Other pesticide standard solutions were obtained the same way and fenitrothion-d_6 was used as internal standard. Recoveries were determined using water samples spiked with different molecules analyzed in this study. Average recovery rates ranged from 91 to 102%.

2.4 Partitioning into Particulate and Dissolved Phases

In order to identify the distribution of pollutants between the dissolved and the particulate phases and estimate their availability, the partition coefficient (K_d in g L^{-1}) of each pollutant was calculated as follows:

$$K_d\left(g.L^{-1}\right) = \frac{C_{dissolved}\left(\mu g.L^{-1}\right)}{C_{particulate}\left(\mu g.g^{-1}\right)} \quad (1)$$

$C_{dissolved}$ is the concentration of the pollutant in the filtered water and $C_{particulate}$ is the concentration of the pollutant in the TSM. The concentration of the pesticide in particulate fraction in micrograms per gram is obtained by difference between the concentration (micrograms per liter) in unfiltered and filtered water, weighted by the TSM concentration in grams per liter. For metals, the concentration in particulate fraction was obtained as described in Section 2.3.3.

2.5 Hydrograph Separation

Separation of different storm flow components (surface runoff SR, subsurface runoff SSR, and groundwater flow GF) was conducted using two different methods: the hydrological approach based on a hydrograph-separation technique and a mixing model using physico-chemical tracers of the different reservoirs.

2.5.1 Hydrological Approach

Early techniques to separate storm hydrographs into different flow components involved graphical separation or recession analysis to determine the portion of stream flow that originates from groundwater or base flow. The graphical decomposition method used is based on Maillet's law (1905) in which the discharge follows an exponential decrease as a function of time during the recession period:

$$Q_t = Q_0 e^{(-\alpha t)} \quad (2)$$

Where Q_t stands for the discharge at time t, Q_0 refers to the initial discharge at $t = 0$, and α is the recession constant.

This exponential equation was used by several authors (Barnes 1939; Roche 1963; Chow 1964). In this approach, river total discharge during storm flow is considered as a mixture of three main flow components: SR, SSR, and GF. Each component has a specific recession constant α which reflects the physical characteristics of the reservoir. When plotting the recession curve of the hydrograph in logarithm, it becomes possible to identify three linear segments, each segment corresponding to the recession of one reservoir according to

Maillet's law (1905). Practically, by plotting log(Q_t) as a function of time, the graphical separation method mainly helps identify the GF component of a flood hydrograph event, including the point where the base flow intersects the falling limb. There is usually a time-lag between the rainfall and the increase in the total river discharge. Before this increase and after the point where the base flow intersects the falling limb of the hydrograph, GF is considered as the sole contributor to the total discharge. The GF starts to increase only at the peak of the total discharge where SR stops contributing. In addition, the peaks of SR and SSR must coincide with the peak of the total discharge. Therefore, the rising limbs of the different flows corresponded to the line linking the beginning of the total discharge increase to the peak of each flow. The principle of this storm flow component separation was already used by many authors (Chow 1964; Singh and Stall 1971; Linsley et al. 1975; Anderson and Burt 1980).

Even though this method is based on well-known hydrological principles, the results obtained were compared with another independent method using chemical tracers for the different components.

2.5.2 Physico-Chemical Approach

Newer techniques involve separating hydrographs into source components using naturally occurring tracers. The well-established two to *n*-component mixing model (Pinder and Jones 1969; Ladouche et al. 2001; Mul et al. 2008) was used to separate the stream flow components. This approach was based on two mass conservations—one for water and one for the geochemical tracer—and allows separating the relative contribution of the different components which originate from different hydrological reservoirs. The use of geochemical tracers allows identifying the three-dimensional origins of the storm flow components. It requires, however, that the tracer signatures be conservative; that is, they do not change through a storm or the changes can be corrected for.

Choosing the appropriate natural tracers for each flow was based on the results of the high frequency sampling and analysis of water during the flood event. The TSM content was used as a natural tracer of the SR (Tardy et al. 2005) and PO_4^{3-} concentration in water was used as a tracer of GF (Hannigan and Bickford 2003; Turner 2009). These two tracers had opposite behaviors during the flood

event: TSM increased with discharge due to the increase of SR contribution responsible for physical erosion and for the transport of suspended matter to the river while PO_4^{3-} content decreased due to a dilution effect of groundwater by surface water and rain water.

The mixing model is based on the steady state form of the mass balance equations for water and a conservative tracer,

$$Q_t C_t = \Sigma Q_i C_i \qquad (3)$$

$$Q_t = \Sigma Q_i \qquad (4)$$

Where Q_t is the total river discharge and C_t is the tracer concentration in the river water at the outlet of the catchment; Q_i and C_i represent, respectively, discharge and concentration of each flow component *i* (SR, SSR, and GF).

The relative contribution of SR, SSR, and GF can then be calculated at any given time *t*.

2.6 Statistical Analysis

STATISTICA 8.0 was used to carry out graphical and statistical analysis of the data set. The significance of correlations was tested by using Pearson and Spearman tests.

3 Results

3.1 Controlling Factors and Major Elements Variations During the Flood Event

Despite the input of precipitations, stream water pH remained between 8.0 and 8.5 decreasing only weakly during the event (Fig. 3a). Electrical conductivity presented also low variability around 500 $\mu S\ cm^{-1}$.

TSM and DOC concentrations increased with increasing discharge during the flood (Fig. 3b, c). However, TSM reached its maximum of concentration before the peak discharge and decreased rapidly afterwards, whereas DOC concentration reached a delayed maximum but remained high during the recession period. Other studies showed the same patterns during storm flows in the same catchment (Oeurng et al. 2010; Taghavi et al. 2011). POC decreased with increasing
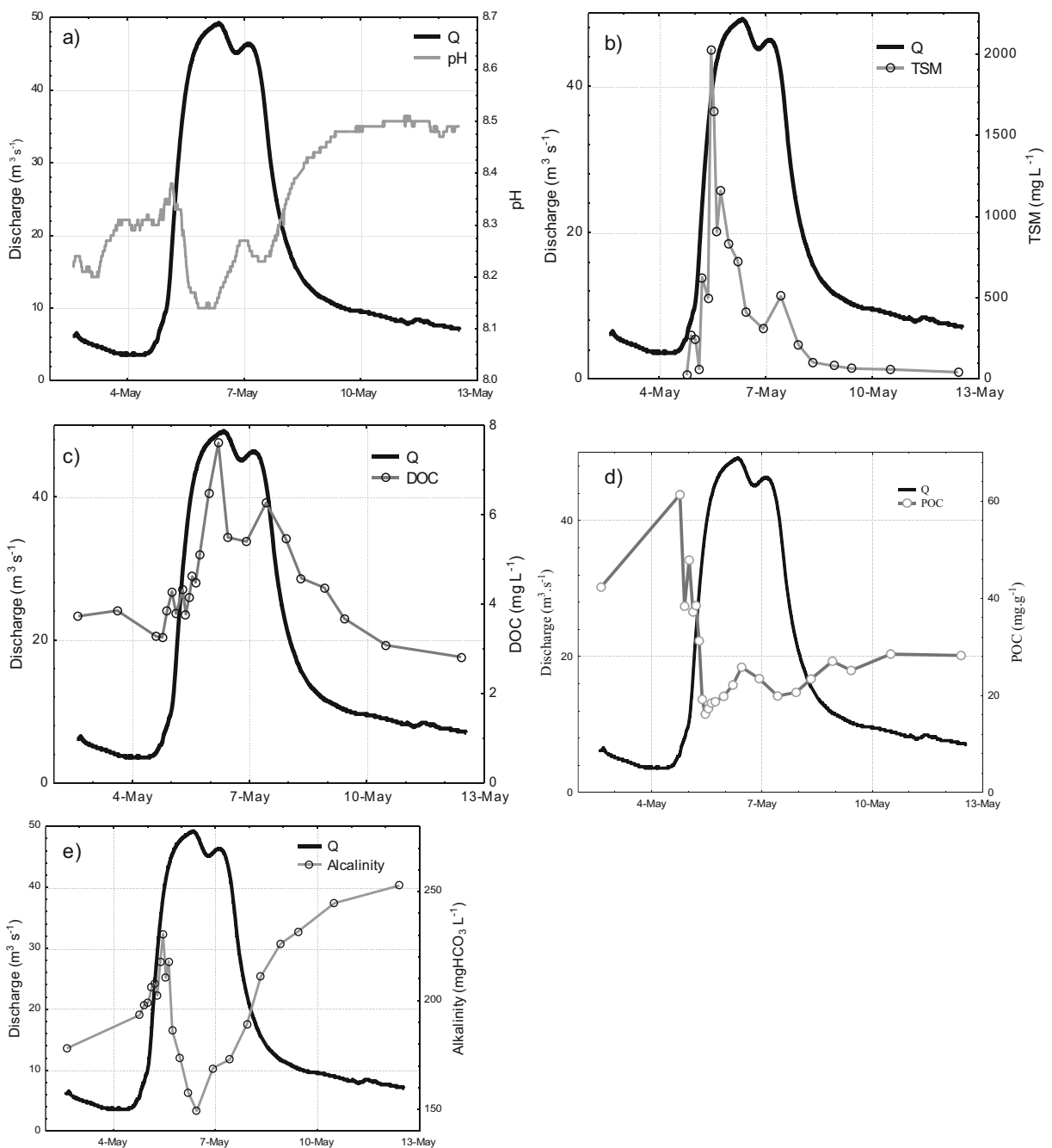
Fig. 3 Variations of **a** pH, **b** total suspended matter (TSM), **c** dissolved organic carbon (DOC), **d** particulate organic carbon (POC), and **e** alkalinity during the storm event of May 2010 at the outlet of the Save catchment

TSM concentration (Fig. 3d). Similar relationships were observed in the same catchment during the period 2008–2009 (Oeurng et al. 2011) and in many world river systems (Ludwig et al. 1996; Gao et al. 2002). These authors mainly associated the decrease of POC percentage in TSM during high floods to a dilution by the increasing input of mineral matter eroded from soils.

Alkalinity (expressed in mg HCO_3^- L^{-1}) remained high decreasing from around 250 to 150 during the storm event (Fig. 3e).

Variations of major anions and cations during this flood event are shown in Fig. 4. Thus, different patterns can be identified depending on the chemical behaviour with respect to stream discharge at the outlet.

Pattern I: TSM, DOC, K^+, and NO_3^- which contents increased with increasing discharge.

Pattern II: Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, PO_4^{3-}, and Cl^- which are strongly diluted with increasing discharge.

3.2 Contributions of the Different Streamflow Components

Hydrograph separation results are represented on Fig. 5a for the hydrological method and Fig. 5b for the physico-chemical approach using TSM and PO_4^{3-} concentrations.

The results showed that (1) GF was the unique contributor at base flow, (2) SR was the first to exhibit the peak, and (3) the maximum of SSR followed that of the

Fig. 4 Variations of discharges and of major **a** cations and **b** anions during the flood event of May 2010 at the outlet of the Save catchment. Q is the total discharge
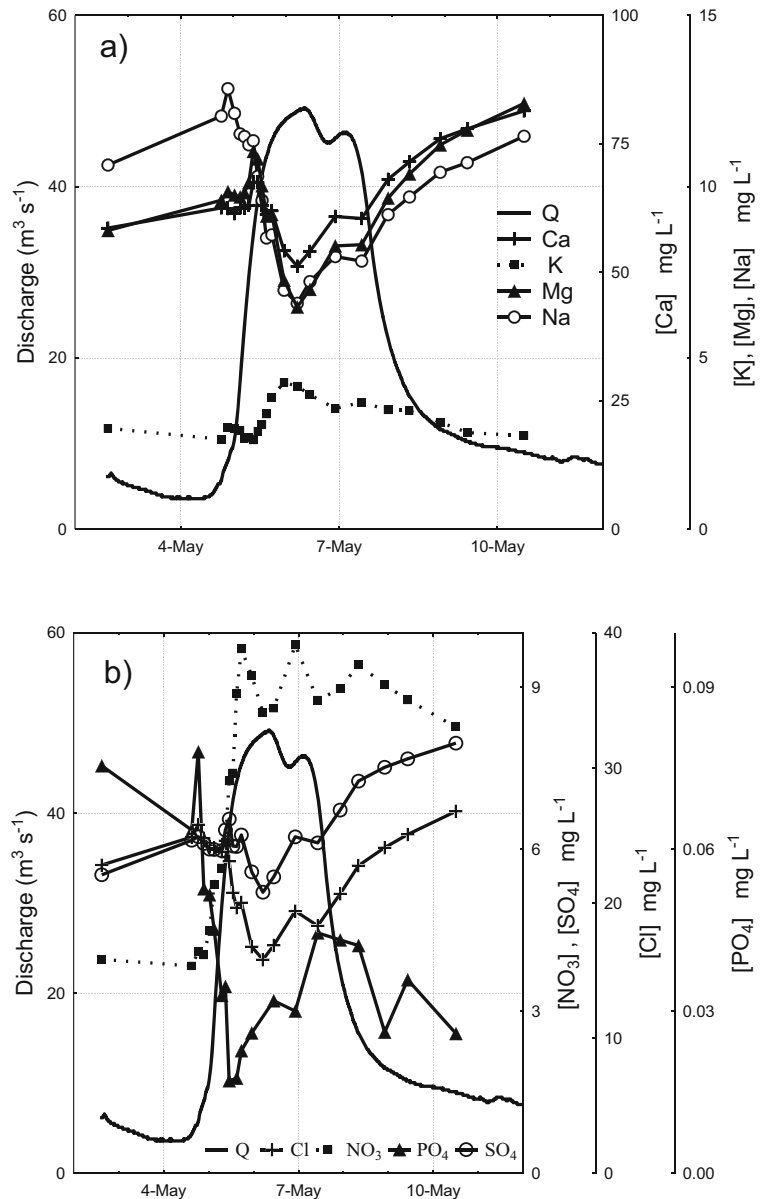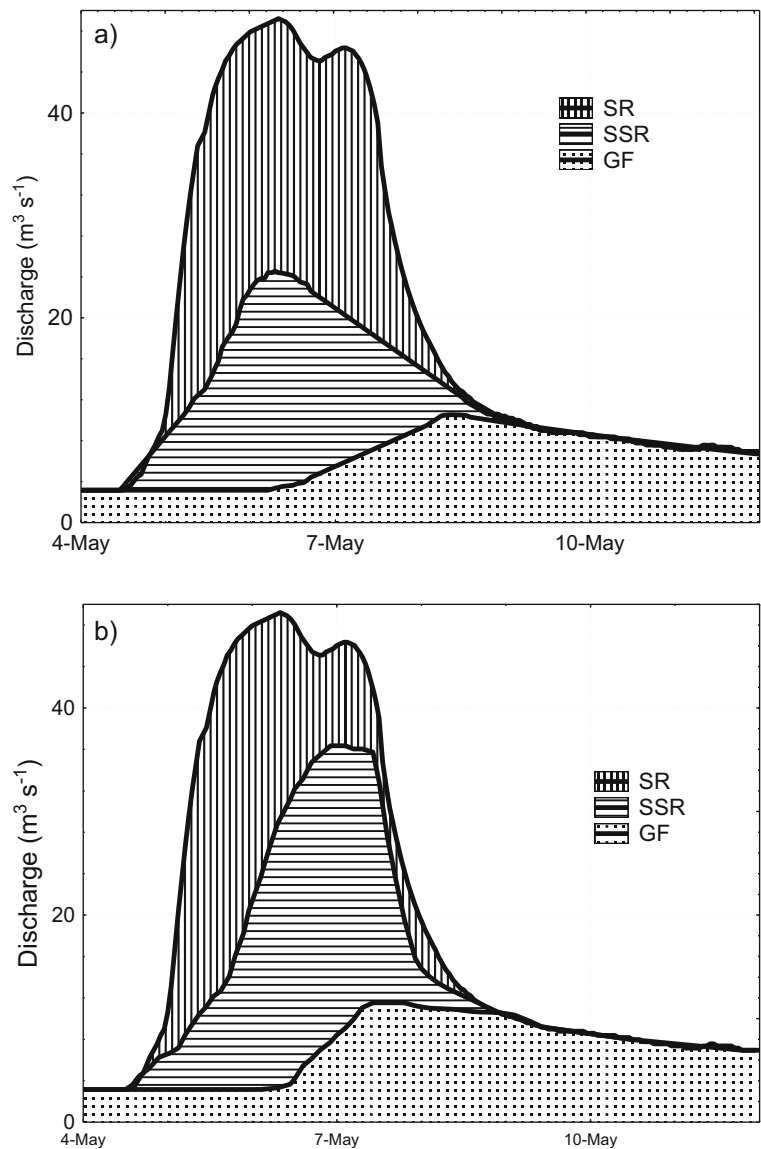
Fig. 5 Hydrograph separation of the different storm flow components (*SR* surface runoff, *SSR* subsurface runoff, *GF* groundwater flow) during the flood event of May 2010: **a** using the hydrological approach based on Maillet's law and **b** using the chemical approach in which TSM was used as tracer of SR and PO_4^{3-} as tracer of GF

SR decreasing slower. When compared, flow component contributions estimated by both method showed significant correlations: $r^2 = 0.81$ for SR, $r^2 = 0.86$ for SSR, and $r^2 = 0.90$ for GF. All correlations were significant at $p < 0.05$ with $n = 22$ sampling periods.

The lag observed between the shapes of the SR and SSR contributions estimated in the two methods is mainly due to the TSM tracer used in the mixing model. Indeed, TSM reached its maximum before the discharge peak. The SR contribution was maximum during the rising limb of the hydrograph and appeared greater than the SR contribution estimated by the graphical hydrological approach. In the same way, TSM decreased

rapidly during the recession period and the SR contribution became very limited. This difference between the rising and falling periods is probably excessive compared to the result obtained from the hydrological approach. In fact, the TSM decreasing during the recession probably includes the sedimentation processes. Therefore, TSM cannot be considered as a conservative tracer during the recession period.

Both methods showed the important contribution of SR (33%) and SSR (40%) in the total discharge during storm flow. During the rising water, both SR and GF contributed to the flow, whereas during the last stage of falling water, SSR and GF contributed to it. At the

maximum discharge, all three reservoirs contributed together. Probst (1986) and Etchanchu and Probst (1986) obtained the same patterns using hydrograph separation for the Girou river draining, in the same region, a molassic agricultural catchment (520 km^2) similar to the Save catchment.

3.3 Variations of Trace Element Concentrations

The concentration of the analyzed trace elements (Cd, Co, Cu, Ni, Pb, and Zn) in water varied from less than 0.1 (for Cd) to more than 8 µg L^{-1} (for Zn; see Table 2). Independently of their range of concentration, trace elements in dissolved fractions followed different patterns during the storm (Fig. 6).

The first group showed increasing concentrations with the water discharge during the storm event. This is the case not only of Cu (Fig. 6a), but also of Co, Ni and Pb. These elements may have been accumulated in soils and sediments of the watershed, then transported to the river during the flood by erosion and leaching of soils.

The second group showed decreasing concentrations with the rising discharge during the flood. This is the case of Zn (Fig. 6b). This pattern indicates a dilution of the concentration in river water during high discharges due to higher contributions of SR and SSR, which are less concentrated in these elements. This pattern characterizes a major transfer of these elements through GF.

Other elements like Cd (Fig. 6c) had less evident patterns with regard to river discharge. Cd content showed a rapid decrease when discharge increased during the rising period (probably due to a dilution by SR). Then at the peak discharge, the Cd content increased due to higher contribution of SSR and a flash input of Cd from soil leaching of available Cd from fertilizers. The transfer of such elements was done via more than one stream flow component and further investigation still needs to be done.

Cd, Co, Cu, Ni, Pb, and Zn were also detected in the particulate phase (Table 2). Their concentrations per gram of suspended matter decreased during the flood (Fig. 6) because of higher TSM contents.

Both concentrations in dissolved and particulate phases were close to ranges advanced for watersheds in the same region (N'guessan et al. 2009; Roussiez et al. 2013) and most slightly below other small agricultural watersheds worldwide (Xue et al. 2000; Vesper and White 2003; Oursel et al. 2014).

The studied trace elements showed different K_d patterns during the flood : (1) for Pb, K_d increased rapidly at the beginning of the flood and decreased gradually after; (2) Cd, Co, Cu, and Ni had K_d that increased and remained high throughout the flood event; and (3) the K_d of Zn decreased during the flood. It was found that the ability of the Save TSM to adsorb trace metals decreased in the order Zn > Cd > Pb > Cu > Co > Ni. Differences were related to SPM loads and DOC levels in the river and their associated influences on the partitioning of the metal (Shafer et al. 1997; Roussiez et al. 2013). The relationship with each of the controlling factors explained each of these K_d variations. For instance, Cu and Ni showed positive and significant relationship with DOC (respectively, $r^2 = 0.9$ and 0.8, $p < 0.05$, $n = 22$). Therefore, the richer the water is in DOC, the more concentrated these two elements will be. Some of the metals showed poorer correlations, because of the variability in the composition of DOC, POC, and SPM and in the metal forms present.

3.4 Variations of Pesticide Concentrations

Pesticides were detected in all filtered and unfiltered samples (Table 3). Pesticides can be classified in three groups of concentrations in filtered and unfiltered waters.

Group I with low concentrations (<0.1 µg L^{-1}) contains trifluralin and fungicides (epoxiconazole, fenpropimorphe, and fluzilazole). Trifluralin is one of the most used pesticides in the catchment during this period, but showed low concentrations in the water. In fact, trifluralin is a poorly soluble chemical ($S_w = 0.221$ mg L^{-1}, log $K_{ow} = 4.83$).
Group II with high concentrations (0.1 to 0.3 µg L^{-1}) contains herbicides like acetochlor, aclonifen, atrazine, isoproturon, and linuron.
Group III with very high concentrations (>1 µg L^{-1}) contains metolachlor with, respectively, 7.1 and 6.4 µg L^{-1} in unfiltered and filtered waters. Metolachlor is a highly soluble chemical ($S_w = 488$ mg L^{-1}, log $K_{ow} = 2.9$) and is one of the most used herbicides during the period of the study. All detected molecules had the same pattern with discharge variations. In fact, most of the pesticide concentrations (filtered and unfiltered) increased with the increasing discharge (Fig. 7), except for very low soluble molecules like trifluralin in the
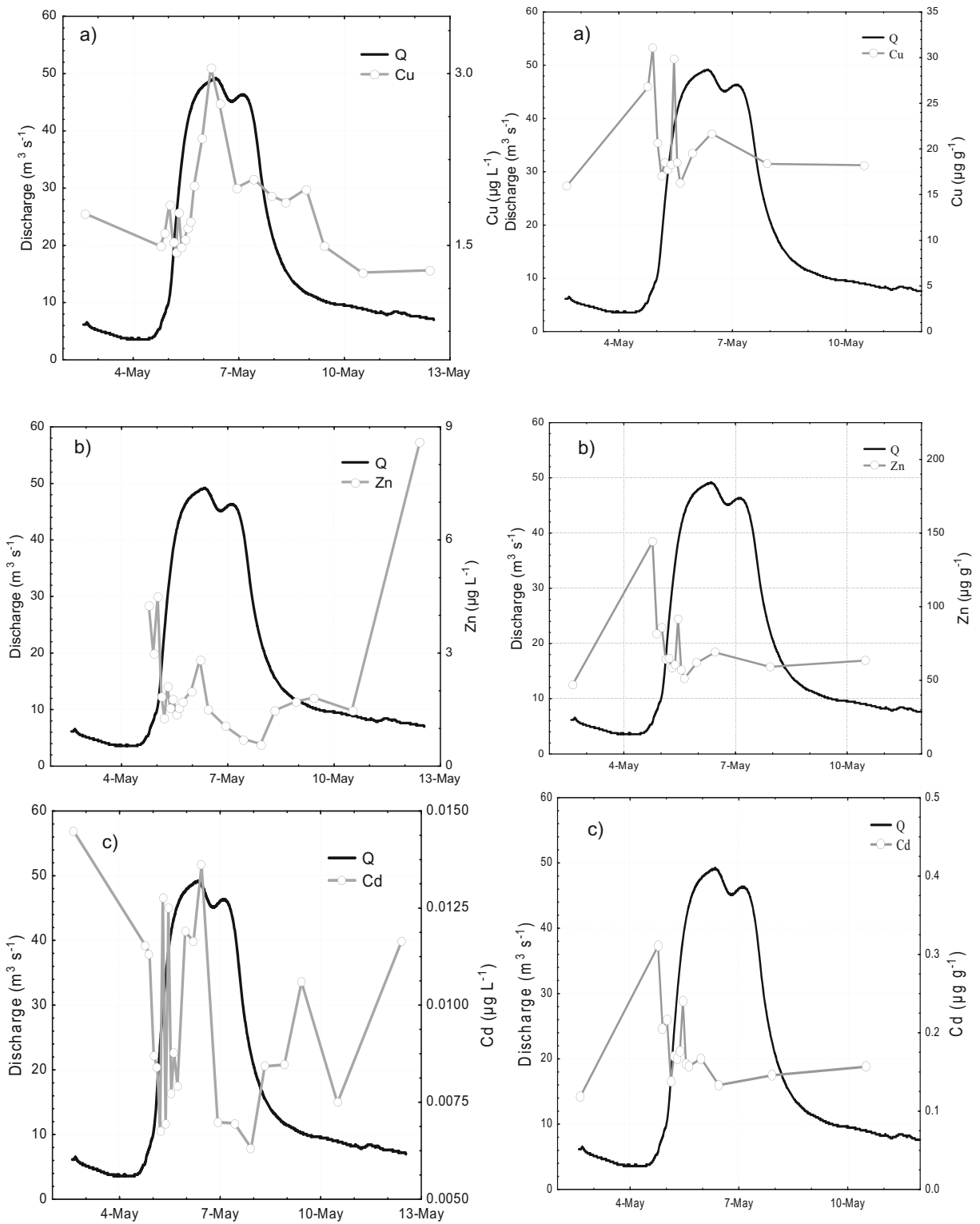
Fig. 6 Variations of discharge (*Q*) and trace element concentrations during the flood event of May 2010: **a** Cu, **b** Zn, and **c** Cd; the *left column* represents the dissolved concentrations in micrograms per liter whereas the *right column* represents the particulate concentrations in micrograms per gram

filtered waters. The same patterns were observed by Goolsby et al. (1991), Thurman et al. (1994), and Taghavi et al. (2011).

The study of pesticide concentrations in both unfiltered and filtered waters helped estimating, by difference, the concentration of pesticides exported by the suspended matter. This export depends on each molecule's characteristics, particularly, the water solubility (S_w mg L^{-1}) and the octanol-water partitioning coefficient, K_{ow} (Tomlin 2006). As an example, there were few differences between unfiltered and filtered waters for highly soluble molecules like metolachlor for which the particulate fraction (unfiltered minus filtered) averaged only to 11.6% during the storm event of May 2010 (Fig. 7a). On the contrary, for low soluble molecules like trifluralin, the difference between unfiltered and filtered water was significant especially at the peak (Fig. 7b). In fact, during the storm event of May 2010, 78.8% of the total fluxes of trifluralin were exported with the suspended matter. Taghavi (2010) studied the same watershed for 2 years collecting more than 120 samples at the outlet during high and low flows and the results of our study fall within the average annual intervals advanced.

Most of the studied pesticides presented increasing K_d at the beginning of the flood. This K_d decreased gradually after. Thus, the presence of pesticides in soluble unstable phases was proven at the beginning of the flood event. The increasing K_d, despite the increase of TSM, showed not only a decrease in the number of available fixation sites on TSM due to interactions between particles and to probable obstruction (Lu and Allen 2001), but also an increase in the DOC contents that are capable of complexing these pesticides (Taghavi et al. 2010).

4 Discussion

The thorough sampling of the flood event made it possible to estimate the contribution of each flow component to the total river discharge. Correlations were therefore possible between pollutants, flow components and controlling factors. These correlations helped identifying potential transfer pathways of the pollutants from the soils to the river water.

4.1 Concentration-Discharge Relationships

Hysteresis is a dynamic relationship between the dissolved or particulate concentration and the river discharge during storm events and this relationship may be represented in a circular pattern (Toler 1965; Johnson and East 1982; Davis and Keller 1983; House and Warwick 1998; Bača 2008). It helps understanding how discharge is affecting a pollutant's concentration and the potential the soil-river transfers, and hence, its controlling factors. These relationships showed that the element's concentration was different between the rising and the falling period of the hydrograph for the same river discharge.

Clockwise hysteresis was observed for elements or molecules primarily controlled by SR such as TSM, POC, linuron, trifluralin, Cd, and Zn (example in Fig. 8a). In fact, results showed that TSM and POC presented the best correlation with SR (respectively, $r^2 = 0.98$ and $r^2 = 0.60$ at $p < 0.05$ and $n = 22$).

Anticlockwise hysteresis was observed for elements or molecules primarily controlled by SSR such as DOC, aclonifen, metolachlor, and Cu (example in Fig. 8b).

The major role of SR and SSR detected in this study was stressed in previous studies (Flury et al. 1995; Johnson et al. 1996; Duffner et al. 2012).

These results were validated by significant correlations established between each pollutant's concentration and the discharge of the flow component which is mainly responsible for its soil-river transfers. Copper content-discharge relationship exhibited an anticlockwise hysteresis showing that during the recession period when the SSR contribution was higher, Cu content was higher (Fig. 8b). Then, Cu content presented the best correlation with SSR discharge (Fig. 9b) estimated using hydrograph separation, while the correlations with SR and GF discharges were not significant. Probst (1985, 1986) showed the same kind of relationships for TSM with SR and for nitrate concentration with SSR.

4.2 Vectors of Pollutant Transport

Properties of the pollutants play a major role in their transfer. They can be either adsorbed onto particulate matter (including POC) or complexed by dissolved organic carbon. Many studies reported relationships between the total river discharge, DOC, POC, and TSM concentration and total pollutant concentration during storm events (Taghavi et al. 2011). However,

Fig. 7 Variations of discharge (Q) and metolachlor (**a**) and trifluralin (**b**) concentrations measured in unfiltered (*circles*) and filtered (*squares*) waters during the flood event of May 2010
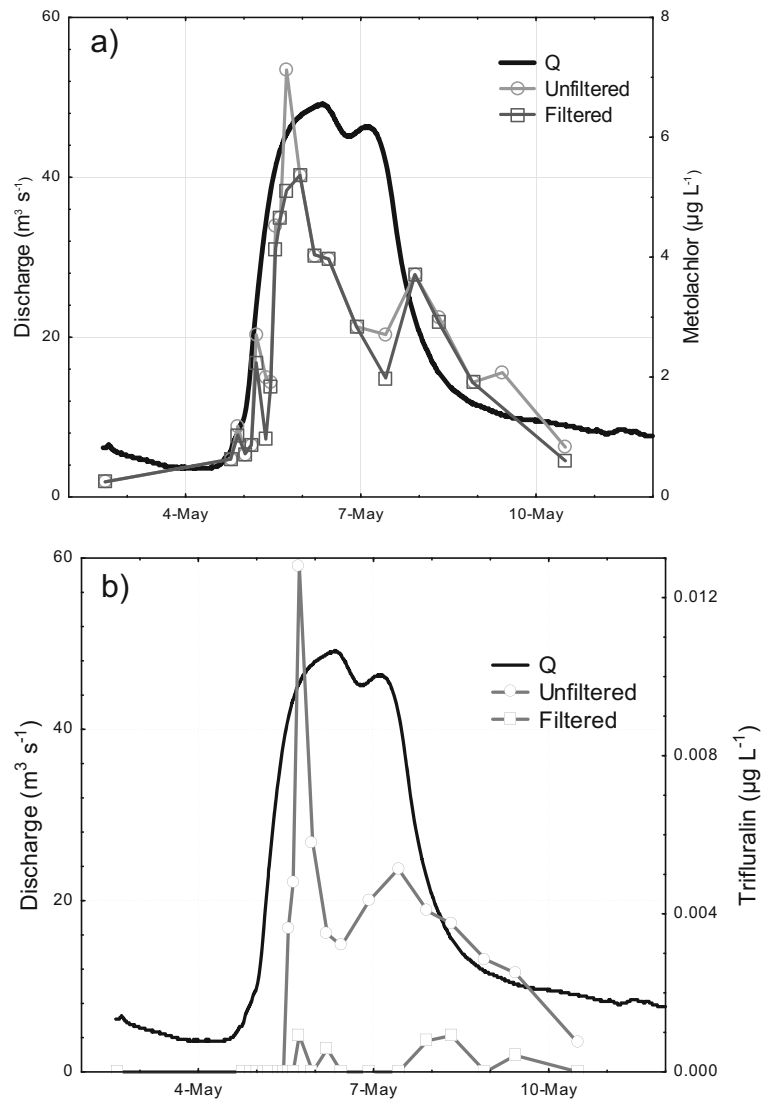
none combined pollutants and vectors' concentrations with hydrograph separation techniques. In fact, when combining hydrograph separation with concentration-discharge relationships and correlation analysis, possible pathways and controlling vectors were proposed.

Simple correlations between the estimated discharges of SR, SRR and GF during the flood and the total pollutant concentrations gave an idea of the possible pathway of the pollutant. On the other hand, correlations between the concentration of the pollutant and the concentration of each controlling factor gave insight on the probable controlling vector.

A summary of results obtained for the studied pollutants were presented in Table 1.

Pesticides with low solubility such as trifluralin showed significant correlations with TSM and POC and were therefore mainly transported via SR where suspended matter is concentrated. In fact, the unfiltered water content of trifluralin presented a correlation with TSM content ($r^2 = 0.7$ at $p < 0.05$ and $n = 22$). Previous studies also showed the important role of surface water in the transport of TSM and low-soluble elements (Probst 1985; Probst and Bazerbachi 1986; Kattan et al. 1987).

Pesticides with moderate solubility such as isoproturon showed significant correlations with both SR and SSR, respectively, linked to either POC/TSM or DOC.
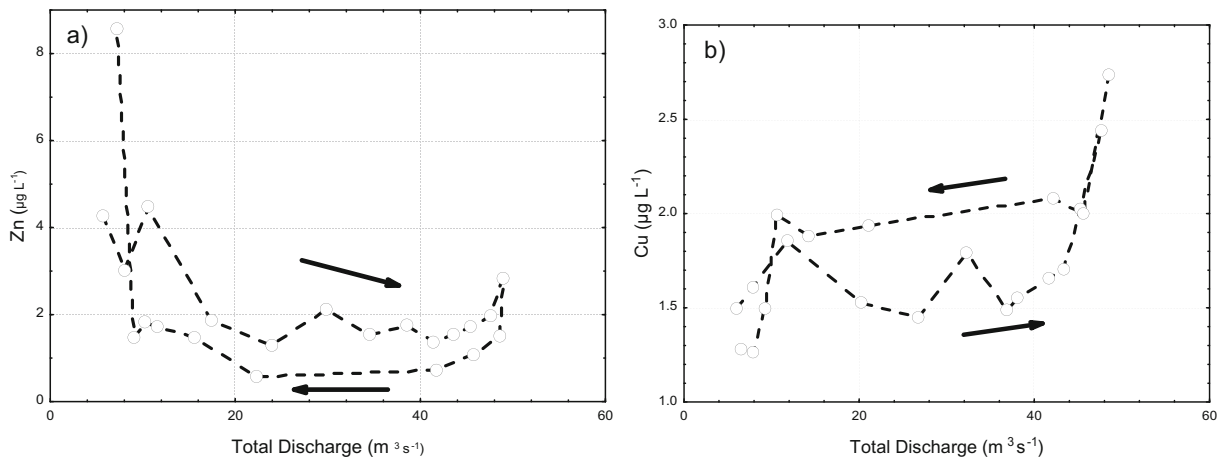
Fig. 8 Relationships between **a** dissolved Zn and the total discharge and **b** dissolved Cu and the total discharge. The direction of the hysteresis pattern is given by the *arrow*

Pesticides with high solubility such as metolachlor showed significant correlations with DOC (for unfiltered water content in metolachlor and DOC: $r^2 = 0.50$ at $p < 0.05$ and $n = 22$) and are,
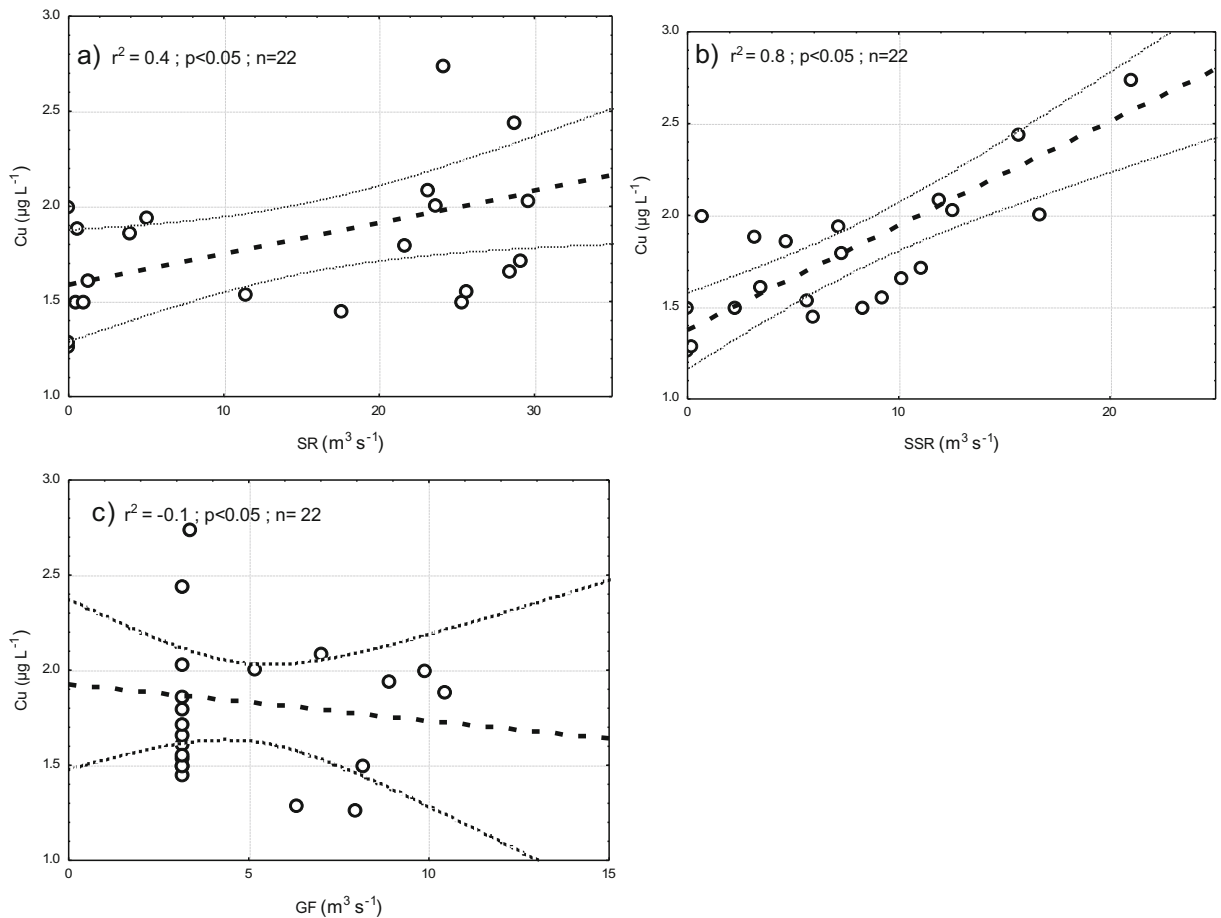

Fig. 9 Relationships between dissolved Cu concentration and the discharge of the different storm flow components: **a** surface runoff (SR), **b** subsurface runoff (SSR), and **c** groundwater flow (GF)
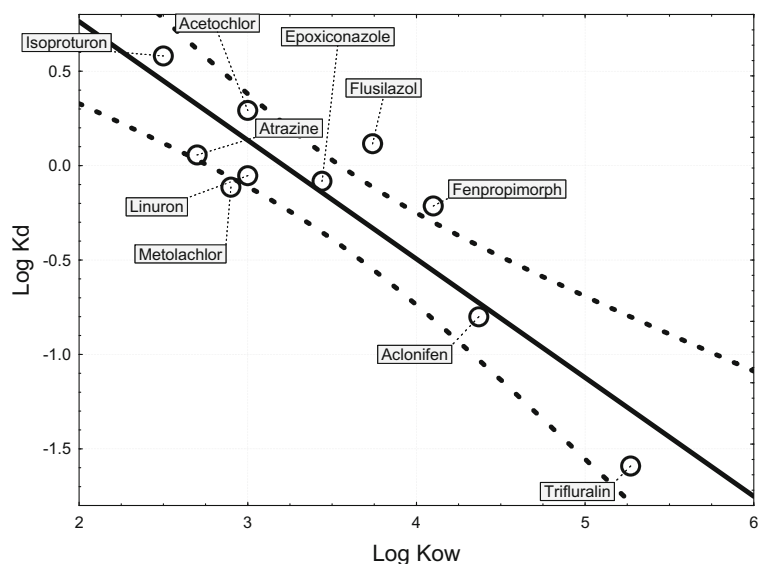
Table 1 Summary of estimated transfer dynamics of trace elements and pesticides in the Save River during the flood event of May 2010

	Main contributing flow (R^2)	Main controlling vector (R^2)
Trace metals		
Cd	SR (0.6)	POC (0.8)
Co	SSR (0.9)	DOC (0.8)
Cu	SSR (0.8)	DOC (0.9)
Ni	SSR (0.9)	DOC (0.9)
Pb	SSR (0.5)	DOC (0.6)
Zn	GF (0.5)	–
Pesticides		
Acetolachlor	SSR (0.6)	DOC (0.5)
Aclonifen	SSR (0.7)	DOC (0.5)
Atrazin	SR (0.6)	DOC/POC (0.6/0.6)
Epoxiconazol	SR (0.8)	POC/TSM (0.7/0.7)
Fenpropimorph	SR (0.6)	DOC/POC/TSM (0.6/0.5/0.6)
Linuron	SR (0.7)	POC/TSM (0.6/0.7)
Fluzilazol	SR/SSR (0.6 / 0.5)	DOC/TSM (0.6/0.7)
Isoproturon	SR/SSR (0.9 / 0.6)	DOC/TSM (0.7/0.6)
Metolachlor	SSR (0.7)	DOC (0.6)
Trifluralin	SR (0.6)	TSM/POC (0.5/0.5)

SR surface runoff, *SRR* subsurface runoff, *GF* groundwater flow, *DOC* dissolved organic matter, *POC* particulate organic matter, *TSM* total suspended matter

therefore, mainly transported via SSR. Similar results were also found in previous studies (Taghavi et al. 2011).

On the other hand, trace elements showed significant correlations with DOC and POC (e.g., dissolved Cu-DOC: $r^2 = 0.90$ at $p < 0.05$ and $n = 22$). The important role of organic matter in the transfer of trace elements was largely described previously (Lu and Allen 2001; Gaiero et al. 2003; El Azzi et al. 2013). Consequently, trace elements were mainly transported by SSR and originated from soil leaching, except Cd which was supplied by SR originating mainly from fertilizer inputs (see N'Guessan et al. 2009) and Zn exported mainly by GF. These results corresponded with those found when studying the variation of K_d of these elements during the flood. In fact, the studied trace elements showed different K_d patterns during the flood: (1) for Pb, K_d increased rapidly at the beginning of the flood and decreased gradually after; (2) Cd, Co, Cu, and Ni had K_d that increased and remained high throughout the flood event; and (3) the K_d of Zn decreased during the flood.

4.3 Pesticides Partitioning into Particulate and Dissolved Phases

The octanol-water partition coefficient K_{ow} is generally listed in databases and easily available. It was interesting to check the existence of a relationship between K_d and K_{ow} (Fig. 10) and the equation found is:

$$\text{Log}K_d = -0.63\log K_{ow} + 2.02 \quad (5)$$

with $r^2 = 0.8$, $p < 0.01$, $n = 10$.

Equation 5 is similar to the equation proposed on the Montousse catchment (a sub-basin of the Save river

Fig. 10 Relationship between the average log K_d (resulting from this study) and log K_{ow} (from the literature) of pesticides studied during the flood event of May 2010 at the outlet of the Save catchment

basin) for simazine, chlorotuluron, isoproturon, DEA, terbuthylazin and tebuconazole (Taghavi et al. 2010):

$$LogK_d = -0.99logK_{ow} + 2.01 \qquad (6)$$

On the Save River, Boithias et al. (2014) expressed the partition coefficient K_d as a function of K_{ow} and TSM, easily measurable and commonly simulated in pesticide fate models:

$$K_d = ((0.094/(TSM-5)) + 0.21)$$
$$\times \left(7.55x10^{-3}.K_{ow}^{0.36}\right) \qquad (7)$$

It was interesting to show here that even if we change the scale of the study, the relationship between K_d and K_{ow} remains more or less the same for pesticide molecules used in this region. The study of Taghavi et al (2010) was on a very small catchment (320 ha) whereas in this study the save river basin is draining 1200 km^2.

One of the main objectives of pesticide science is to predict, with little laboratory and field experiments, the environmental impact of a pesticide before its release in the environment (Briggs 1981). Equations (5) and (6) can predict water pollution potential by estimating the tendency of a pesticide to undergo leaching and runoff (K_d) only by knowing its chemical characteristic (K_{ow}). When important TSM variations exist, Eq. (7) can be used. Similar studies allowed successful environmental decision-making (Kanazawa 1989; Wauchope et al. 1992) and predicted the toxicity and accumulation of pesticides in food-webs.

Equations (5) and (7) are specific for the Save river and can help future management, modelling and estimation of pollutant transfers during floods. It is, however, still unclear how precisely this kind of equation can be extrapolated to other sites under different set of conditions (Wauchope et al. 1992).

5 Conclusion

The studied storm flow event led to high fluxes of pollutants exported to the outlet of agricultural catchment. In fact, the majority of studied pollutants, mainly originating from diffuse sources, exhibited high concentration during the flood event. These storm flow events are also very important to estimate the transfer dynamic of pollutants and the main hydrological processes that control them. Surface and subsurface runoffs were identified as the main contributors to pollutant transfer during floods. DOC, POC, and TSM concentrations increased during the flood and significant relationships between the controlling factors (DOC, POC, and TSM), the contributors to storm flow (SR, SSR, and GF), and the pollutants were advanced. DOC was proved to be highly correlated to SSR while POC and TSM were more linked to SR. The presented approach combining a hydrological hydrograph separation method with mixing models using physico-chemical tracers helped to estimate the contribution of each storm flow components to the total discharge of the river and to better understand the pathways and the controlling factors of different pollutants.

Understanding and quantifying the flow pathways by which the pollutants from diffuse sources are transported from the soils to the surface water are valuable for the implementation of appropriate agricultural practices that may reduce the transport of pollutants to the river and thus improve water quality.

Appendix

Table 2 Minimum, maximum, and average dissolved ($\mu g\ L^{-1}$) and particulate ($\mu g\ g^{-1}$) trace metal contents ($n = 22$ samples) during the flash flood event of May 2010 in the Save River basin (LD between 1 and 100 ng L^{-1})

	Dissolved ($\mu g\ L^{-1}$)			Particulate ($\mu g\ g^{-1}$)		
	Min	Max	Average	Min	Max	Average
Cd	<LD	0.01	0.00	0.02	0.31	0.17
Co	0.11	0.26	0.14	<LD	14.28	8.52
Cu	1.26	3.06	1.85	<LD	31.12	19.45
Ni	0.54	1.50	0.81	0.07	35.07	25.42
Pb	0.03	0.27	0.06	1.45	24.7	15.97
Zn	0.59	8.59	2.22	<LD	144.05	67.33

Table 3 Characteristics and minimum, maximum and average of pesticide contents (µg L^{-1}, $n =$ 22 samples) in unfiltered (UF) and filtered (F) water during the flash flood event of May 2010 in the Save River

µg L^{-1}	Solubility (mg L^{-1})	Log K_{ow}		Min	Max	Average
Acetochlor	223.00	3.00	UF	0.005	1.461	0.450
			F	0.003	1.817	0.413
Aclonifen	1.40	4.37	UF	0.000	0.217	0.057
			F	0.000	0.139	0.025
Atrazin	35.00	2.70	UF	0.007	0.204	0.062
			F	0.006	0.161	0.051
Epoxiconazol	7.00	3.44	UF	0.000	0.082	0.027
			F	0.000	0.054	0.016
Fenpropimorph	4.32	4.10	UF	0.000	0.019	0.005
			F	0.000	0.008	0.002
Flusilazol	54.00	3.74	UF	0.000	0.023	0.006
			F	0.000	0.012	0.003
Isoproturon	70.20	2.550	UF	0.000	0.243	0.067
			F	0.000	0.236	0.051
Linuron	63.50	3.20	UF	0.000	0.128	0.032
			F	0.000	0.091	0.024
Metolachlor	488.00	2.90	UF	0.000	7.124	2.368
			F	0.000	6.394	2.239
Trifluralin	0.22	4.83	UF	0.000	0.013	0.002
			F	0.000	0.098	0.004

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