POLITECNICO DI TORINO

Master's Degree in Environmental Enginnering

Master Thesis

A Mixing method to trace diffuse pollutions during floods on a wine-growing catchment

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On ne se construit pas seul, et les plus simples partages sont les plus grands architectes.

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1 Introduction and aims of the study

1.1 Surface water contamination during floods: insufficiently known mechanisms

Use of pesticides, particularly in viticulture, can lead to a significant pollution in the different compartments of the environment. These micro pollutants can migrate from cultivated parcels to surface water exported by different flow components during floods. During important rainfall events, pollutant concentrations can drastically increase and these events can be responsible, on their own, of the majority of the delivery of pollutants in surface water in terms of exported quantities.

Potential solutions applicable in order to prevent or limit these transfers depend on the flow component participating to the transfer. For example, flows transferred by surface runoff can be mitigated by the implementation of grass strips while transfers by the groundwater can only be reduced by a limitation in the use of pesticides.

As a result, quantifying pesticides exportation for each flow components becomes necessary in for an efficient basin management.

Some studies have previously worked on these problematics. In a non-exhaustive manner, we can cite the separation of hydrograph in four components on the Coet Dan catchment carried out by (Durand & Juan Torres, 1996). Going further, (El Azzi & Probst, 2016) studied the consequences for pesticides transport on the Save river performing correlations between flow components discharges, after the hydrograph separation, and pollutants concentrations along with vectors of contamination such as total suspended matter.

This provided a hierarchy in flow components levels of contamination but little information on the magnitude of these and neither real possibility to confront pesticides exportation from a given component between two events.

Irstea has been performing experimentations on a wine-growing catchment for many years. Despite this, on this sandy catchment with a high slope, the different flow components participations at the flood's discharge as well as their dynamic of exportation are not well known.

In this context, the first aim of this study is trying to identify and quantify the different flow components on the Morcille experimental watershed during floods. Several methods, of increasing complexity and similar to the ones used in the previous studies will be applied at two rainfall events. Secondly, the possibility of using these results in a method allowing understanding pollutants exportation dynamic more precisely will be studied.

1.2 Hydrograph definition and applications to environmental sciences

Many studies have focused on the analysis of hydrograph which is the flow's chronicle in a section of a stream as a function of time. This flow is the flow resulting of the various flow components in the watershed. Quantifying streamflow has always been fundamental for land management and flood prevention or the management of water resource. This preoccupation was then extended for the different flow components for the question of water resource quality management. A broad range of methods is available in an attempt to answer to this question. In our study, the aim is the deconvolution of hydrograph during flood events. It means that for an observed signal, here the flow variation we're trying to determine the proportion of the different flow components.

Several methods of hydrograph deconvolution are available presenting different scales of complexity. First method –purely hydrological – is based on a graphical recession analysis of flow (Barnes, 1939), (Remenieras, 1965) ; the second one uses physicochemical tracers which are characteristic of the different flow components (Pinder, 1969) ; finally, recent progresses in the domain of hydrogeology, hydrochemistry and statistics have offered more precise models such as the EMMA model (End-Member Mixing Analysis) (Christophersen, et al., 1990). In this study, these 3 different methods will be applied on the Morcille experimental watershed (Beaujolais, France).

Consistent results will then be used in order to study consequences for pesticides transfers with a similar approach to (El Azzi & Probst, 2016).A multilinear regression on pesticides concentrations will be performed as a second deconvolution to assess the degree of contamination of each contaminant. Finally an estimated mass balance of exported pesticides by each flow components will be calculated using the two previous deconvolutions.

1.3 Deconvolution basis and applications to this study

A convolution or composition is defined as:

$$h(x) = \int_{-\infty}^{+\infty} f(t)g(x-t)dt \qquad (1)$$

or :

$$h(x) = f(x) * g(x) \qquad (2)$$

f is the input signal and g is the frequency response or transfer function. h is the impulse response and is the result of the convolution of the function f by the function g .

A deconvolution, under its strictest expression, is the resolution of a convolution equation. Many approaches exist to solve a convolution equation. One of the most common methods is performing a direct inversion of the convolution matrix (Biraud, 1976).

$$f^* = g^{-1} * h \qquad (3)$$

In this study, the impulse response h is a solute or a pesticide concentration at the outlet. However the input signal and the transfer function are not known. The transfer function f_1 will be the varying participations of the different flow components[1].

Finding g with methods in the literature, the participations of the different flow components requires a first deconvolution[2] where total discharge and the flow

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[1] Reduced model

[2] This first deconvolution of hydrograph is also called separation or decomposition of hydrograph.

components participations are respectively h and f. The transfer function will differ with the three different methods used in this study. A second deconvolution using f_1 previously calculated provides a signal on pesticides concentrations in each flow component. The approach of the study is described in Figure 1.

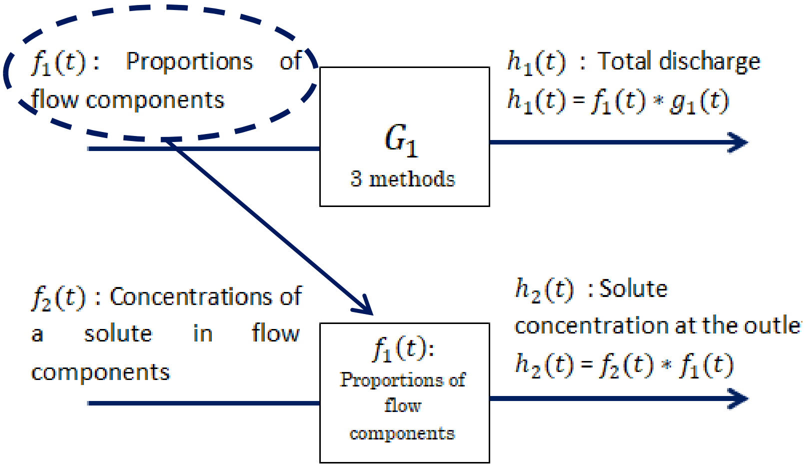

Figure 1: Two step deconvolution performed in this study

2 Soil water and flow components on a watershed

In this chapter we will present the characteristics of soil water and the main processes at the origin of flow in a watershed.
Presenting the different flow components presents a double interest°:

- Define the used term used for a given flow component ;
- Physically characterize these components and their participation to the river flow

2.1 Soil water

All the variables used to characterize the storage and the circulation of water in the soil are based on the concept of Representative Elementary Volume (REV) which involves that we can allocate to a point in the space: permeability, porosity or any other variables of interest of a given soil volume. It is then possible to set the definition of an average property for the concerned volume. This is classical space integration. The REV must be sufficiently important in order to cover heterogeneities at the microscopic scale but sufficiently small in order to be considered as homogeneous for the macroscopic properties.

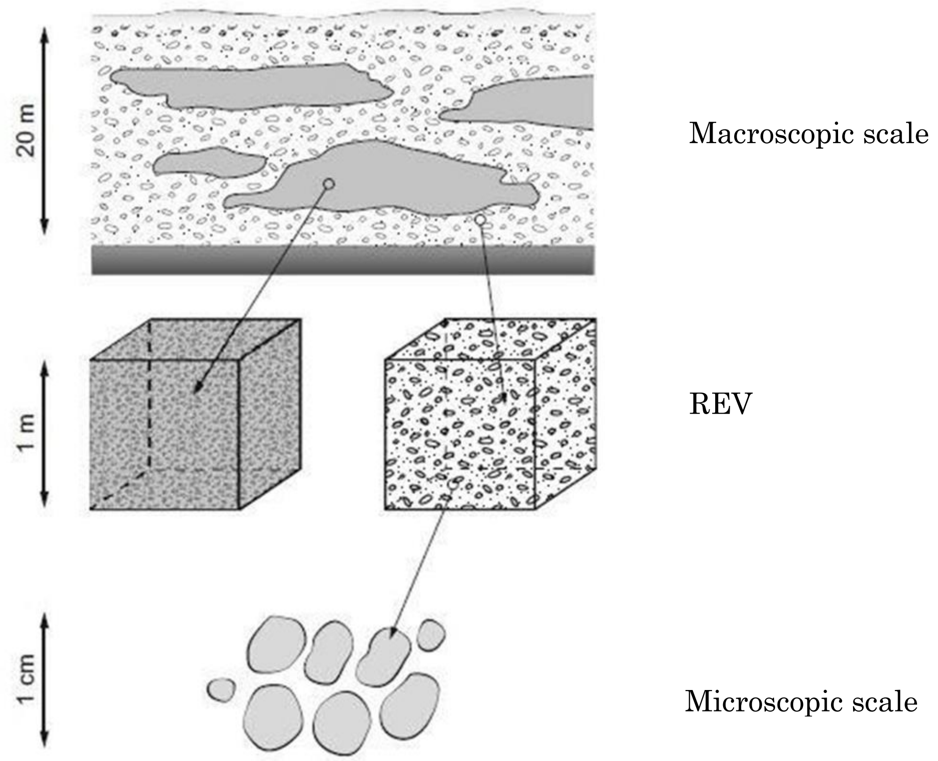

Figure 2 : The concept of REV (Sethi&Molfetta 2012)

Let us look at few elementary definitions characterizing the soil ability to store water (porosity) and to let it flow (notion of permeability).

- Porosity n : ratio between pore volume (void volume) V_v of the sample and V_t the total volume of the sample, V_s being the solid volume of the sample

$$n = \frac{V_v}{V_t} = \frac{V_v}{V_v + V_s} \qquad (4)$$

A soil is saturated when all its porosity (cracks, sediments or rocks pores) is filled by water. This water splits in:

- Bound water, attached at the grain face through the molecular force attraction ;
- Free water, lying outside of the solid particles attraction field, it's likely to move due to gravity or pressure gradients.

Molecules adsorption's phenomenon may sometimes be important (especially for clays) and can limit water circulation, as do few not connected REV pores.

- Consequently, we define the effective porosity (or drainage porosity) of a saturated media as the ratio between water volume V_{wg} released by the only effect of gravity drain and the total volume.

$$n_e = \frac{V_{wg}}{V_t} \qquad (5)$$

- In the configuration of an unsaturated environment, we define water content θ as the ratio between stored water volume V_w and total volumeV_t.

$$\theta = \frac{V_w}{V_t} \qquad (6)$$

With $0 < \theta < n$ and $V_{wg} < V_w$

The hydraulic conductivity K is a variable quantifying the capacity of a porous media to let a fluid flow in response to a pressure gradient. It is homogeneous to a celerity, generally expressed in m/s. The hydraulic conductivity is a function of the porous media intrinsic permeability k (in m^2), specific density of the fluid ρ (kg/m^3), the acceleration of gravity g and μ the dynamic viscosity of the fluid ($kg.m^{-1}.s^{-1}$) :

$$K = \frac{k.\rho.g}{\mu} \qquad (7)$$

An usual profile of water stored in the soil according to the depth is showed Figure 3:

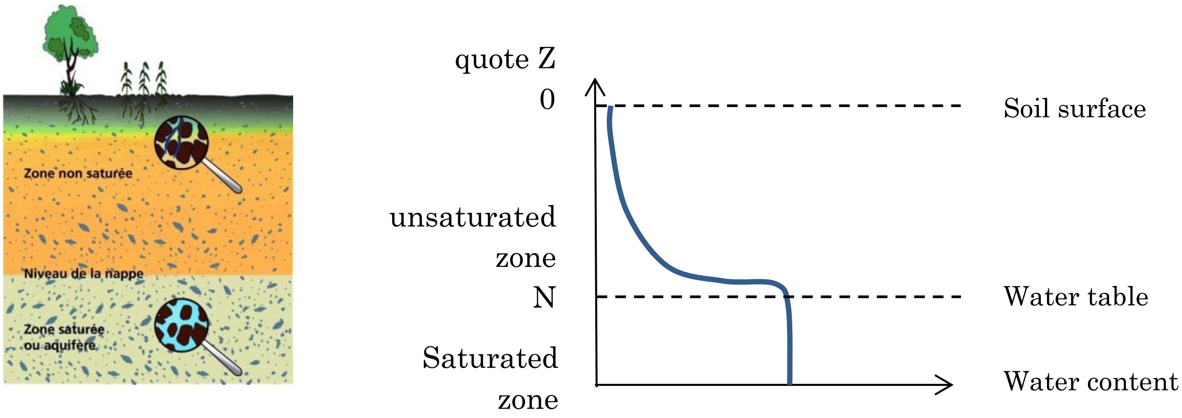

Figure 3 : Profile of water content of the soil. (inspired by De Marsily 1981) and BRGM

Below a given depth N, the soil is saturated and the water content no longer increases. A body of permeable rocks with a saturated zone and able to conduct groundwater allowing the pipping of a sufficient flow is called an aquifer (Castany & Margat, 1977).
This groundwater is essentially subject to gravity forces, capillary forces being negligible. The average velocity of flow U in saturated zone is described by Darcy's law°:

$$\vec{U} = -K\overrightarrow{grad h} \qquad (8)$$

$\vec{K}$ being the saturated hydraulic conductivity expressed as a tensor and h the hydraulic head.
$h = \frac{u^2}{2g} + \frac{p}{\rho g} + z$
U being the flow velocity, p the static pressure and z the quote upwardly positive. In porous media, velocities are slow, we neglect the kinematic term and we only consider the static load, the piezometric quote: $h = \frac{p}{\rho g} + z$ assimilated to the hydraulic head
For an unsaturated media, we talk about pressure potential : $\varphi = \frac{p}{\rho g}$ (with p negative).
Above the depth N the soil is unsaturated and its interspaces contain simultaneously water and air. The water is subject both to gravity and capillary forces. Water flows are governed by Darcy's law in unsaturated medias, also called Richards equation°:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}(K(\theta)\left(1 + \frac{\partial\varphi}{\partial z}\right)) \qquad (9)$$

In the following paragraphs we will describe the genesis of the different flow components following a water layer generated during rainfall and propagating itself in and on the soil.

2.2 Infiltration and surface runoff

When the water arrives at the surface of the soil, it starts by moistening the superior fraction of the soil on few inches. The capacity of soil to adsorb water when he receives efficient water is called infiltrability . This infiltrability depends on, the texture and the structure of the soil, through hydraulic conductivity,. It also depends on the initial water content of the profile and the water pressure imposed at the surface. Infiltrability is expressed in mm/h (or in m/s in IS).

This water flows vertically when gravity force is greater than capillary forces, which means when water content exceeds a specific value called specific retention capacity. In a homogeneous soil, the moisture profile presents:

- sometimes a saturated zone directly located under soil surface when this one is overwhelmed.
- a zone close to saturation called transmission zone, seemingly uniform
- a moisturation/humidification zone characterised by water content strongly decreasing with the depth. This important moisture gradient also called moistening front delimits moist soil from the subjacent dry soil.

During the infiltration, the transmission zone progressively elongates while the zone and the front of humidification are moving into depth. The water movement is subject to the Richards equation *(9)* above-mentioned.

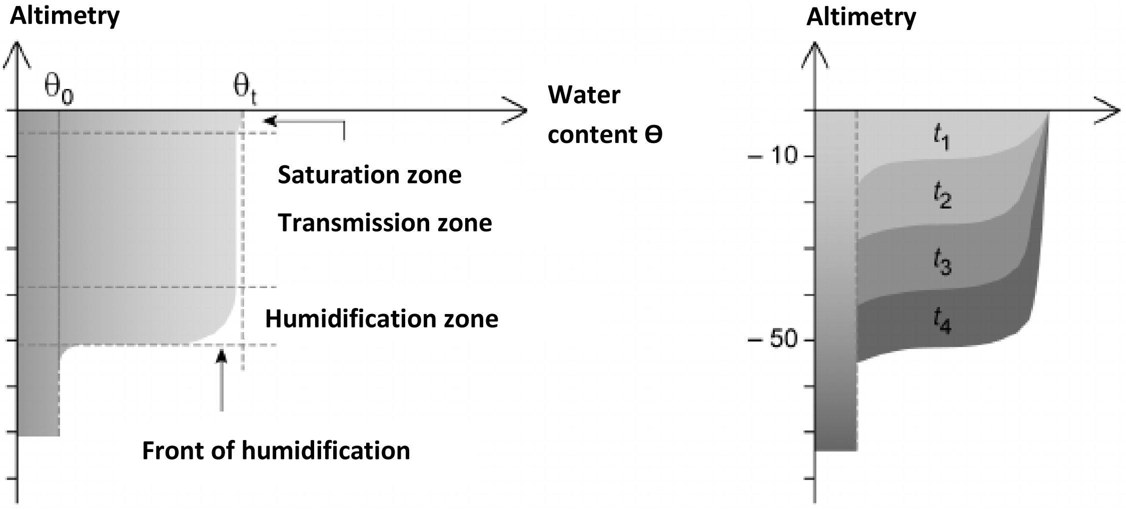

Figure 4 : Infiltration front of soil. Hydrologie et niveaux d'eau dans le sol (Fouché 2013)

2.2.1.1 Surface runoff by exceedance of the infiltration capacity: the Horton overland flow

At the rain beginning, the soil infiltrability is often higher than the rain intensity and the fallen water layer infiltrates integrally in surface. Subsequently, due to the water saturation of the first inches of soil the infiltrability decreases sometimes until being inferior to the rain intensity. The soil cannot absorb water and an excess of water appears in surface. The evolution of a water layer's infiltration precipitated during a rainfall event is showed Figure 5.

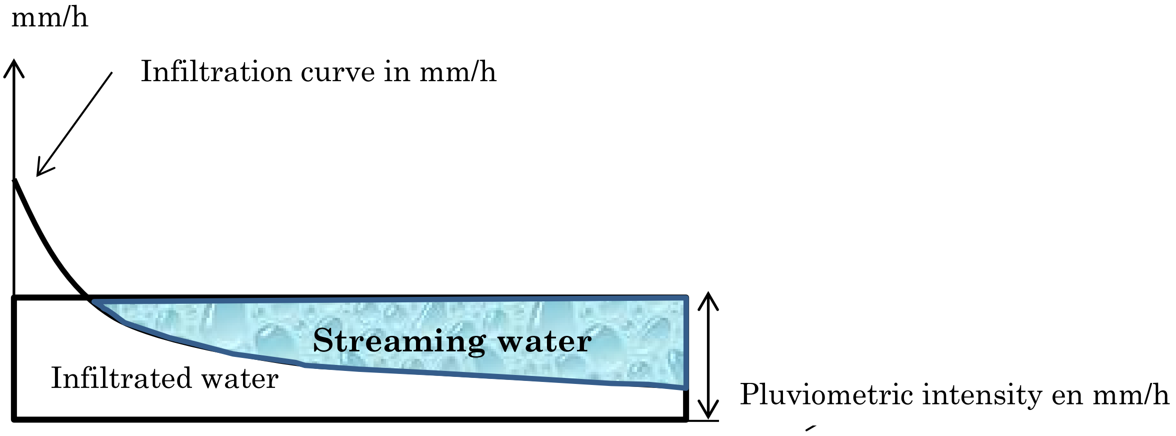

Figure 5 : Infiltration and surface runoff of a water layer precipitated during rainfall

This film of surface water can then flow on the soil by gravity and moves upslope to downslope. We use the equation of the kinematic[3] wave :

$$q = vh = \alpha h^m \qquad (10)$$

With the flow velocity $v\ (m.s^{-1})$, m the parameter depending on the type of flow and α the hydraulic coefficient.

The Horton overland flow is typical of the hydrological answer for watershed in semi-arid climates with very dry soils and low permeability or/and during high intensity rainfalls.

However, it is possible to observe it on more temperate watersheds even if they present a higher hydraulic conductivity in their soils.

Depending on the soil condition and the importance of the water layer, this one can then vertically flows (as defined in this chapter's introduction) until a horizon of lower permeability (lower K) or an already saturated zone is encountered. The water accumulates creating saturated zones here and there (or feeding the already existing ones). Once this accumulation is initiated, three situations can appear.

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[3] Saint-Venant's equation simplified : The acceleration is negligible and the friction slope is equal to the free-surface slope

2.2.1.2 Surface runoff by soil saturation in water

If the interface slope is low or non-existent, the water continues to accumulate at the interface, the water table rises until the saturated zone flushes and generates a surface runoff by saturation of soil as illustrated Figure 6. It is also called groundwater ridging.

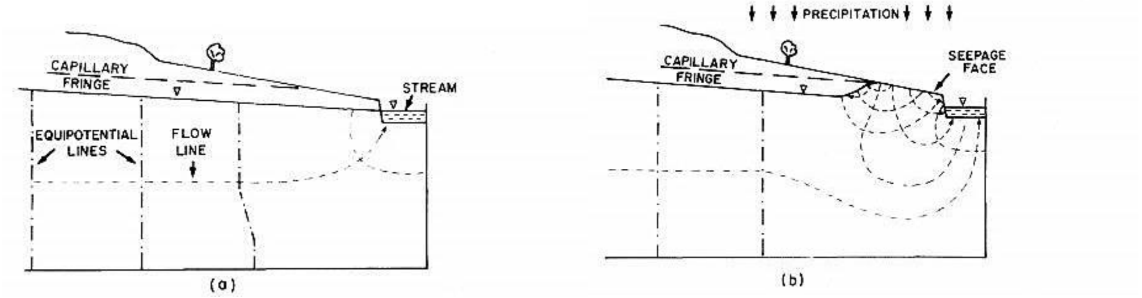

Figure 6 : Modification of the hydraulic gradient and thus of the flow, by groundwater ridging (Gillham 1994)

As opposed to the Horton overland flow which was a saturation « above ground », depending on the rain intensity, it is a saturation « from below » depending on the rainfall accumulation. There can be conjunction of these different runoffs in proportions varying with the context. The differences of functionement between these two types or runoff are summarized Figure 7.

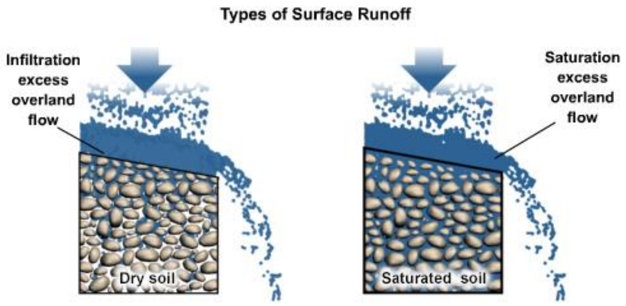

Figure 7 : Differences between Horton runoff and runoff by saturation (Basic Hydrologic Science Course Runoff Processes 2006)

2.2.2 Lateral flow of shallow subsurface

If the interface between these two horizons is a slope, the accumulated water above the interface causes a charge gradient, from upstream to downstream and so a lateral flow to downstream appears according to the Darcy's law Figure 8.

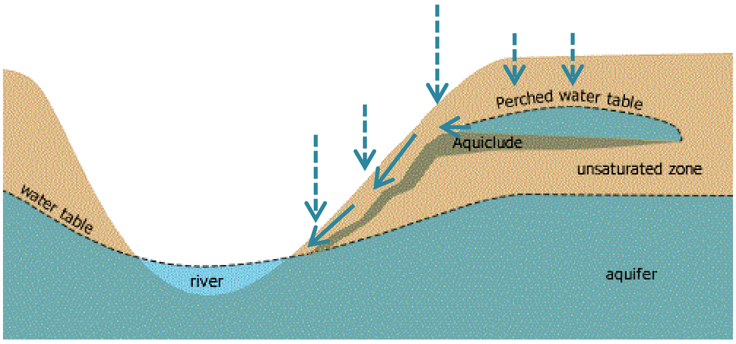

Figure 8 : Perched water table and lateral subsurface flow on a low permeability bedrock

Initially, on the basin's floor the saturation is not sufficiently homogeneous or even insufficient in order to trigger the flow[4]. The infiltrated water layer must be consequent in order to trigger or extend the saturation into the depressions of the topographic permeability ruptures (filling phase). Subsequently, due to the energetic disequilibrium caused by the gravity these perched water tables overflow downstream one by one and interconnect which triggers the flow (spilling phase)). This is the "fill and spill "theory illustrated Figure 9. This threshold effect is ruled by the initial water content of the system and by the depressions connections more or less facilitated which determine the water volume required to fill these depressions.

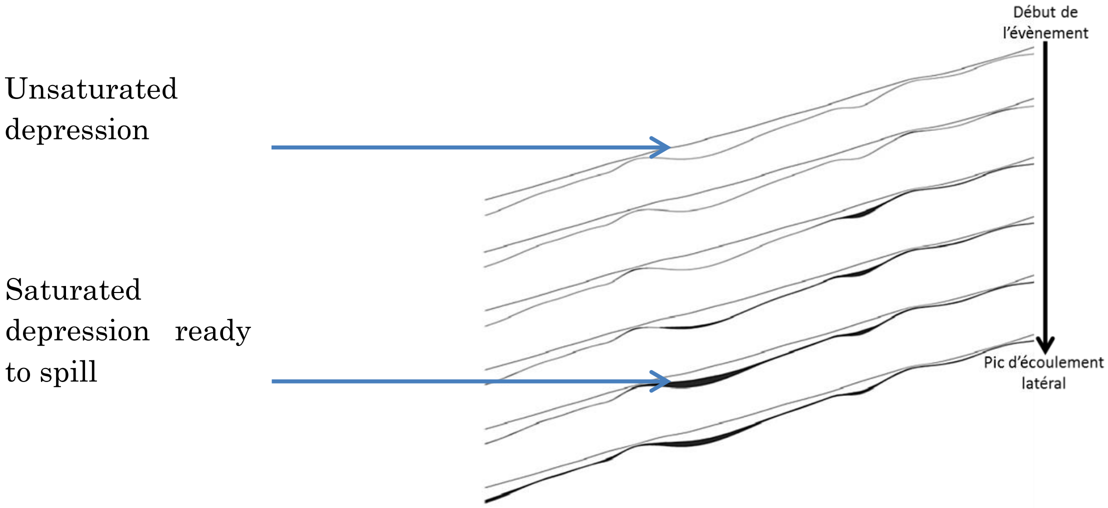

Figure 9 : Schema of the fill and spill process (Tromp-van Meerveld et McDonnell,2006)

2.2.3 Percolation and groundwater flow

An hydrogeological basin can contain one or more aquifers separated by near impermeable geologic formations that do not allow the circulation of water (ex : clay), called aquiclude. However, such a geologic formation can also present a low permeability (aquitard) and allows the flow between two aquifers, providing a vertical refilling of the one with the minor hydraulic charge. It's called percolation and it's the third situation. A silty formation or silty-sandy is a typical example of aquitard. The groundwater ability to move is governed by Darcy's law. Due to the low velocity of water percolation in the subsoil, the groundwater flow accounts for a low proportion in the flood discharge.

2.2.4 Preferential flows : Case of macropores

Sometimes, a fraction of water infiltrates through macropores. A macropore is defined here as a pore greater than REV pores by at least one order of magnitude. This kind of porosity can lead to vertical or horizontal water movements (depending on whether the macropore is horizontal or vertical) essentially governed by gravity. Depending on their continuity (entirely passing or not through the surface horizon), they will bypass the matrix flow (Richard's law) and trigger "preferential flows". Macropores often play an important role in the transfer of reactive contaminants because this flow bypass can drastically reduce the adsorption and degradation capacity of the soil. Theses

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[4] Unsaturated lateral flow on bedrock according to the Richard's law may occur but their participation in the total discharge is anecdotic.

macropores can have a biotic or abiotic origin and can sometimes extend over lengths superior to the meter as presented Figure 10.

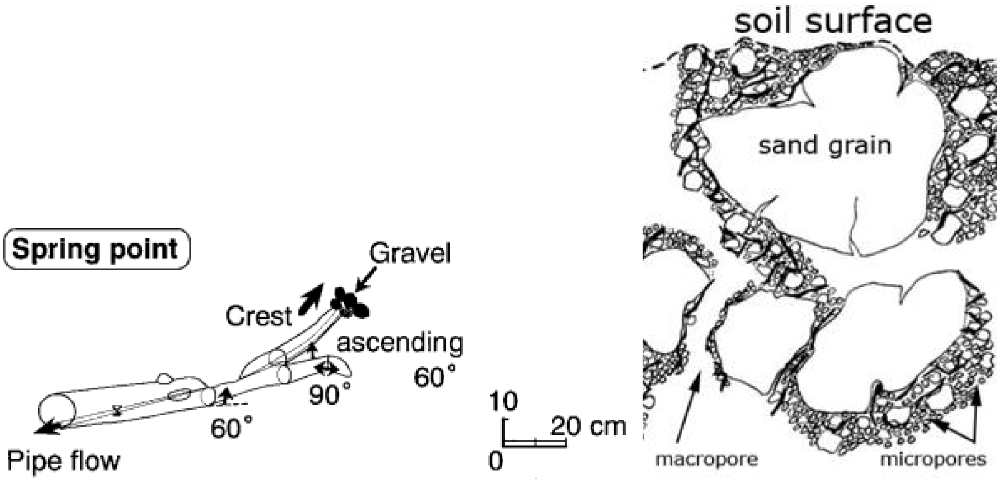


Figure 10 : Macro and micro-porosity of the soil and geometrical description of a tubular macropore (Terajima et al. 2000)

2.2.5 Flow's fates and total discharge participation

The different flow components can end up joining the river and participate to its discharge.

The Horton overland flow will meet the hydrographic network when reaching the river surface.

In the case of subsoil flows (shallow subsurface and groundwater), the water-aquifer exchanges are also governed by Darcy's law and so it's the hydraulic gradient which rules the exchange as described Figure 11 :

- If the water table of the groundwater is greater than that of the river we have the water exfiltration (case A).
- In the opposite case, it's the river which supplies the aquifer and we have water infiltration (case B, not common in temperate environments)).

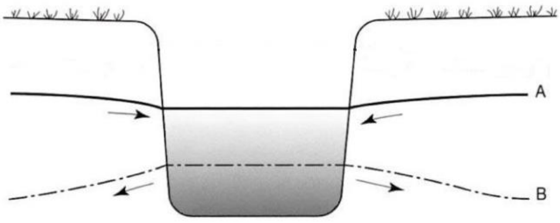


Figure 11 : Exfiltration and infiltration of water illustrating Darcy's law. Hydrologie continentale (Cosandey&Robinson2012)

The lateral subsurface flow can adopt different behaviours depending on the drainage basin morphology:

- If the low permeable bedrock outcrops, this flow can come out in surface (resurgence) and directly flow into the river or indirectly by mixing with the surface runoff.
- Otherwise, close to the riparian area:

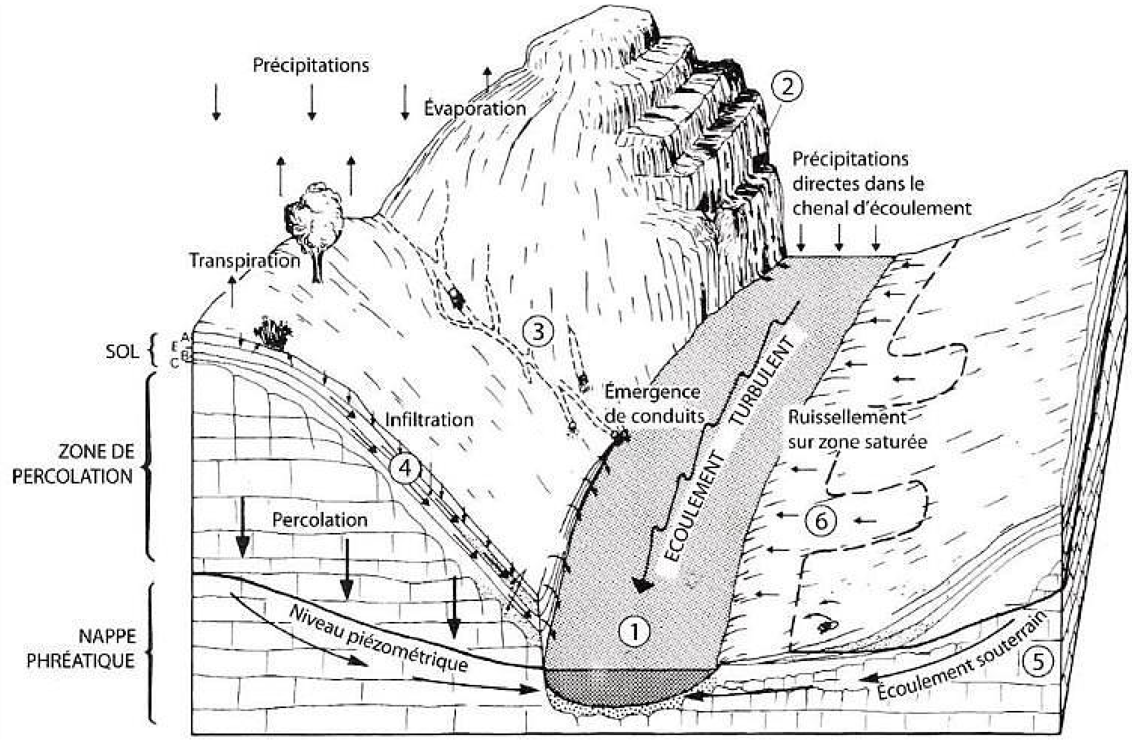
- The soil of the riparian area is already saturated and the lateral flow is directly exfiltrated.
- The soil isn't saturated and the lateral flow connects to the alluvial water table. Then, it will exfiltrate by the riverbanks or the bottom of the river's bed.

2.2.6 Water transfer towards atmosphere: evapotranspiration

The evapotranspiration is the quantity of water redirected toward the atmosphere, by the evaporation from the soil and by plants transpiration. The potential Evapotranspiration (PET) is an essential part in the water balance and is often greater than precipitations. As a result, on a period of hydric deficit, precipitations poorly participate to river flow.

2.2.7 Synthesis

The different flows occurring on a drainage basin and exposed previously are summarized Figure 12.



1. Stream flowing to the outlet
2. Horton overland flow
3. Subsurface lateral flow by macropore
4. Subsurface lateral matrix flow
5. Groundwater flow
6. Surface runoff on saturated zone

Figure 12 : Summary of the different flow components inside a watershed (Arnaud-Fassetta 2015)

Usually, the groundwater flow provides a "base flow" i.e. river's flow in the absence of rain. However, groundwater can participate to flood spike being quickly supplied thanks to preferential flows. Depending on the basin characteristics, some of these flow components can be missing during rain events.

3 Hydrograph deconvolution methods

3.1 Hydrological method for reference: graphical decomposition of the flood hydrograph by analysis of its recession

We chose as a reference a purely hydrologic method, based on a graphical decomposition of the flood hydrograph because it can be quickly applied without needing any data of water quality. This method is documented in (Barnes, 1939) (Roche, 1963), (Remenieras, 1965) (Castany, 1967). More recent authors describe more complex methods with the same aim of analysing graphically the hydrograph. However, in general, they're also based on the same general hydrologic principles.

The aim is to develop a decomposition method sufficiently simple in order to be generalized and performed on all the flood events available while respecting the physical sense as much as possible.

3.1.1 Formalization

The traditional approach in the literature[5], which is used here, is to consider that recessions of the hydrograph components follow a law of exponential decay for their discharges (Q) according to Maillet's law (Barnes, 1939).

$$Q(t) = Q_{0,n}e^{-\alpha_n t} \tag{11}$$

With the discharge flow over the time $Q(t)$ in $m^3/s, \alpha_n$ the recession coefficient (dimensionless) of the n component, $Q_{0,n}$ in m^3/s the initial discharge of the component before recession phase.

We transcribe the decreasing part of the hydrograph in a semi-logarithmic graph, with the logarithmic discharge in Y-axis as indicated Figure 13.

On the logarithmic curve, any significant slope rupture matches with the recession of one flow component. Most of the time, we can fit 2 lines to the different slope ruptures on the logarithmic discharge curve.

A first line represents the sum of the groundwater flow and the shallow subsurface flow (light blue on the graph) and the second represents the groundwater[6] (in dark blue). It is then possible to screen the surface runoff by subtracting the subsoil flows (light blue) to the total discharge. Then, in order to screen the subsurface runoff we subtract the groundwater flow to the subsoil flows.

The subjective part of this exercise consists in plotting the increasing part of each flow component; their beginning and the position over time of their maximums.

The method presented here is called "simplified method", if water table variations data are available we can precise the increase initiation of the base flow (BRGM, 1971).

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[5] There are others possible mathematical formalisms of the flood decay such as the hyperbolic decay or double exponential decay but they are less easy to use.

[6] Usually called baseflow in graphical hydrograph studies

3.1.2 Graphical decomposition of the flood hydrograph rising limb: procedures and plotting justification

While the recessional part of the hydrograph is based on a physical law, the rising limb plotting is usually more subjective.

3.1.2.1 Groundwater and shallow subsurface flows separation: shared methodology for the two methods:

The literature accounting the shallow subsurface flow in the graphic analysis of the hydrograph is less consequent. Indeed, the shallow subsurface flow was usually allocated between the surface runoff and the groundwater flow because it wasn't really identified on the first hydrogeological studies and wasn't needed for land management.

a) Initiation of the groundwater + subsurface component

The rising of the discharge curve starts at the point (C). Sometimes, even under a homogenous rain, a particular configuration of the drainage basin causes, , an anticipated surface runoff of low amplitude in the downstream zone (Roche, 1963) as we can see on Figure 13.
Therefore, we introduce the point C' which reflects the true initiation increase of the flood discharge curve. The point C' is the intersection point between the extension of the discharge recession curve before rainfall and the true rising of the flood discharge curve. Without any other information, the initiation of the increasing discharge is at point C'. However, in some cases this isn't physically accurate. Actually, subsoil flows (subsurface and groundwater) need a significant quantity of water to increase and do not rise from the beginning of the rainfall. As explained in 2.2.2 the water can infiltrate under conditions depending on water content, evapotranspiration and the quantity of water fallen during rainfall.

b) Peak discharge for the groundwater+subsurface

The x-coordinate [7] of the maximum for the subsoil flows is difficult to identify.
Some authors favour a « careful » analysis of hydrograph and hyetograph associated with a rainfall event without surface runoff in order to better identify the hydrograph form of the subsoils flows (Remenieras, 1965) (Roche, 1963).
However, such events are not always recognizable, in particular in wine-growing watersheds where the climate, the slope and the type of soil favour the formation of surface runoff[8].
Studies have shown that once the threshold of imbibition necessary to trigger the subsurface flow is passed, the discharge of this flow presents a linear relation with the volume of fallen rain (Peyrard, 2016).
Logically, as for surface runoff, variations of subsurface flow component should match those of the hyetograph[9] and the X-axis of the maximum subsurface discharge should be the same as the X-axis of the maximum total discharge P.

---

[7] Knowing the X-axis, the Y-coordinate is obtained at the intersection with the recession curve

[8] In fact in a certain extent the fast drainage is wanted in order to avoid the vineyard rot.

[9] Minus the watershed concentration time

3.1.2.2 Pure groundwater flow separation :

Following water table variations it is possible to obtain a response time of groundwater (Δt_1) and a rising period (Δt_2)and apply it to the separation of hydrograph (approached method). Without data on the water table variations, we will use the "simplified" method (Remenieras, 1965) : we define the increase initiation at the point (C') and it's decreasing (E) starts when the surface runoff ends which i.e. at the point A. The overall methodology is disclosed Figure 13.

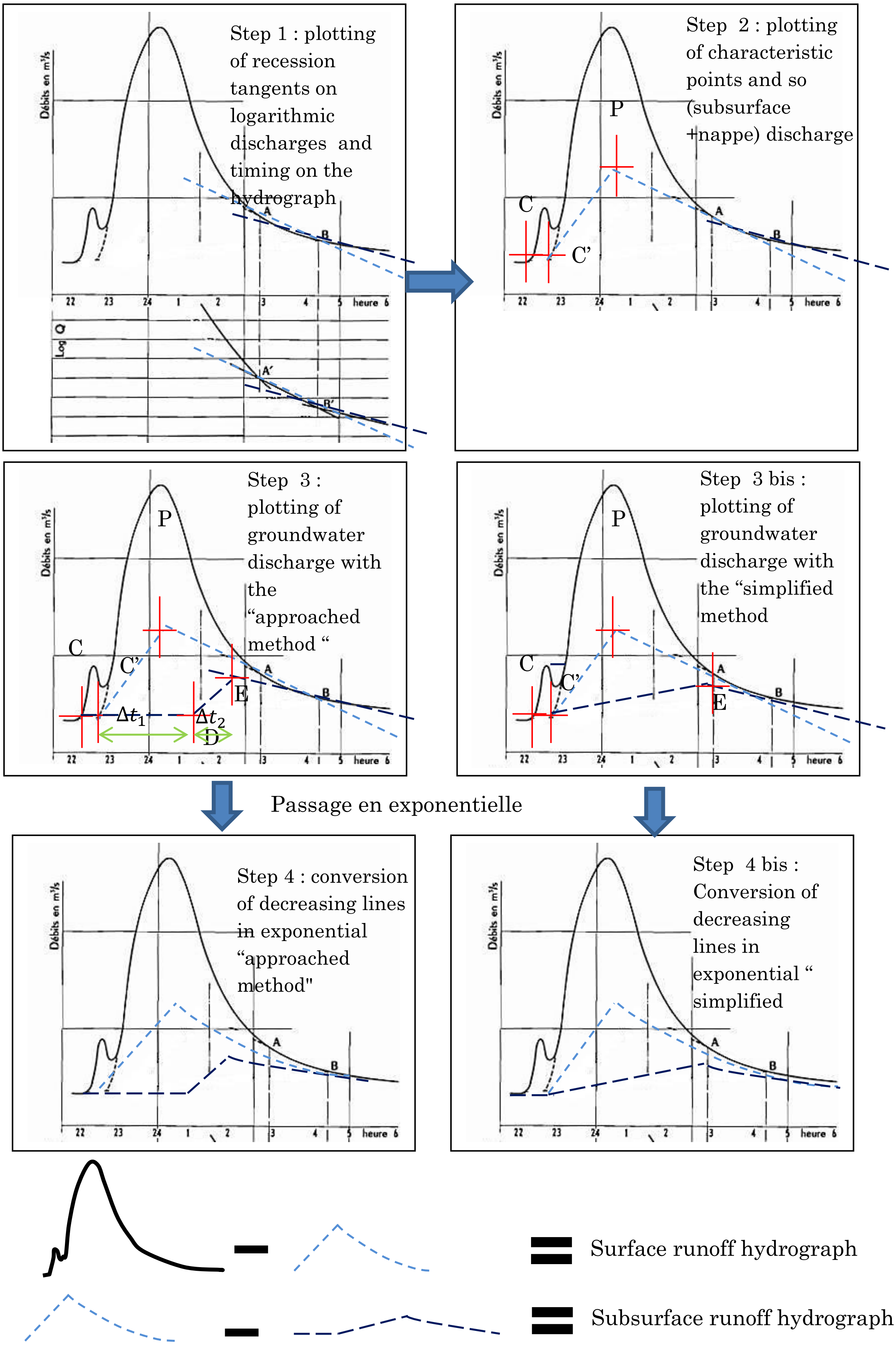

Figure 13 : Graphical separation of hydrograph by recession analysis

3.1.3 Additional Comments

Although being simple in theory, the graphical decomposition of hydrograph proves to be sometimes difficult to use due to the consequent subjectivity in each step. Sometimes the discharges in semi-logarithmic coordinates are curvilinear instead of being lines. This problem questions the validity of the fundamental hypothesis at the origin of the method and makes difficult the layout of the recession lines.

Shallow subsurface flow can be absent in some floods for example if we consider an Horton overland flow, previously defined chapter 2.2.1.1, in the case where the soil forms a "crust" with a weak hydraulic conductivity. The water absorption capacity is nearly null; the water runs off and directly feeds the stream, in addition to groundwater delivering a baseflow.

However, by definition this hydrologic method, , will always provide a result with a non-zero subsurface flow , though sometimes, in very low proportions.

The runoff / subsurface confusion in total water flow is a relatively minor problem, as long as the hydrologist's goal is to reconstruct or predict flow rates. This determination becomes an essential problem when it comes to reconstructing or predicting the quality of river water (Hubert, 1989).

Following the generally more reliable physicochemical methods, the graphical decomposition method of the hydrograph was partly neglected for more precise and less subjective analyses. We will describe two physicochemical methods.

3.2 Physicochemical methods based on Mixing Model

3.2.1 Concepts of the Mixing Model and formalization

The approach is based on the fact that the chemistry of the stream is the result of the mixing from different end-members of the basin mixing in varying proportions. End-members are solutions with fixed compositions that are at the extreme end of a solution series in terms of purity. The fundamental equations of the Mixing Model are based on the conservation at each moment of the mass of fluid on the one hand and of the mass of chemical species on the other hand. Then, this mixture is modelled in the form of a system of at least 2 equations and it becomes possible, by solving this one for each time step to find the contribution of each end-member to the streamflow. Concretely, the flow at the outlet is equal to the sum of the flows from the different end-members of the basin at time t:

$$\sum_{i=1}^{n} Q_i(t) = Q_{tot}(t) \tag{12}$$

Also, the sum of the contributions of end-members in a chemical element is equal to the mass of this chemical element in the stream at the outlet if it is conservative. These chemical elements are thus used as natural tracers of the flows.

$$\sum_{i}^{n} Q_i(t) * C_i = Q_{tot}(t) * C(t) \tag{13}$$

A conservative element (or inert or non-reactive or perfect tracer) is a solution element not undergoing any modification and not interacting with the solid phase when transported through the porous media. In nature there are no inert elements in the strict

sense but at best elements with negligible reactivity and which will be considered as inert to the time scale that interests us. The system of conservation equations for chemical elements and fluxes applied to hydrology was first introduced by Archer and Al in 1967. In contrast to our study, the objective here was to determine outflow concentrations by knowing the proportion and concentration of dissolved species in subsurface flows (groundwater + shallow subsurface) and surface runoff. Then, it was Pinder in 1969 who used the Mixing Model for the decomposition of the hydrograph.
Usually, the end-members chosen for the decomposition are the composition of water in each of the 3 soil layers corresponding to the 3 flow components defined in the state of art[10], supposed homogeneous at the basin scale. For our study, we will look for these classical end-members, However, it could be possible to use multiple decompositions, in basin zones, as long as we identify end-members.

Several hypotheses must be verified in order to use the Mixing Model:

1. The end-members ‘composition in conservative elements remains constant during floods. This hypothesis is questionable due to the possible influence of refill waters of the different compartments during the storm. This phenomenon is rarely highlighted in the literature (Hooper et Shoemarker, 1986) for the deep groundwater; nevertheless it remains possible for the perched water tables at the origin of the subsurface flow, which are more reactive with a shorter water residence time. In general, the shorter the response time the more right this hypothesis (Mul, et al., 2008) ;
2. Concentrations of chemical elements in rainwater are significantly different from those in the stream water before the rainfall (Crouzet et al., 1970). This hypothesis is verified considering the difference of the chemistry between rain waters and the base flow (Kamagaté, 2006) ;
3. The chemistry of the stream during base flow is significantly close to the one of groundwater (Sklash et Farvolden, 1982).
   The concept of Mixing Model is summarised in the scheme Figure 14.

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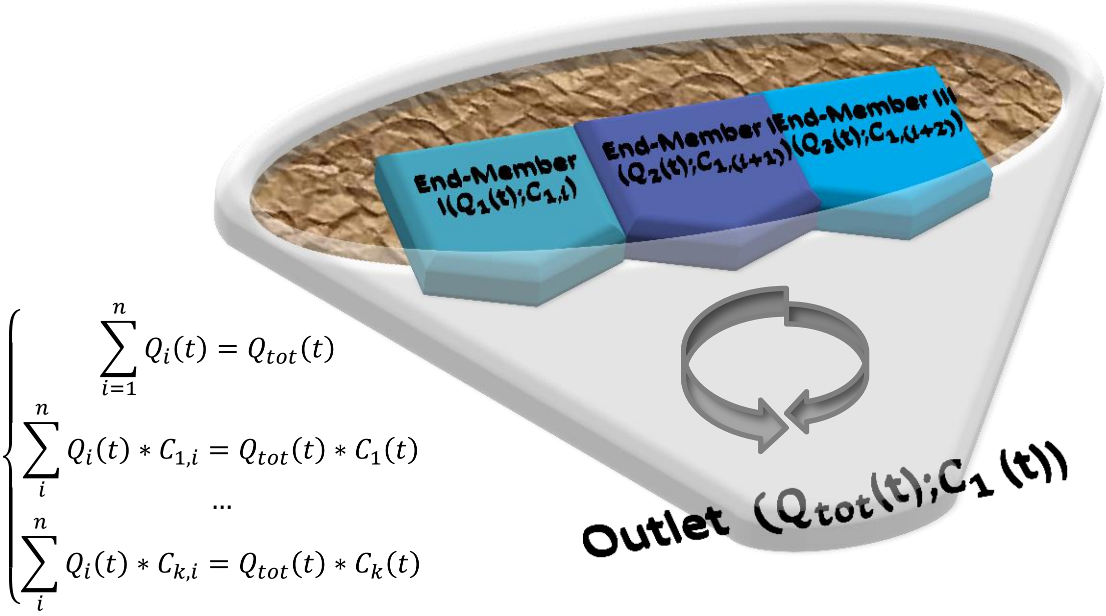
[10] Surface runoff flows (hortonian and by saturation), shallow subsurface runoff and the baseflow provided by groundwater



$$\begin{cases} \sum_{i=1}^{n} Q_i(t) = Q_{tot}(t) \\ \sum_{i}^{n} Q_i(t) * C_{1,i} = Q_{tot}(t) * C_1(t) \\ \dots \\ \sum_{i}^{n} Q_i(t) * C_{k,i} = Q_{tot}(t) * C_k(t) \end{cases}$$

Figure 14 : Mixing Model scheme applied to a drainage basin

n: number of end-member $n \geq 2$
k: number of tracers ($k = n - 1, k \geq 1$)
$C_{k,n}$ concentration of the k-th tracer (constant) in the end-member n en mg/L
Q_i(t) end-member flow involved to the total discharge at time t in m^3
Q_{tot} (t) discharge observed at the outfall at time t in m^3
$C_k(t)$ concentration of the tracer k observed at the outfall at time t in mg/L

The system reduced into the form of a matrix:

$A = BI$

$$\begin{pmatrix} Q \\ Q * C_1 \\ \vdots \\ Q * C_k \end{pmatrix} = \begin{pmatrix} 1 & \cdots & \cdots & 1 \\ C_{1,1} & \cdots & \cdots & C_{1,n} \\ \vdots & . & . & \vdots \\ C_{k,1} & \cdots & \cdots & C_{k,n} \end{pmatrix} \begin{pmatrix} Q_1 \\ \vdots \\ \vdots \\ Q_n \end{pmatrix} \qquad (14)$$

With A, the column vector of the products from multiplying the outfall discharge by the k element concentrations at the outfall at time for a given observation, B the concentrations matrix of the k elements in the current n end-member I the column vector containing the unknowns (which means the n discharges of the n end-members for the given observation. The inversion of the convolution matrix can be done by adopting a least squares objective function. The optimal solution to equation (14) is the normal equations (Draper and Smith, 1981), namely

$$I^* = AB^T(BB^T)^{-1} \tag{15}$$

Equation (15) must be solved for each of the n observations.

3.2.2 Evolution of Mixing Model methods for the hydrograph separation

The fundamental equations of the Mixing Model as well as its hypotheses remain the same, since their introduction, at the end of the sixties to our days: The aim is still solving the system of unknown I. Until 1990, the differences in the use of Mixing Model between two studies lie mainly in°:

- The selection of the End-Members/flow components tracked;
- Chemical species selection (representative tracers of flow differs with the basin geology and geography) ;
- The A matrix filled with the concentrations for each end-member.

First studies, such as (Archer 1967) and (Pinder, 1969) model the input by two flows: deep groundwater and surface runoff. The shallow subsurface was neglected and counted in the two other defined flows depending on its concentrations similarities with these.
Some authors, in the eighties, did the separation in terms of «old water» (soilwater) and «event water» end-members (water brought by the rain) with the help of isotops (Hooper & Schoemaker, 1986) and demonstrated that, in general, the stream during the event is supplied with the «old water» (Hooper & Schoemaker, 1986) using isotopes. Moreover, in the same time it was shown that sometimes, the shallow groundwater isn’t sufficiently consequent to be the unique source of «old water». This “old water” missing from balance is sometimes consequent and can come from the perched water table triggering the subsurface flow. Thus, carrying out a two components separation could be a bit simplistic and it can be necessary to consider it.
However, this third end-member is located into a depth between the two others and its functioning differs a lot from a basin to another, or withing it. It is then necessary to have a good general knowledge of the basin and its hydrogeochemistry (type of soils, rock solubilisation in water) in order to identify the probable components and the maximum of differences between them. At the beginning of the nineties, the Mixing Model has a new impetus, Christophersen and Hooper introduced the End-Member Mixing Analysis (EMMA) where the same system of equations is enhanced with mathematic and statistic tools: the Principal Components Analysis and the mixing diagram. Subsequently, two approaches are suggested in the literature:

- The ones in the continuity of the previous studies considering that the components with similar hydrogeological behaviours can be approached by a simplified end-member consisting in one solute. (Pinder, 1969) ; (Gac, 1979) ; (Tardy, et al., 1995) ; (Mul, et al., 2008); (El Azzi & Probst, 2016)
- EMMA (Christophersen, et al., 1990), (Christophersen & Hooper, 1992), (Durand & Juan Torres, 1996) (Bélanger, et al., 1998) testing complex combinations of solutes as end-members.

We will describe these two methods: the first using predominant tracers (simplified end-member) and the second, EMMA used in (Christophersen & Hooper, 1992).

3.2.3 Natural tracers of flow components

As already mentioned in 3.2.1 for n compartments it is necessary to follow n-1 tracer (s). The studies listed in the table explain that in the case of n flow components, the groups of tracers selected for the conservation of the mass chemical species are those of the flows which are supposed to be the most important and the most distant in terms of functions and compositions. Several chemical elements have been used in the literature, Table 17 on the appendix lists the flow components and their chemical elements used as tracers in different studies.

The bibliography enumerated shows that generally major cations and anions are used. For the groundwater we generally choose an ion coming from the solubilisation of a parent material such as $Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}$. For surface runoff, isotopes such as ($^{18}_{\delta}O,\ ^{\delta}D$)) or suspended matters can work. For subsurface runoff, it depends on the basin, and K^{+}, NO_3^{-} are the most used.

In the case of a two components model, following a groundwater or surface runoff tracer is possible. In the literature, it's generally a groundwater tracer which is chosen because there is a wide range of conservative tracers in it and they are generally similar in one basin to another. In the case of a 3 compartments model we usually select a groundwater tracer and a surface runoff tracer. Sometimes, in basins with a high infiltration (forested watersheds) with no surface runoff, researchers separated in two components: subsurface and deep groundwater (Robson and Neal, 1990). Rigorously, we prefer to avoid subsurface tracers because they are difficult to identify:

- Very high heterogeneity in their concentrations from a zone to another.
- Temporal variations of concentrations: soil water quickly mixes with infiltrated water during the flood which hasn't the same physicochemical characteristic straining the first hypothesis (true groundwater represents a bigger volume of water and is less subject to temporal variations of water concentrations).

Metals are not often used in the decomposition of hydrograph (analysis are generally more expensive compared to the ones for the ions), however metals are used as tracers in many environmental problems. For example, lithium (Kenneth E Bencala 1990) or strontium (E.Schemmel 2006) has been used. We will verify in this study if some ions or metals can be adequately used as tracers for our problematic of a watershed with anthropic activities.

3.2.3.1 Main criteria to account for the selection of chemical elements

a) Conservative element

We have seen that chemical species need to be conservative in order to use them as tracers. However, many chemical reactions and equilibriums occur in aquatic environments and these potential changes during the flood can undermine the conservative nature of the species. Indeed, the mobility of the species depends very much on its speciation and a complexation or adsorption reaction for example will have the consequences of immobilizing the species and underestimating the contribution of a component of the flow. The main chemical reactions taking place in aquatic environments that can influence the conservative character of a species are listed here:

- <u>Acido-basic reactions</u>

The composition of natural waters depends to a large extent on acid-base interactions. For example, the solubility of oxides, carbonate minerals, silicate minerals and metals depends on the H^+ion concentration.

- <u>Redox reactions</u>

  A redox reaction is a chemical reaction during which an exchange of electrons takes place. Redox reactions can be biotic or abiotic. Oxidized or reduced forms of certain chemical species do not have the same mobility in solution.

- <u>Complexation reactions</u>

  Many ligands [11] are present in natural waters. Among mineral ligands, we can find : $HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, F^-, S^{2-}$. Ligands can also be organic.

  A given system containing a metallic ion M and a ligand L which can form the complexes $ML_1, ML_2, .. ML_n$ reactions are :

  $$\begin{cases} M + L = ML_1 \\ ML_1 + L = ML_2 \\ \dots \\ ML_{n-1} + L = ML_n \end{cases}$$

  Heavy metals, for example can form aqueous complexes with differents organic and inorganic ligands found in natural waters.

  Complexation reactions are mainly governed by pH and redox potential.

- <u>Adsorption reactions</u>

  Adsorption is a surface phenomenon by which ions or molecules attach to a solid surface from a gaseous, liquid or solid phase.

  Thus, dissolved substances can adsorb to soil components and suspended solid particles and then be desorbed.

  Such processes contribute to establish metals concentrations (dissolved phase and particulate phase) in water. For example, the clay particles in suspension, are adsorbents and serve as both a mean of transport and a metal reservoir. In first approximation, in the case of low concentrations, adsorption can be described/represented by the following linear relation:

  $C_s = K_d . C_{aq}$ (16)

  Where C_s is the element concentration of the solid phase, C_{aq} the element concentration in aqueous phase and K_d the adsorption coefficient also said distribution coefficient. The adsorption coefficient is generally greater when the organic matter content is high, because of its high adsorption capacity.

  Two important categories of adsorption modes can be distinguished:

  - Adsorption by ion-exchange
  - Adsorption by formation of a covalent bonding bewteen the metal and the terminal –OH groups of the solid surface. It's the case of clay.

- <u>Reactions of precipitation/dissolution</u>

  An aqueous solution can precipitate or dissolve a mineral phase, such as the NaCl salt. The capacity to be precipitated or to be dissolved depends on the saturation of the solution in constituent ions of this salt. The mineral phases can, under certain conditions, precipitate and imprison metallic species or dissolve and

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[11] A ligand is an atom, an ion or a molecule carrying chemical functions that allow it to bind to one or more central atoms or ions.

release them. These balances can be reached at very variable time scales, of the order of the hour to thousands of years (INERIS, 2006).

b) Screening of the different behaviour of the elements during flood

In order to screen the different behaviours of the chemical species and choose the best ones as tracers, we consider their variations of concentration on the one hand and the discharge variation on the other hand during the flood. Species presenting a fall in concentration during flood show an affinity with groundwater flow. Indeed, groundwater flow ensures the greater part of the river baseflow. Thus, during floods extra flow components poor in these species cause a dilution.

However, species presenting a rise in concentration show an affinity with surface or subsurface runoff because these extra flows are essentially present during floods (especially the surface runoff), therefore an increase of concentration reflects the fact that these element have been brought by flood flows (surface and shallow subsurface runoff).

3.2.3.2 General approach to identify classical End-Member and structure of the simplified End-Member matrix

a) Groundwater

The concentrations of the tracer of the groundwater can be assimilated to the concentrations of the stream during periods of low water (Sklash et Farvolden, 1982), (Pinder, 1969)). This hypothesis can be supported by chemical analyses of representative aquifers by sampling piezometers

b) Surface runoff

The concentration in the runoff may be similar to the concentration in the temporary stream formed during the flood. (Pinder, 1969), (Buttle, 1994)

c) Shallow subsurface runoff

The concentration in the subsurface may be similar to the concentration of water flowing into the subsoil at the level of a rupture of permeability, supported by traces of hydromorphy. This water can be taken by a trench or piezometers on different depths (Bélanger, et al., 1998) (Peyrard, 2016).

It is also clear that these zones should be investigated first for the EMMA method because they are possible relevant End-Members.

d) Structure of the simplified End-Member matrix

Overall, for two compartments (groundwater and surface runoff) there is only one chemical element monitoring needed. The matrix of concentrations becomes:

$$\begin{bmatrix} 1 & 1 \\ C_{1,\text{groundwater}} & C_{1,\text{surface runoff} \cong 0} \end{bmatrix}$$

However, for a three compartments system, it becomes necessary to follow 2 chemical species:

$$\begin{bmatrix} 1 & 1 & 1 \\ C_{1\text{groundwater}} & C_{1,\text{surface runoff}\cong 0} & C_{1,\text{subsurface}\cong 0} \\ C_{2,\text{groundwater}\cong 0} & C_{2,\text{surface runoff}} & C_{2,\text{subsurface}\cong 0} \end{bmatrix}$$

Note that concentrations close to 0 are ideal concentrations and should be comforted by analysis.

3.2.4 Enhanced end-members tracking: End-Members Mixing Analysis (EMMA)

The EMMA method also derives from the Mixing Model. This method has been firstly described by Christophersen and Hooper in 1990 on the Panola Mountain and the Birkenes catchments and then used in other articles (Burns, et al., 2001) (Bélanger, et al., 1998); however, it has been less applied on watershed with agricultural activities (Durand & Juan Torres, 1996).

The hypothesis and equations remain the same as before, the main difference lies on the end-members screening. The previous Mixing Model method consisted first in identifying the main end-members based on a preliminary idea of the hydrogeological functioning of the basin (simplified end-members). The second step was to find the most relevant tracer for each flow component. In opposition, EMMA consists in iteratively trying, no longer using our perception of the system[12], the available combinations of solutes until finding the ones that fit and explain the chemistry of the stream at best, these combinations are the end-members. In order to perform this, EMMA needs additional tools.

3.2.4.1 Mathematical definition of convexity and end-members capacity to explain the mixing

Let's consider the case of f End-Members ($f \geq 2$), mixing in a conservative manner, without any chemical reactions ; the mixture is a "convex combination" of these end-members (Renner, 1993). A set is said convex when for two random points taken in this set, the segment connecting the points must be entirely contained in this set. An example of convex set is shown Figure 15.

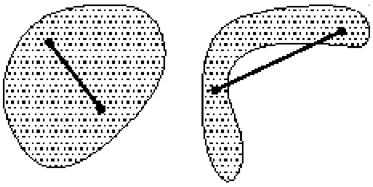

Figure 15 : Convex set on the left and not convex set on the right

Given two chemicals elements 1 and 2 and n observations of water chemistry, a mixing diagram is the graph $C_1 = f(C_2)$where the n observations are plotted .

Observations on the chemical composition of the river water, resulting from the end-members mixing is progressing in a convex set. The extremities of this mixing are the end-members. For two end-members the possible mixing set is a portion of a line. For three end-members, the set is a triangle.

The whole data describing water chemistry must be convex, which means that a maximum of observations must fit into the geometrical figure.

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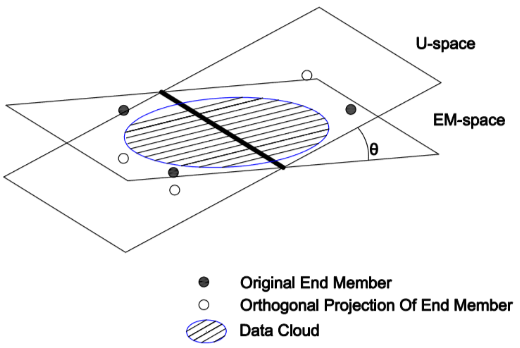
[12] However, this perception of this system should stay on the « background » because results, beyond being just mathematically should be realistic.

This notion of convexity is also used in the identification of potential end-members (Renner, 1993). This method being complex, it will not be described here and we will only use the convexity as verification.

3.2.4.2 Principal Components Analyses

In 1992 the same authors published a new article on the same Panola Mountain basin using a Principal Component Analysis (PCA) to express the mixture in a vector manner. The PCA is a multivariate analysis method which involves transforming the observations data (here the concentrations at the outlet) linked together (correlated) into new uncorrelated variables, linear combinations of the old variables. The axes used to describe these new variables (called principal components), or main axes are orthogonal. These axes define a new U space.

The PCA allows to un-noise data on the concentrations of several chemical species and to compress them, in order to create a "chemical identity" no longer expressed in concentrations for the end-members and the stream water. We return to the same system of equations as in the previous method but using the new variables that contain information on a mix of tracers. The notation changes however because we work in the subspace U. $U_k(t)$ are the variables of the space U obtained after projection of the concentrations after the ACP:



$$\begin{cases} \sum_{i=1}^{n} Q_i(t) = Q_{tot}(t) \\ \sum_{i}^{n} Q_i(t) * U_{1,i} = Q_{tot}(t) * U_1(t) \\ \quad\quad \dots \\ \sum_{i}^{n} Q_i(t) * U_{k,i} = Q_{tot}(t) * U_k(t) \end{cases}$$

Figure 16: Three End-Members in a two dimensional space spanned by a PCA

The approach is:

- geometric because the observations are represented in U according to maximum directions of inertia
- statistic because the axes are defined in such a way to explain the variability of the data cloud as best.

If the mixture results in k linearly independent End-Members the data can be encompassed in k-1 dimensions. The PCA gives an indication on the number of required end-members to explain the variability, the sum of variability (sum of eigenvectors) of the first dimensions should rise at least up to 80% of the total variability (Christophersen & Hooper, 1992).

The EMMA method is less restrictive in the choice of suitable solutes because each end-member is no longer described by a predominant solute but by a chemical identity, ie a combination of solutes. This is made possible by the PCA which frees the over determination problem and allows the use of more than k-1solutes. However, it is still necessary to verify the assumptions made previously and make sure to use only the relevant species in the different methods of the Mixing Model.

3.2.4.3 Selection of End-Members and goodness of fit

a) Selection of End-Members

The potential end-members are usually the solutions described in 3.2.3.2. As explained in 3.2.4.2 the PCA gives an indication on the number of required End-Members.

A practical criterion is to choose after projection on the U space the set of bounding End-Members that are closest to the cloud of observations among all available End-Members (Christophersen & Hooper, 1992).

b) Goodness of fit

It is possible to predict concentrations in the stream by "unstandardizing" end-members[13], back-projecting them in the original space (orthogonal projection) and finally mixing them in the proportions given by the model.

Global goodness of fit is measured by performing a regression of predictions against observations. The scatter is indicated with the coefficient of determination (R^2).

Relevance of a chosen experimental end-member can be measured by comparing one by one its solutes concentrations with the solutes concentrations of its back-projected version. After verifying the physicochemical plausibility of the back-projected end-members, they can replace the experimental end-members and usually slightly improve the goodness of fit (Christophersen & Hooper, 1992).

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[13] Multiplication by the standard deviation and adding the average

4 Material and methods

We will describe in this chapter the strategy of the study and the avalaible data.

4.1 Study strategy

4.1.1 Hydrograph separation

In this study we will apply 3 methods of hydrograph decomposition on available data on different recorded flood events.

4.1.1.1 Hydrological method

To apply this method, discharge recordings at the outlet during the rainy episodes and the rainfall intensities corresponding are necessary.

4.1.1.2 Mixing Model methods

In addition, for Mixing Model methods it is essential to follow the evolution of the concentrations of the chemical species that can be used as tracers during the flood episode. That is to say that from the available data (major parameters and metallic trace elements) it is necessary to sort the potential tracers, according to the criteria selected.
In addition, it is necessary to decide which end-members are considered (watershed areas / "flow layers"). For this, an important data is probably the punctual analysis of the water at the outlet of the watershed. Firstly, this data is required in order to compare the difference in water quality between before and during the flood. Secondly, this data presents other interests:

- Some samples were taken during periods of major recession of the watercourse; these analyses represent the typical average concentrations of the water table of the basin (Sklash and Farvolden, 1982), (Pinder, 1969).
- Apply the EMMA method: build the U space from these observations describing the evolution of river chemistry in the time (Burns, et al., 2001).

Subsequently, samples should be taken or data extracted from the samples in the other conventional layers of the basin as described in 3.2.3.2.

4.1.2 Consequences for pesticides concentrations

Because the second part of our study aims to give information on pesticides exportation dynamics, data on pesticides concentration during the flood are necessary.
In a first step, we will perform correlations between pesticides concentrations and the estimated mixing ratios of flow components for each event.
Consequently, we will perform a multilinear regression of pesticides concentrations on mixing ratios (reverse Mixing Model) in order to screen more easily the contribution of each flow component to the exported mass in pesticides.

4.1.3 Mathematical resolution

For the hydrological method, the logarithmic transformation and plotting of hydrograph is performed on the R software with the package ggplot.
In most articles, for the Mixing Model system is solved by the least squares method.
The "nnls" package of R (non negative least squares) was used in our study for the first Mixing Model method. The Principal Component Analysis of EMMA was performed on R

with the package FactoMineR, results were then used on an excel sheet inspired from the excel sheet used by (Christophersen & Hooper, 1992).
Finally, the multilinear regression is performed on R using"lm".

4.2 The Morcille watershed

The methods previously described in the state-of-art will be applied on the Morcille watershed. The study of the Morcille drainage basin started on 1986 in order to identify pesticide transfers, erosion phenomenon in connection with the cultural practices. It was chosen because it shows interesting characteristics in order to study anthropic activities on water quality. Actually, the basin particularities are:

- A proven degradation due to various anthropic activities (no more fish life in the river since a few decades) (Orquevaux, 2010)
- Vulnerability to soil erosion
- The area devoted to vines is very consequent (70%)
- A small surface area (approximatively 9 km^2).

A presentation of the Morcille catchment is showed Figure 17.

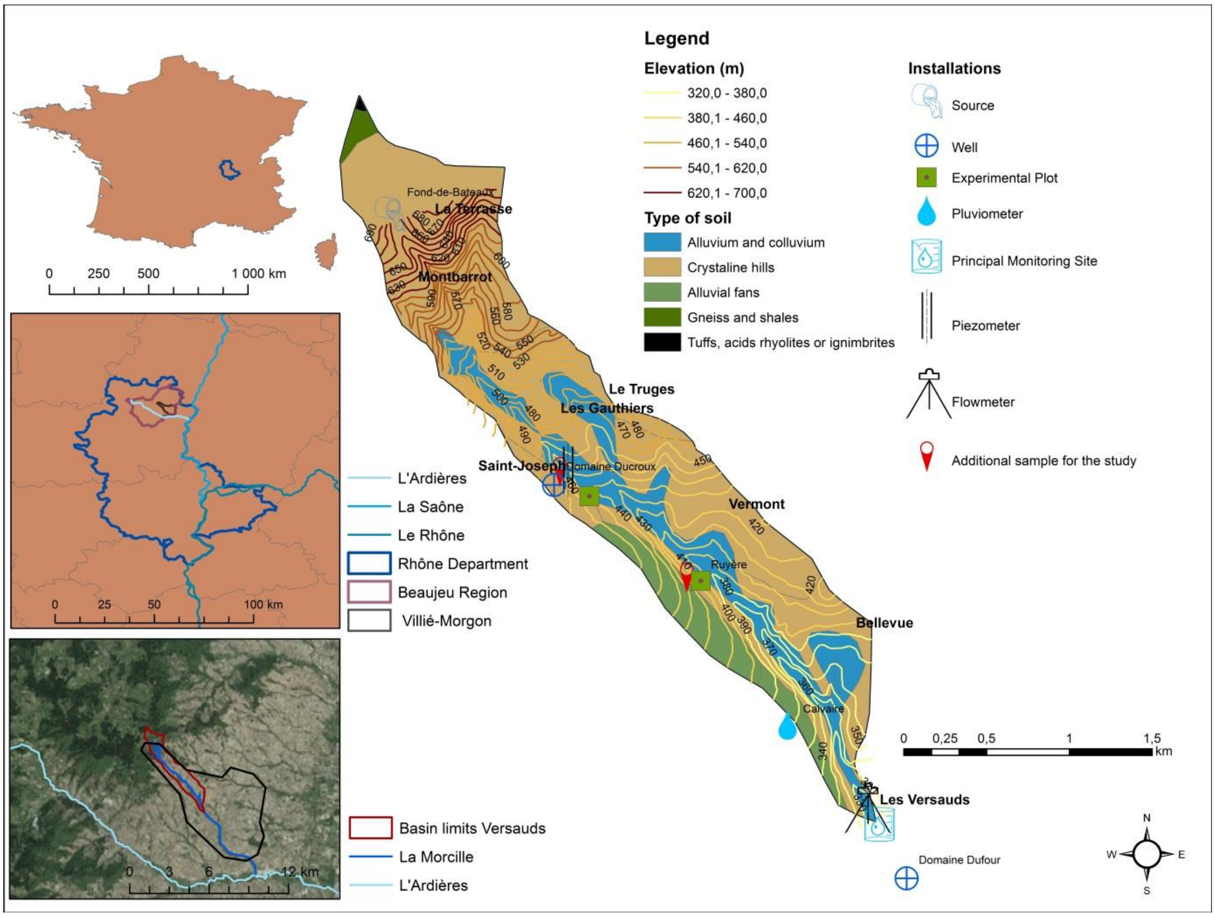

Figure 17 : Map of the Morcille experimental watershed and its installations

4.2.1 Geography

The Morcille basin is located in the North Rhône department, in the Haut-Beaujolais, between the Massif Central oriental border and the west Saône valley.

It is the Ardières sub-basin (220 km²) which meets the Saône (Rhône affluent), near Belleville. The Morcille extends over 9 km[14], from the “Fonds de Bateaux” a hamlet located near a municipality called Villié-Morgon until the junction with the Ardières. Figure 17.

4.2.2 Nature of the substrate and soils

The substrate is an altered crystalline basement, essentially granitic. Soils are mostly sandy (or even silty, rarely clayey) and erodible (granular disintegration) and are generally poor in organic material. Sandy soils are on the top of hillsides while more clayey soils are at the bottom of the valley.

4.2.3 Climate characteristics :

The climate is temperate with contrasting seasons and significant temperature disparities between summer (30°C and more) and the winter (- 10°C). Medium annual temperatures range between 7°C and 16°C. The annual pluviometry is 770 mm. Rainfall repartition is quite regular during winter while in summer one event out of two is a storm.

4.2.4 Morcille hydrology :

The discharge varies very widely and can oscillate between 5 and 700 L/s or even higher (8000 L/s). This site is characterised by important hydrologic events (strong and quick floods) with a very short response time due to the high slopes and high hydraulic conductivities on the catchment. The bed is rarely dried up.

4.2.5 Hydrological arrangements :

In order to protect the agricultural lands from the erosion, heavy structures have been implemented including a dense and structured ditch system: the intra-parcel ditches are linked with canalisations (nozzle pipe) whose purpose is to lead out water from the parcel to an outfall which is the stream.

4.3 Previous studies and available data

The Morcille watershed has been studied many times during the last years, (Peyrard, 2016), (Orquevaux, 2010), (Rabiet, et al., 2015), the first step was doing a synthesis of all the available and useful data for this study (Table 1 and Figure 17). Then, some samples have been taken in order to complete the missing data such as physicochemical parameters on surface runoff.

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[14] Most of the studies carried out on this basin use as an outlet the site study called "Versauds" thus reducing the field of study to a sub-watershed
with an area of 4.8 km².

Table 1 Summary of the installations and available data for this study on the Morcille watershed and choice in the available data.

Installations	Available data	Used data
Source	14 analysis of major parameters, metals and pesticides 2008 to 2011 (upstream to Saint-Joseph)	
Wells	3 private owner's wells : Ducroux, Dufour, Bereziah (Bereziah being out of map, to the South), 17 analysis of major parameters and pesticides from 2008 to 2015.	Two wells used on three. Bereziah's well isn't on the same catchment with a deeper water table and a different hydrochemistry.
Experimental plots	Analysis of major parameters, metals and pesticides in the Morcille streamwater from 2006 to 2014. 1 Analysis of major parameters, metals and pesticides in Ruyères. Analysis of TSS in surface runoff for different rain events in 2013.	
Pluviometer	Precipitations chronicles from 1992 to 2017.	
Sampling (streamwater)	-Fractionated flow-proportional sampling in 2007, « les Versauds » station. Analysis on metals, major parameters and pesticides (nearly 10). -Punctual sampling from 2004 to 2012 (nearly 40 per year). Averaged sampling for year 2007	
Piezometers	Water-table variations from 2012 to 2016, ½ h intervals. 3 analysis of major parameters in 2012 and 2013 (excepted pH) on the set of piezometers o Saint-Joseph grass strip.	
Flowmeter based on streamwater heights	Discharge's chronicles from 2002 to 2016	Mainly discharges in 2007
Cette étude	2 series of ponctual sampling of major parameters and metals in 2 piezometers (2P and PV) and in the Morcille streamwater at Saint-Joseph. 1 rainwater sample on Saint-Joseph. 1 runoff sample on the experimental parcels Ruyères and St Joseph 1 sample of water on the trench of Ruyères.	

Description and disposition of piezometers is showed Figure 18

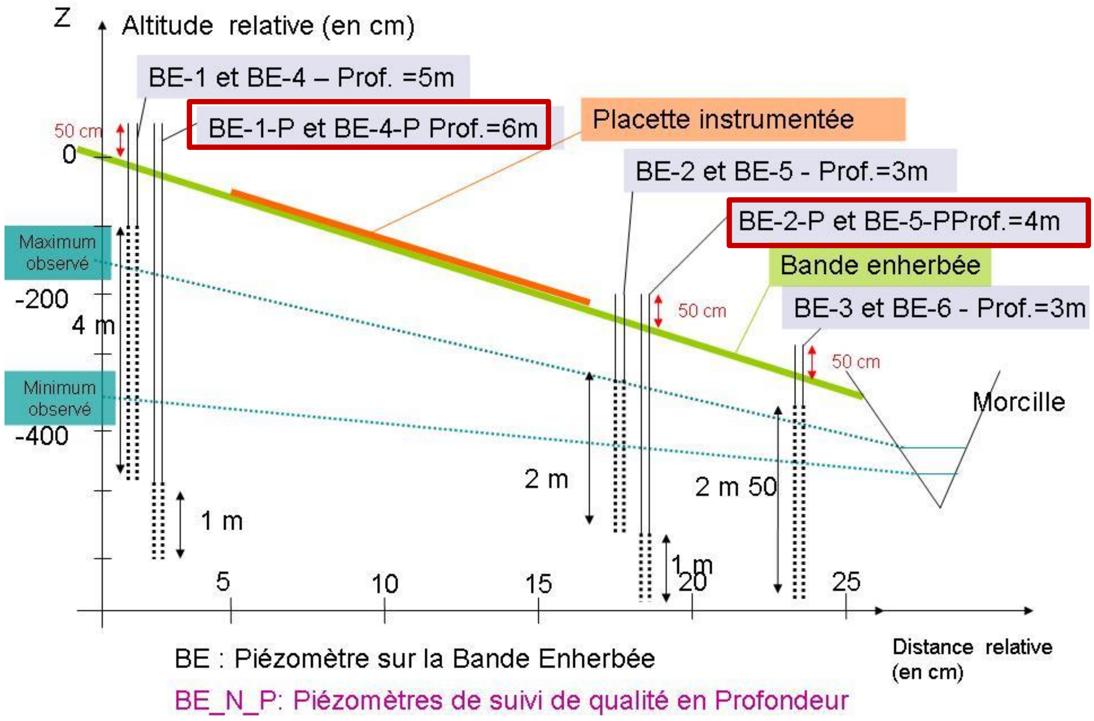

Figure 18 :Piezometers disposition on the Saint-Joseph transect (Rousseau 2011)

Piezometers in red were the most used piezometers in this study.

5 Preliminary work and results

5.1 Selection of rainfall events

The data collection on water quality during the studied flood events wasn't initially designed in order to apply the Mixing Model and the deconvolution of hydrograph. We had to select the events with enough data in order to perform this study according to « material and methods » A decisional pyramid is presented Figure 19.

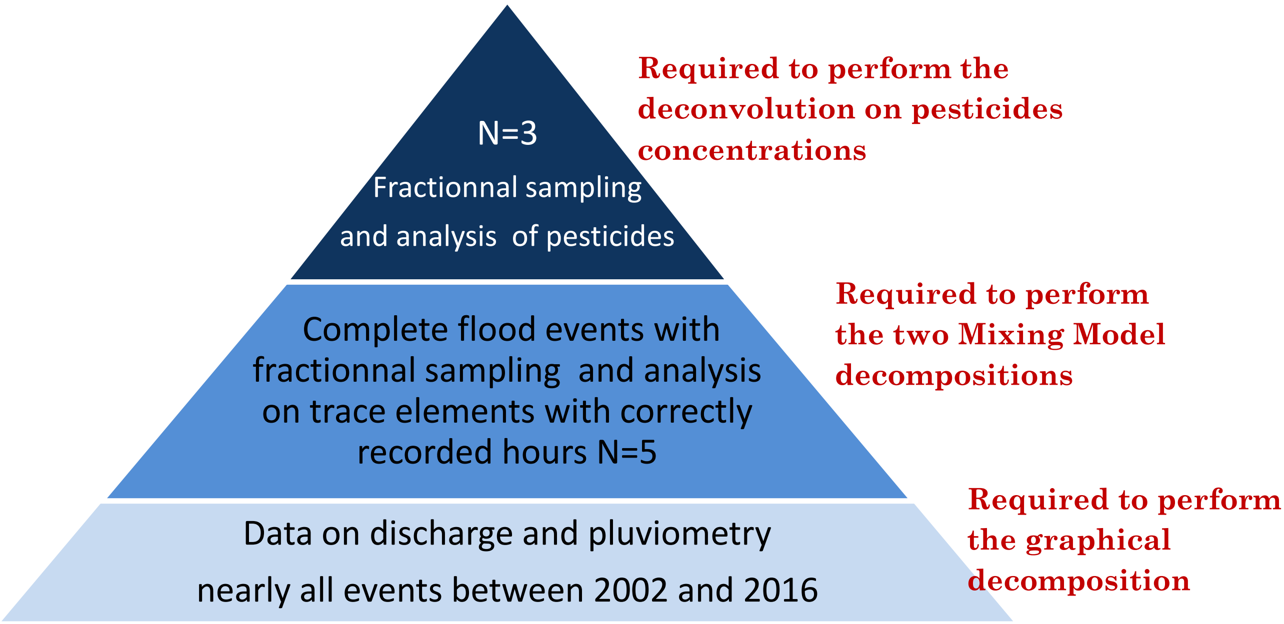

Figure 19: Decisional pyramid to select the potential flood events with enough data for this study

As a result, the complete study will focus mainly on 2 rainfall events, with the highest discharge : The event of the 01/07/2007 and 07/08/2007 . The same events are studied in (Rabiet, et al., 2015). More events are, when it's possible, treated in order to study limits of a method on more than two rainfall events.

Characteristics of these flood events are registered Table 2.Table 2 : Characteristics of the selected flood events in this study

Characteristics	**1 July 2007 event**	**7 August 2007 event**
Baseflow (L/s)		
Before	13	4
After	20	19
Flow max (L/s)	101	188
Cumulative rain (mm)	18,5	20
Duration (basetime) h	13h	8h
Maximum intensity (mm/h)	4,43	5,94

5.2 Selection of tracers

This is to eliminate among all chemical species available these that do not meet the criteria to be used as tracers in this study. Also, this preliminary work is necessary partially or entirely for methods based on the Mixing Model.

A decisional pyramid based on all criteria found in the state of art 3.2 is showed

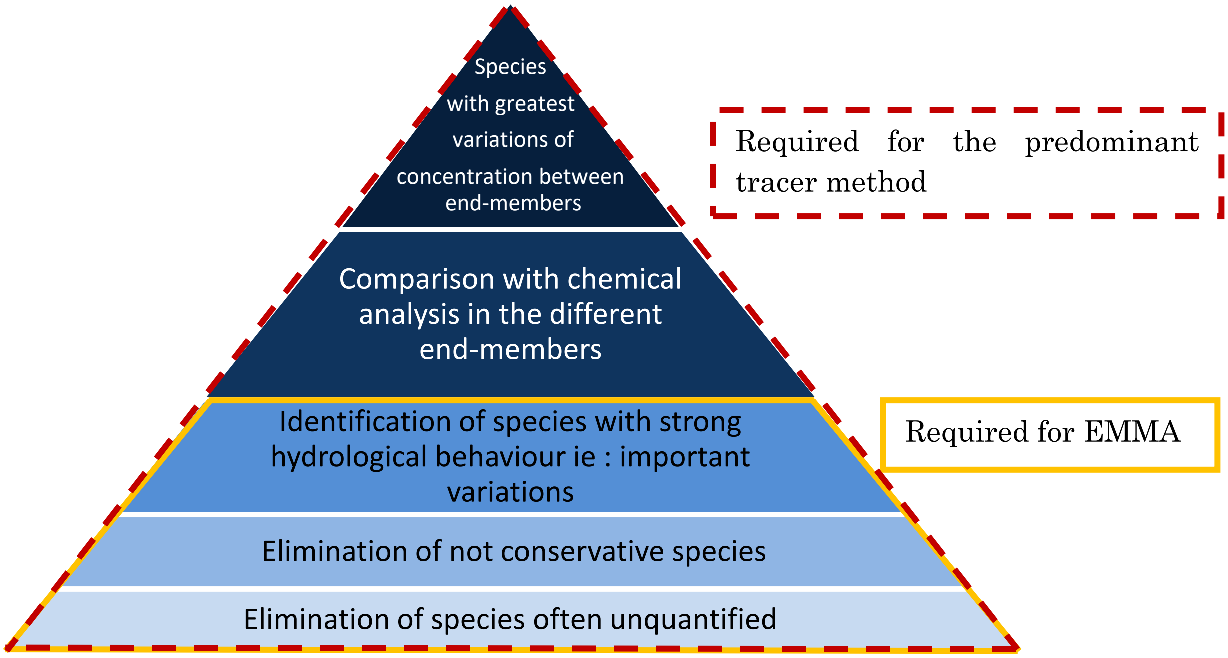

Figure 20: Decisional pyramid to identify the potential tracers for two Mixing Model methods in this study

EMMA shows to be faster and more objective in the characterisation of the potential End-Members thanks to the mathematical tools.

The most relevant tracers in this basin were $Cl^-Sr, Na^+$and $Mg^{2+}$for the aquifer and Al,Cu, K^+, Total Suspended Solids (TSS) and Rb for quickflows.

The pyramidal path is described in the following paragraphs.

5.2.1 Quantitative approach: elimination of species often unquantified

Some species are present in water with too low concentrations, sometimes below the limit of quantification. They do not provide usable information for our study. If these non-quantifications are too frequent, the chemical species must be eliminated. Also, species with concentrations close to the limit of quantification have higher analytical uncertainties and must be eliminated too. Table 3 and

Table 4 record the frequency of non-quantification of each element in the Morcille water at the Versauds station for each flood studied. If the species has a quantification frequency greater than 1/3 or an average value less than 2 times the quantification limit in more than one event it is excluded.

Table 3: Elimination of anions/cations and major non-quantified parameters in water samples from Morcille at the Versauds station

Major parameters								
Anions, cations and conductivity	Quantification limit in mg/L	Frequence of non quantification Green :FNQ=0 Orange : FNQ<1/3 Red :FNQ>1/3			$Cmoy \ll 2 \times LQ$ exceeded limit in red $5 \times LQ \ll Cmoy \ll 2 \times LQ$ in orange (Cmoy/LQ indicated in the boxes)			Selected elements
		26/05/07	02/08/07	17/09/07	26/05/07	02/08/07	17/09/07	
Conductivity	☒	🟩	🟩	🟩	🟩	🟩	🟩	Conductivity
TSS	8	12/38	🟩	🟩	🟩	🟩	🟩	TSS
Cl^-	1	🟩	🟩	🟩	🟩	🟩	🟩	Cl^-
SO_4^{2-}	1	🟩	🟩	🟩	🟩	🟩	🟩	SO_4^{2-}
PO_4^{3-}	0,03	🟩	🟩	2/12	🟩	🟩	🟩	PO_4^{3-}
Mg^{2+}	1	☒	🟩	🟩	☒	4,4	🟩	Mg^{2+}
Na^+	1	☒	🟩	🟩	☒	🟩	🟩	Na^+
Ca^{2+}	4	☒	🟩	🟩	☒	🟩	4,9	Ca^{2+}
K^+	1	☒	🟩	🟩	☒	3,76	🟩	K^+
NH_4^+	0,02	19/38	🟩	🟩	1,73	🟩	4,29	NH_4^+
NO_2^-	0,02	6/38	2/28	1/12	2,18	3,25	1,5	NO_2^-
NO_3^-	1	🟩	🟩	10/12	🟩	🟩	1,04	NO_3^-
HCO_3^-	30	☒	🟩	☒	☒	2	☒	HCO_3^-

Table 4: Elimination of non-quantified metals in the Morcille water samples at the Versauds station

Metallic trace elements												
Metals	Quantification limit in µg/L	Frequence of non-quantification Green :FNQ=0 Orange : FNQ<1/3 Red :FNQ>1/3					$Cmoy \ll 2 \times LQ$ exceeded limit in red $5 \times LQ \ll Cmoy \ll 2 \times LQ$ in orange (Cmoy/LQ indicated in the boxes)					Selected elements
		26/05	02/08	17/09	07/08	01/07	26/05	02/08	17/09	07/08	01/07	
Al	5,0	11/38	🟩	🟩	🟩	🟩	1,9	🟩	🟩	3,5	3,4	Al
Cu	0,05	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Cu
Fe	0,5	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Fe
Li	0,05	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Li
As	0,05	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	As
B	2,0	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	B
Cr	0,05	🟩	☒	🟩	🟩	🟩	🟩	☒	🟩	4,8	3,62	Cr
Co	0,10	☒	22/28	🟩	🟩	28/30	☒	1	4,2	4	1	Co
Ni	0,05	🟩	🟩	🟩	29/32	1/30	🟩	🟩	🟩	<1	2,4	Ni
Zn	0,5	13/38	3/28	🟩	3/32	11/30	2	1,1	🟩	1,3	<1	Zn
Rb	0,05	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Rb
Sr	0,5	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Sr
Mo	0,05	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	4,3	3,4	Mo
Cd	0,01	🟩	🟩	🟩	1/10	2/30	1	1,5	2,7	1,3	1	Cd
Ba	5,0	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Ba
Pb	0,10	28/38	🟩	🟩	🟩	1/30	1,8	3	🟩	1,35	2,5	Pb
U	0,10	🟩	🟩	🟩	🟩	🟩	2,9	3,4	3,2	2,2	2,7	U
Ag		38/38	28/28	☒	32/32	30/30	0	0	☒	0	0	Ag

HCO_3^- fullfills the criterions but was followed only for a flood so it cannot be used and was also excluded. **Finally, the following parameters were retained in the first stage for the major parameters: Conductivity, TSS, $Cl^-, SO_4^{2-}, PO_4^{3-}, Mg^{2+}, Na^+, Ca^{2+}, K^+ et\ NO_3^-$**[15]
For metallic trace elements°: $Al, Cu, Fe, Li, As, B, Cr, Ni, Rb, Sr, Mo, Ba, U$.

5.2.2 Qualitative approach: Elimination of potentially non conservative species

The aim is to assess whether the potential chemical reactions mentioned, in particular the acid-base and redox reactions do not undermine the conservativity of the chemical elements previously retained.
To identify the conservative character of an element we can use Pourbaix diagrams, also called « potential-pH diagrams » as a first approach. These diagrams in E-pH coordinates indicate the domains of predominance (or existence in the case of solid species) of the different forms of an element. Thus, the first parameter to look at is the pH variation within the Morcille basin.
Figure 21 illustrates a weak variation of the pH on the Morcille, the average pH is illustrated by a vertical line:

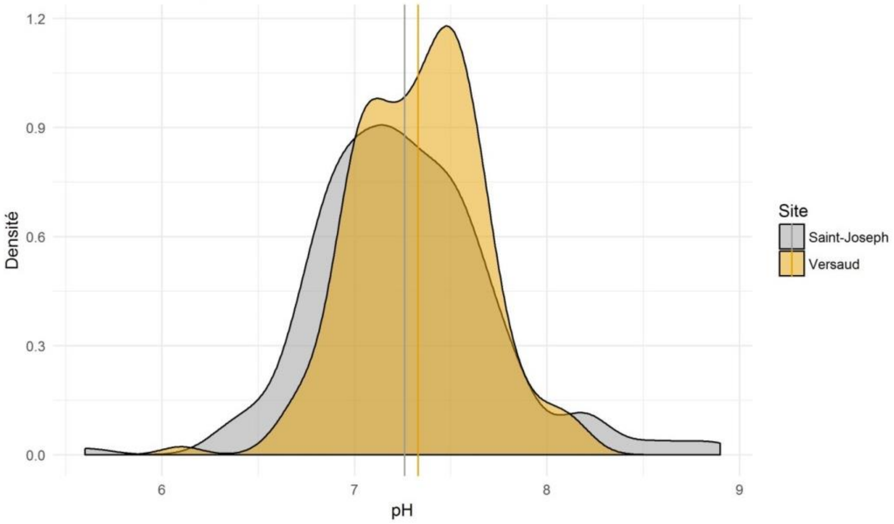

Figure 21 : PH distributions of the Morcille at the upstream and downstream point from 2004 to 2010

The distribution curve shows that pH presents a low geographical and temporal variation: majority of values are between 6,6 and 7,8 over six years. Spatially, pH distributions for the two sites are almost superimposable with very close averages and a slight tendency of the pH to increase from upstream to downstream.
In addition, measures of pH performed during this study or before are reported in Table 5 for different waters: Source Morcille, wells, piezometers, surface runoff, subsurface runoff at Ruyères and rainwater Table 5.

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[15] However, NO_3^- cannot be used as tracer on the 17/09/2007 event

Table 5: pH of different water in the Morcille watershed

Water samples		Source Morcille (n=14)	Wells (n=14)		Groundwaters Piezometers		Surface runoff n=2	Soilwater subsurface runoff n=1	Stream in recession	Rainwater n=1
			Ducroux	Dufour	vine n=2	2P				
pH	Average	6,4	6,3	6,5	6,0-6,1	6,3-6,4	7,5-7,6	6,7	7,4	6,7
	Standard variation	0,26	0,16	0,17					0,26	

The selected pH interval for the Morcille waters is then included between 6 and 8 with a comfortable margin.

The second parameter to consider is the redox potential. We admit that in natural waters, redox potential is included between -0,2 and 0,2 V including the alluvial water table (Bossy, 2010).

Once the intervals have been determined, using Pourbaix diagrams makes it possible to check whether the chemical species are likely to change from a solid to a dissolved form or vice versa during the rain event, depending on the observed variations in pH. and redox potential. Figure 22 presents the methodology for the lithium, iron and chrome:

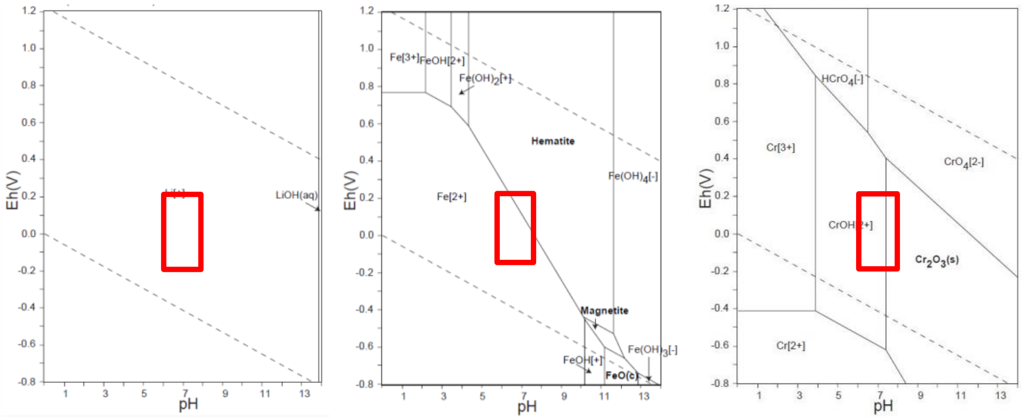


Figure 22 : Pourbaix diagrams of lithium, iron and chromium and delineation of the redox-pH potential range of Morcille waters (red rectangle). Original diagrams from (Takeno, 2003).

As for lithium (and many other species), its physico-chemical form (hydrated ion) does not evolve in the range of pH and potential of the Morcille's waters.

In the case of chromium and iron, according to the Pourbaix diagrams a change of speciation and phase of the species is possible (cation-solid precipitate).

Following this qualitative analysis, iron and chromium were excluded. The exclusion of iron is confirmed by considerations of soil: indeed from 2 meters of depth the soil presents traces of hydromorphy and the iron is grey indicating that it is already in reduced form according to the equation:

$$Fe^{3+} + e^{-} = Fe^{2+}$$

It should be noted, however, that the Pourbaix diagrams give information on the thermodynamic nature of the reaction (favoured or not) but none on the kinetics of the reaction. Some balances are reached on a minute scale while others are on the scale of thousands of years. Thus, some reactions can be slow enough at the scale of a day to make the hypothesis of the conservative character during a flood event on the Morcille basin.

5.2.3 Identification of strong hydrological behaviours

As mentioned in 3.2, only 2 tracers are necessary for three end-members. Generally, the most appropriate choice is to take a tracer from the group of species characteristic of the aquifer and the second from the group of species characteristic of surface runoff.

This choice is justified by the presence of significant quick flows on this basin and that the contribution of the subsurface is not yet well known.

Additional sampling was necessary to identify more precisely the chemical composition of the subsurface and the runoff (1 sample for the subsurface runoff, 0 for the surface runoff until there except for TSS). Sampling was also necessary to know more precisely metallic elements concentration in the Saint Joseph groundwater. Table 6 lists the expected criteria of potential tracers for the different chosen flow components.

Table 6 : Required criteria of potential tracers resumed

Flow components	**Selection criteria of selected species**	
Groundwater	Physicochemical	Poorly adsorbable. Mobile species resulting from the solubilization of the parent rock, called "geochemically controlled" Ex : Na^+, Mg^{2+}, Sr^{2+}
	Hydrological	Species with declining concentration in the watercourse with the flood and high concentration during periods of recession
Surface runoff	Physicochemical	Adsorbable on the erosive material, or erosive material itself. Ex : TSS,Cu
	Hydrological	Species with low concentration in the stream before the flood and with a peak of concentration generally correlated with the peak of flood

Some examples of these trends are graphically illustrated Figure 23 and Figure 24.

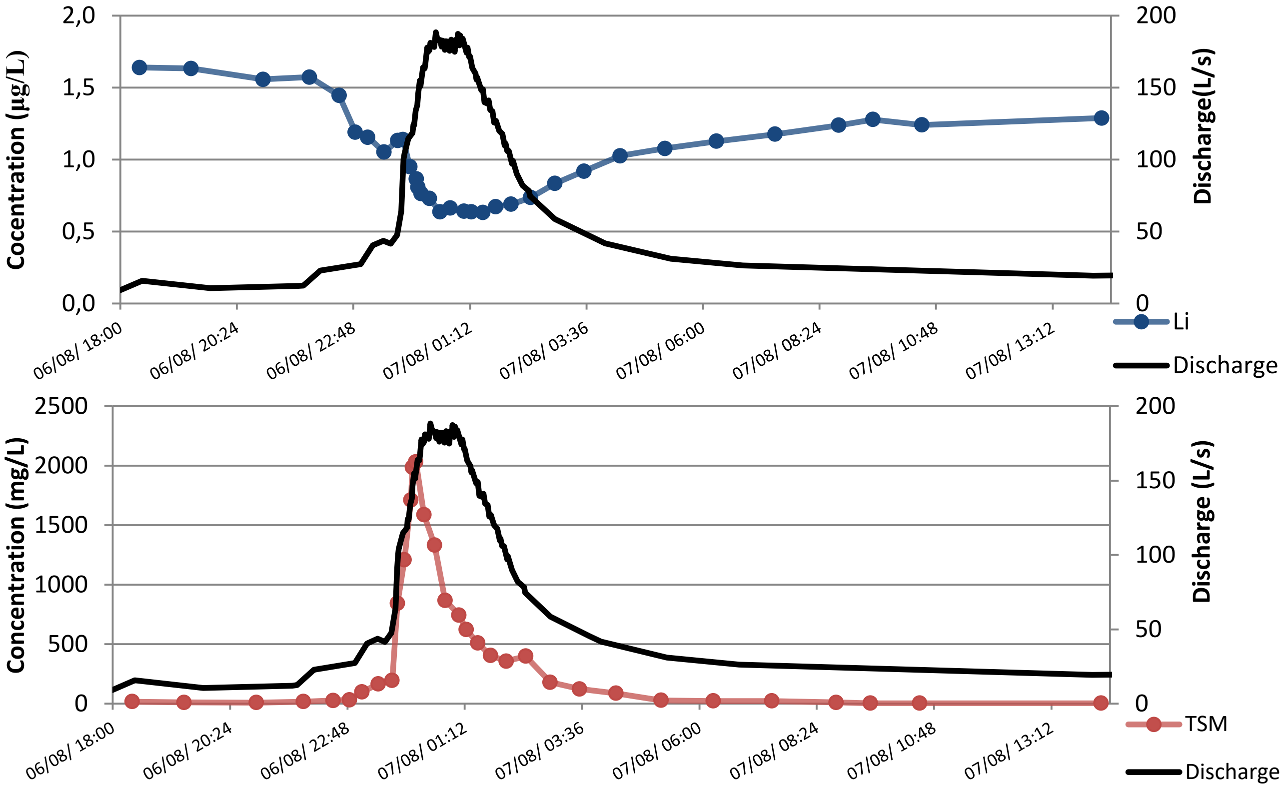


Figure 23 : Evolutions of concentration in lithium and TSS during the flood of the 07/08/2007

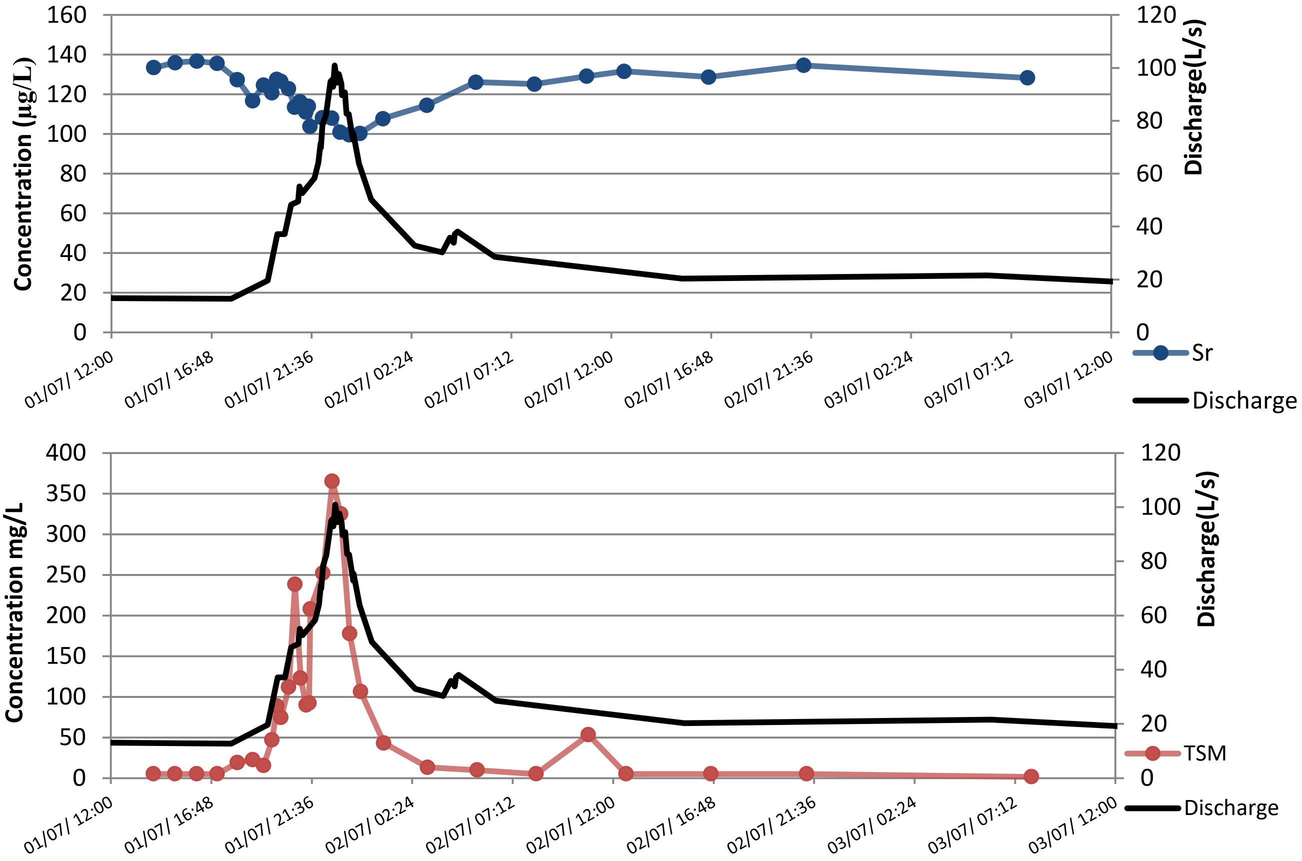
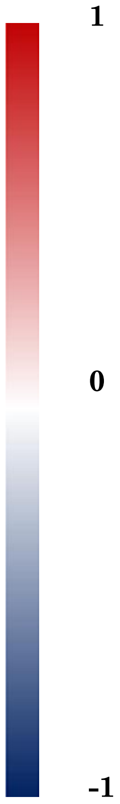


Figure 24 : Evolutions of concentrations in strontium and TSS during flood of the 01/07/2007

We observe, as expected, the concentration of TSS increases quickly at the beginning of the flood while the concentration of strontium or lithium for example decrease significantly and then rise thereafter at the end of the flood. The correlations between the flow and the concentrations of the different species during 4 floods are registered in the Table 7. These correlations make possible to observe trends more easily in order to systematically sort the elements, and to judge whether these trends can be generalized over all the floods.

Table 7 : Correlations between concentrations of the species and the flows of the different floods. Significative correlations in bold α=0,05.

Events **Species**	26/05/2007	02/08/2007	07/08/2007	17/09/2007
Number of samples	n=38	n=38	6<n<34	n=13
TSS	**0,92**	**0,79**	**0,82**	**0,69**
Copper	**0,26**	**0,44**	**0,88**	**0,69**
Aluminium	**0,65**	**0,56**	0,34	**0,67**
Potassium	0,71	0,35	**0,99**	**0,82**
Boron	0,15	0,35	**0,57**	0,30
Phosphate	**0,38**	0,34	**0,94**	-0,41
Rubidium	**0,27**	**0,42**	**0,53**	-0,11
Molybdenum	**0,50**	0,36	**0,87**	**-0,67**
Arsenic	-0,63	-0,32	**0,35**	0,04
Nitrate	-0,04	0,43	-0,25	**-0,76**
Uranium	0,21	**0,58**	**-0,81**	**-0,65**
Sulfate	-0,28	0,45	**-0,86**	-0,55
Calcium	-0,77	0,08	**-0,98**	-0,47
Conductivity	**-0,63**	0,09	**-0,99**	**-0,65**
Barium	**-0,75**	-0,15	**-0,77**	-0,49
Strontium	**-0,77**	-0,04	**-0,82**	**-0,64**
Chlorine	**-0,59**	0,02	**-0,98**	**-0,75**
Magnesium	**-0,88**	-0,09	**-0,81**	**-0,69**
Sodium	**-0,90**	-0,02	**-0,99**	**-0,71**
Lithium	**-0,85**	**-0,54**	**-0,85**	**-0,73**



We observe 3 differents dynamics of concentration during floods :

- The elements with strong negative correlations with the flow, it is the case of $Li, Na^+, Mg^{2+}, Cl^-, Sr, Ba, Conductivity\ and\ Ca^{2+}$. These elements seem to form the group of majority species in groundwater.
- The elements with positive correlations with the flow more or less important, it is the case of $TSM, Cu, Al\ , K^+, B\ et\ Rb$. These elements seem to form the group of the majority species of runoff and / or subsurface.
- The elements with very different correlations from an event to another, this is the case of $SO_4^{2-}, U, NO_3^-, As, Mo, PO_4^{3-}$. These weak and variable correlations can be explained by the presence of these elements in significant quantities in all the

compartments of the basin while having eventually a variable concentration during the flood in some of these compartments.

These weak correlations can be explained by the presence of these element in concentrations close in all compartments of the basin. In addition, the comportment of these species seems to be different from event to another, in particular for the 2 august which can be explained by a variation of concentrations in these elements between 2 flood events.

5.2.4 Comparison with analysis in the different compartments: case of major parameters

These last steps are not needed for EMMA.

5.2.4.1 Groundwater

Data on punctual samples carried out in the Morcille surface water at the Versauds site from 2004 to 2011 during periods of prolonged flow recessions were selected and averaged.

At these periods, the stream is theoretically only fed by the groundwater. These physicochemical analyses make it possible to approach the concentrations of Morcille aquifers for cations / anions and metals[16].

However, among the selected dates the river water may not be completely fed by the water table but also by the subsurface resulting already in a diluted mixture and a possible underestimation of the concentrations of characteristic species of the water table.

These concentrations of the anions and major cations in the Morcille at the Versauds station were confronted with the concentrations of the samples in the Saint Joseph piezometers and the wells of the two individuals in the Figure 25.

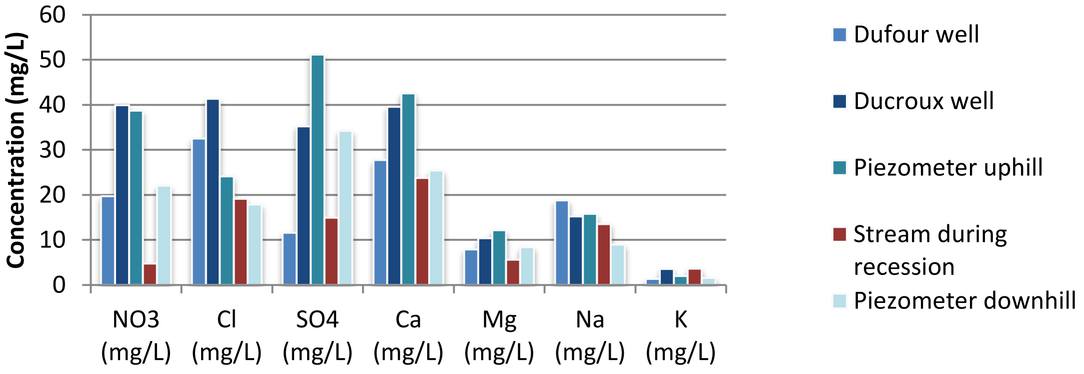


Figure 25 : Confrontations of medium concentrations of major anions and cation in different Morcille's groundwater (Saint Joseph piezometers and wells) and surface water in recession (Versauds Station) (Cf. Table 1 and Figure 17)

The concentrations in recession of geochemically controlled anions and cations in the stream are often included between the concentrations of upstream and downstream piezometers. Concentrations of these chemical species are higher in private wells than in the river during recession. However, the repartition on the different elements is similar

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[16] Phosphates have been sampled only two times in the piezometer and once in a concentration above the quantification limit. As a result, phosphate has been removed of the study.

to the stream in recession or the piezometers, which seems to confirm the hypothesis of the contribution of a "diluent" component (subsurface) to the flow, even in recession already resulting in a mixture and an underestimation of the concentrations of the characteristic species of groundwater.

The wells as well as the piezometers have a higher load in nitrates and sulphates than the stream. These differences in concentrations could be explained by a greater biological activity in stream during its recession.

Using the watercourse concentrations during a recession for the chemical signature of the water table seems to be valid for the Morcille watershed for the species regularly found in the literature ($Cl^-, Mg^{2+}, Na^+, Ca^{2+}$).

For the method using “predominant tracers”, we defined the global concentration in groundwater as the average of the watercourse in recession with the two groups of piezometers located at Saint Joseph's. Indeed, many doubts remain about the nature of the groundwater taken by the different wells and it is better to dismiss them. Table 8 lists the average concentration of each species and its standard deviation within the 3 differents groundwater and between these, each with a weight of 1. We observe a generally low variation (RSD <35%) of the concentrations over time for each groundwater. Variations are also low between the different groundwater for most chemical elements[17]. This allows to gather these groundwater in a unique simplified end-member using the adequate tracer.

Table 8: Medium concentrations of the Morcille’s groundwater and observed variations (RSD)

Major anions and cations		Conductivity µS/cm	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	K^+	NO_3^-
Retained concentrations (mg/L)		292	12,8	31,0	8,7	33,4	21,0	2,4	21,8
RSD	Upstream piezometer 1P+4P n=7	6,4%	20,2%	4,9%	2,9%	7,3%	3,7%	15,0%	8,4%
	Downstream piezometer 2P+5P n=10	3,0%	13,5%	5,2%	8,6%	7,8%	16,8%	94,3%	29,9%
	Stream in recession 10<n<27	28,0%	33,0%	32,5%	34,4%	31,4%	15,2%	47,5%	52,1%
RSD between concentrations of the 3 different groundwater		32,3%	33,0%	32,5%	34,0%	29,4%	15,2%	45,2%	77,7%

5.2.4.2 Surface and subsurface flow components

Two samples and analyses of surface runoff were performed the 07/06/2017 after the event of 06/06/2017[18] on the plots located at Saint-Joseph and Ruyères Samples and

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[17] Except for potassium and nitrates

[18] 4,615 mm of rain fallen, maximal intensity of 3,3 mm/h

analyses performed on the Ruyères subsurface in february 2013 and may 2017 are also recorded Table 9.

Table 9:Anions/cations analyses on different shallow components in the Morcille watershed

Major anions and cations		Conductivity (µS/cm)	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	K^+	NO_3^-
Surface runoff concentrations (mg/L)	Saint-Joseph	188	2,8	25,3	2,2	25,9	6,8	5,6	3,0
	Ruyères	199	9,4	12,6	2,9	31,4	1,4	5,7	4,0
Subsurface concentrations (mg/L)	Piezometer. February 2013 PhD thesis	55	1,8	9,3	1,3	13,0	1,0	1,1	0,83
	Trench May 2017 master thesis	90	2,3	5,9	2,0	19,8	5,9	7,2	5,7

Concerning the major parameters, the surface runoff is poor in "characteristic" species of groundwater as expected in the literature, with the exception of calcium, sulphate and potassium, present at values sometimes as high as in the aquifer. From one site to another, the conductivity, nitrates, magnesium, sulphate and potassium have similar concentrations. In contrast, for sodium, calcium, chlorine and phosphate it differs significantly. The subsurface is also an end-member with very low concentrations overall with a low conductivity between 55 and 90 µS / cm and varying concentrations of potassium, chlorine and nitrates. Only calcium and sulphates observed at different dates remained high for these which seem to confirm a presence of these two elements in the soil and explain their correlations with the low flow rate during the flood. The sample taken at the spring shows concentrations higher in nitrate, potassium and sulphate compared to the one done during winter. This can be explained by an higher use of fungicides and fertilizers during spring.

5.2.5 Comparison with analysis in the different compartments: case of trace elements

5.2.5.1 Groundwater

As for the major parameters, the groundwater data are summarized in the histogram Figure 26. The data relative to metals are less numerous for the Saint-Joseph water table: 4 samples taken in the framework of the study allocated on 2 piezometers.

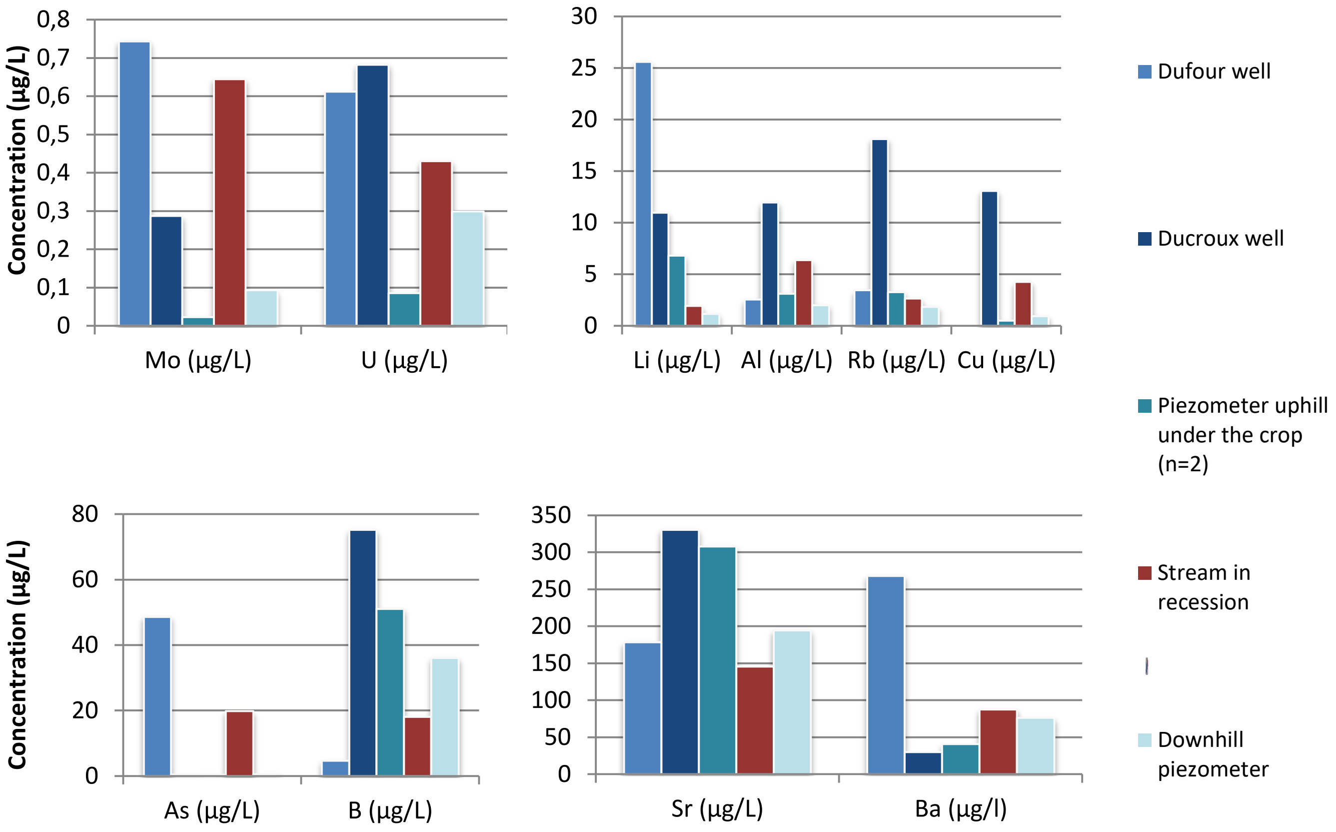

Figure 26 : Confrontations of medium concentration in metallic trace elements on the Morcille groundwater

The Dufour well is contaminated by metals of anthropic origin used on crops (Cu,Ni,As,Zn…)[19]. Concentrations in stream in recession are very high, such as arsenic. For all metal elements except for strontium (30% RSD), the concentrations are very different from one groundwater to another (107% for lithium, 96% for barium). The absence of additional samples to establish more precisely the concentrations of the other characteristic metallic elements of the aquifer means that only strontium is retained as metal tracer of the aquifer.

To establish strontium and other species concentrations in the aquifer, the same procedure was used as for the major parameters, taking the mean of the piezometers available with that of stream in recession.

5.2.5.2 Surface and subsurface flow components

As for the major parameters two samples of surface and subsurface runoffs were made on the same date and analysed for metals and are presented Table 10.

---

[19] For scale concerns, the medium value of copper in Dufour well (795 µg/L) isn't on the chart.

Table 10: Metallic trace elements analyses on different runoff in the Morcille watershed

Metallic trace elements		Li	B	Al	Cu	As	Rb	Sr	Mo	Ba	U
Surface runoff concentrations (µg/L)	Saint-Joseph	0,58	16,2	26,5	48,0	11,6	9,30	69,5	0,47	55,0	0,204
	Ruyères	0,24	32,2	135	35,7	13,2	3,54	67,3	1,30	33,8	0,331
Subsurface runoff concentrations (µg/L)	Ruyères Piezometer February 2013 thesis			123	21,1	15,0		11,4			
	Ruyères trench May 2017 master thesis	0,99	49,5	17,4	5,83	1,46	2,45	36,4	0,04	65,4	0,022

For surface runoff, concentrations of lithium, uranium, strontium, barium and arsenic concentrations are lower than in the stream in recession as expected. The concentrations of aluminium, copper, rubidium and boron are higher, which is consistent with calculated correlations in Table 7. Concerning molybdenum and arsenic, we cannot say anything because the concentrations from one sample to another are really different.

From one sampling site to another, concentrations of strontium, copper and arsenic are close but differ greatly for rubidium and aluminium.

For the subsurface, we see the same trend as for the major parameters: many elements have the lowest concentration of the 3 compartments in the subsurface. This is the case of the strontium of uranium, molybdenum and rubidium.

Finally, the large variation in sample concentrations at the same site for copper, arsenic, aluminium and strontium shows the difficulty in defining with precision the chemistry of the subsurface.

The sites of Ruyères and Saint-Joseph have different types of soil and there are probably differences in the chemistry of the water in subsurface from one site to another.

5.2.6 Predominant tracer: synthesis and last criteria

The analysis of the correlations of the concentrations with the flow, the concentrations in the different compartments as well as the viticulture practices make it possible to suspect anthropic pollutions on more than one flow component. This pollution is difficult to quantify[20]. This is the case of arsenic, sulphate, calcium which are excluded for this method of Mixing Model.

Ultimate exclusions are done in two steps°:

I. The decomposition of the hydrograph is based on the concentrations of only two species, it is essential that the tracer characteristic of the aquifer has a well-controlled and reliable concentration for this end-member. Thus, the elements whose concentration in the aquifer is very different from one site to another have been removed. The species removed following this criterion are NO_3^- and all the metals (RSD >35%, (Table 8 and Figure 26)) except Sr.

   Table 11 lists the concentrations of the species retained in the different simplified end-members.

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[20] The pollutions limited to a compartment such as surface runoff, of the basin are more easily quantifiable, in particular when it is agricultural practices generalized on all the parcels.

Table 11 : Retained concentrations for the different flow's tracers.

Tracers		**Groundwater tracers**					**Surface runoff tracers**				
Simplified End-Member		Conductivity µS/cm	Na^+ mg/L	Mg^{2+} mg/L	Cl^- mg/L	Sr µg/L	TSS Mg/L	Al µg/L	Cu µg/L	K^+ mg/L	Rb µg/L
Grondwater		292	12,8	8,7	21,0	170,1	0	3,7	2,59	2,4	2,20
Surface runoff	St Jo Ruy	188-199	2,8-9,4	2,2-2,9	6,8-1,4	69,5-67,3	200-5000	26,5-135	48,0 35,7	5,6-5,7	9,30-3,54
Subsurface runoff		55-90	1,8-2,3	1,3-2,0	1,0-5,9	11,4-36,4	≅ **0**	123-17,4	21,1-5,83	1,1-7,2	2,45
$\frac{C_{groundwater}}{C_{surface\,runoff}}\%$		151%	450% 140%	400% 300%	310% 2100%	250%	≅0%	13% 2,7%	5,4% 7,3%	42%	23% 62%

Thus the species retained as predominant tracer for the groundwater are conductivity, Na^+, Mg^{2+}, Cl^- and Sr.
Potential tracers of the surface runoff are: TSS, Cu, K^+ and Rb. Al has high concentrations in both surface and subsurface and is highly variable so it is difficult to conclude on its nature of tracer.

II. Species with the greatest differences in concentration from one end-member to another and with greatest variations during floods should be retained.

- For groundwater tracers, chlorides potentially have the largest differences in concentration between the different flow components, while having the lowest variability in the aquifer (RSD <15%). However, given the available surface and subsurface runoffs data, a concentration cannot be defined. Magnesium and strontium appear to have more regular concentrations on other end-members. Additional samples are needed to determine the concentrations of Na^+ and Cl^- in the surface and subsurface runoffs. Given the current knowledge of the data, **the best tracers appear to be strontium and magnesium for groundwater.**
- For runoff tracers, the concentrations of TSS in the subsurface and the groundwater are zero because of the functioning of these flow components[21]. In addition, there is additional data on the concentrations of TSS in the surface runoff, so this parameter is chosen as tracer. The concentration in TSS chosen in surface runoff for each event is explained in appendix.

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[21] Filtering effect from the sandy soil, confirmed by samples in the piezometers

6 Results: Separation of hydrographs

The percentages of participation of the various components in the flood for the two most important events (01/07/2007 and 07/08/2007) as well as their runoff coefficients at the peak of flood are recorded in Table 12.

Table 12: Summary of flow components' participations to the flood depending on the different methods of hydrograph separation.

Events		**Graphical method**	**Predominant tracer (simplified end-member)**	**EMMA**
01/07/2007	Surface runoff	12%	6%	10%
	Shallow subsurface runoff	22%	27%	36%
	Aquifer	66%	67%	54%
	Mixing ratio of surface runoff at peakflow	0,62	0,31	0,35
07/08/2007	Surface runoff	29%	10%	30%
	Shallow subsurface runoff	11%	42%	39%
	Aquifer	60%	48%	31%
	Mixing ratio of surface runoff at peakflow	0,81	0,3	0,5

6.1 Hydrologic method

After passing through the natural logarithm, the tangents of recessions of the different flows were identified on the hydrographs. An example of the tangents plot is described Figure 27

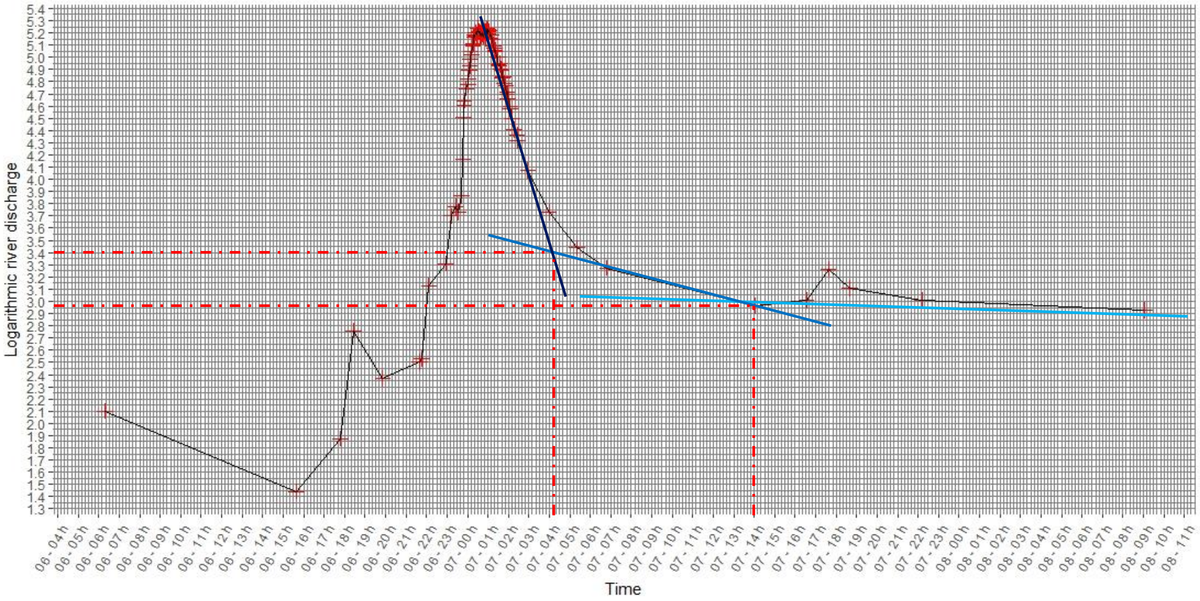

Figure 27 : Plotting of recession tangents and characteristic points of the hydrograph ln(discharge) of the 1 July 2007 event

After graphical construction and transition from recessions to exponential decomposed hydrographs are obtained, the other 3 floods plotting of recession curves are presented in appendix 10.4

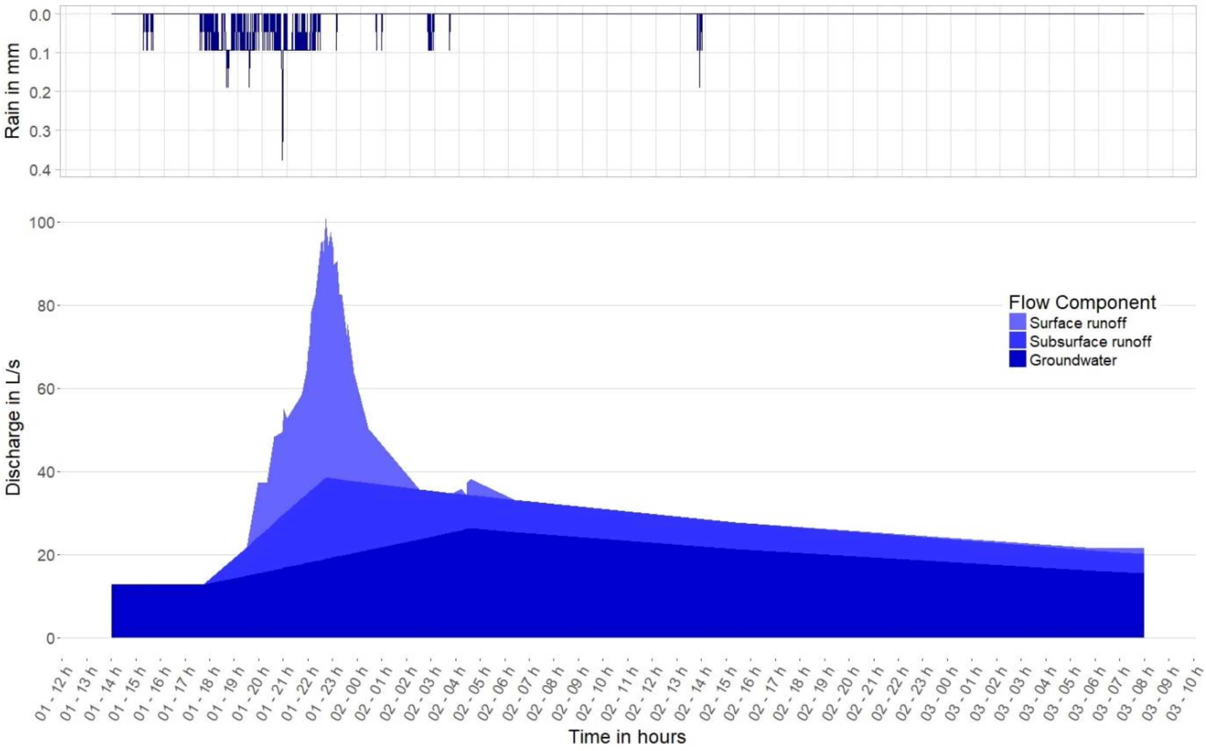

Figure 28 : Hydrograph separation by recession analysis on the 01/07/2007 event

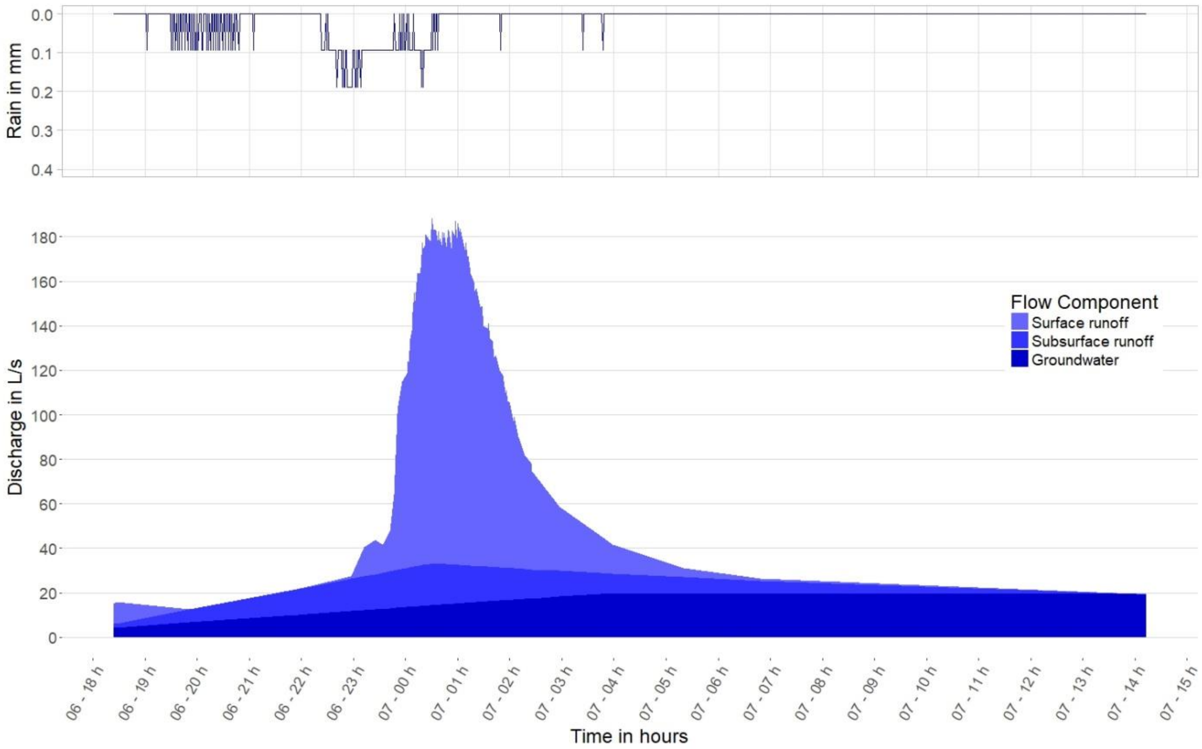

Figure 29: Hydrograph separation by recession analysis on the 07/08/2007 event

Table 13 shows the slopes values for every flow components for five rainfall events including the two main studied. Hydrographs are showed in appendix 10.4.

Table 13 : Recession tangents slopes for each flow component in different rainfall events

Event **Tangents slope in $10^{-3} min^{-1}$**	**May 26**	**July 1**	**August 2**	**August7**	**September 17**
Surface runoff	$-4{,}870$ $-5{,}510$	$-6{,}633$	$-5{,}153$	$-10{,}62$	$-10{,}19$ $-9{,}584$
Subsurface runoff and groundwater	$-0{,}2585$ $-1{,}346$	$-0{,}6245$	$-1{,}053$	$-0{,}716$	$-1{,}102$
Groundwater	$-0{,}01264$	$-0{,}3264$	$-0{,}1576$	$-0{,}0430$	$-0{,}2481$

The highest the absolute value of the slope is, the quickest is the recession of the concerned flow component. It is noted that the surface runoff tangent slopes are all of the same order of magnitude and very important in comparison with the other components confirming the presence of very quick flows in the basin.

The identification of the subsurface is less satisfactory: for example, the episode of May 26 generally has longer time steps it was more difficult to identify the second tangent (subsurface+groundwater).

The tangent selected has a high coefficient in absolute value leading to an overestimation of this recession during the exponential transition. However, the order of magnitude is the same compared to other events. At the same time the guideline coefficient of the tangent of the groundwater is low:$-1{,}264.10^{-5}min^{-1}$ an order of magnitude below the others probably because several millimeters of rain continue to fall and support the flow. The subsurface portion resulting from the difference between (subsurface + water table) low on this event on the one hand and high water table on the other results in a subsurface component dried up before surface runoff, which is physically difficult to interpret since runoff is a faster flow.

There are also many disparities in the recession coefficient of the water table. One hypothesis could be that the recession coefficient is important in the case where the rainwater has actually managed to infiltrate into the water table and thus that it initiates a significant decrease after the rain. On the other hand, an event without recharge of the aquifer would lead to few changes in the recession of the aquifer. The events with the most important groundwater recessions (August 1st and September 17th) are, by their characteristics, likely to have had a more substantial recharge of the water table.

An important limitation to this method is the configuration of the basin; horizontal ditches can sometimes capture the subsurface flow when it's really close to the surface, it's the case on the Ruyères parcel for example where we observe shallow subsurface runoff at 1 m depth (Peyrard, 2016). As a result, subsurface runoff is bypassed and feeds the ducts. Because this method is based on the flow velocities, subsurface runoff can be accounted as surface runoff.

Overall, the graphical decomposition of the hydrograph can give a first idea of the behaviour of the different components during a flood, but leads to several inconsistencies and weaknesses.

6.2 Predominant tracer or simplified End-Member separation

The separation of hydrographs of July 1 and August 7 by the tracer majority method are presented Figure 30 and Figure 31.

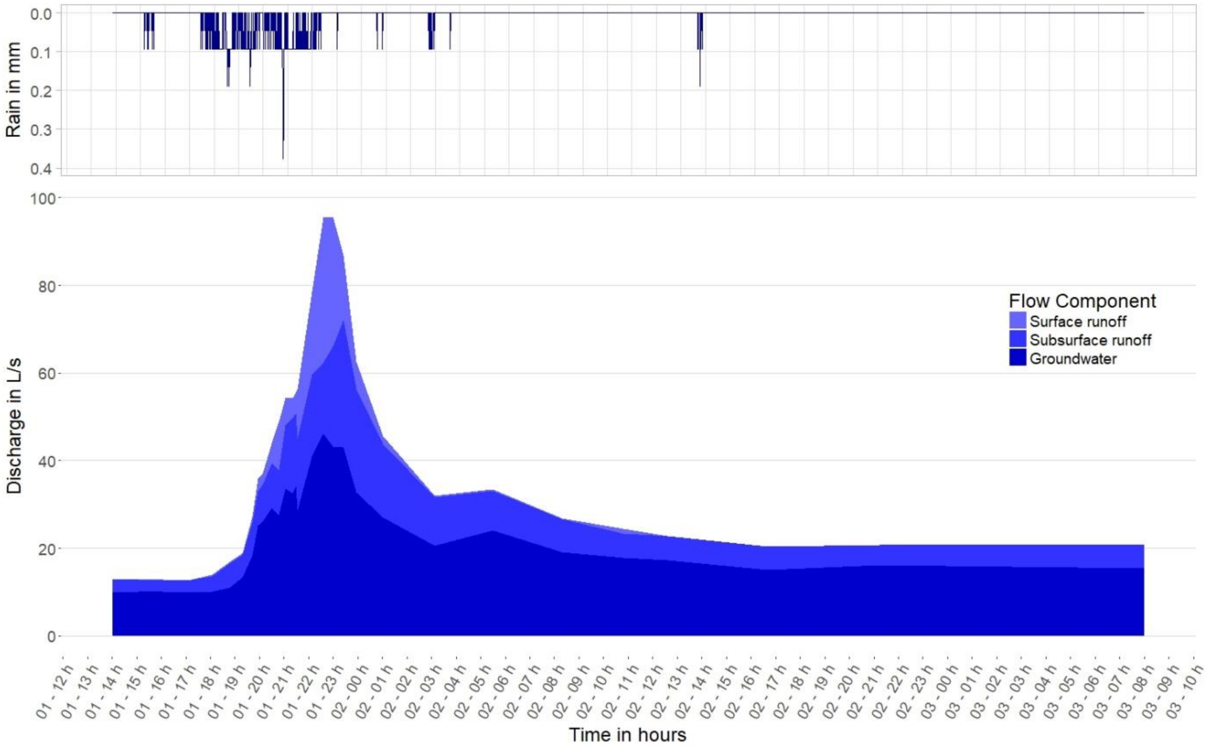

Figure 30 : Separation of hydrograph with predominant tracer : TSS and Strontium for the flood of 01/07/2007

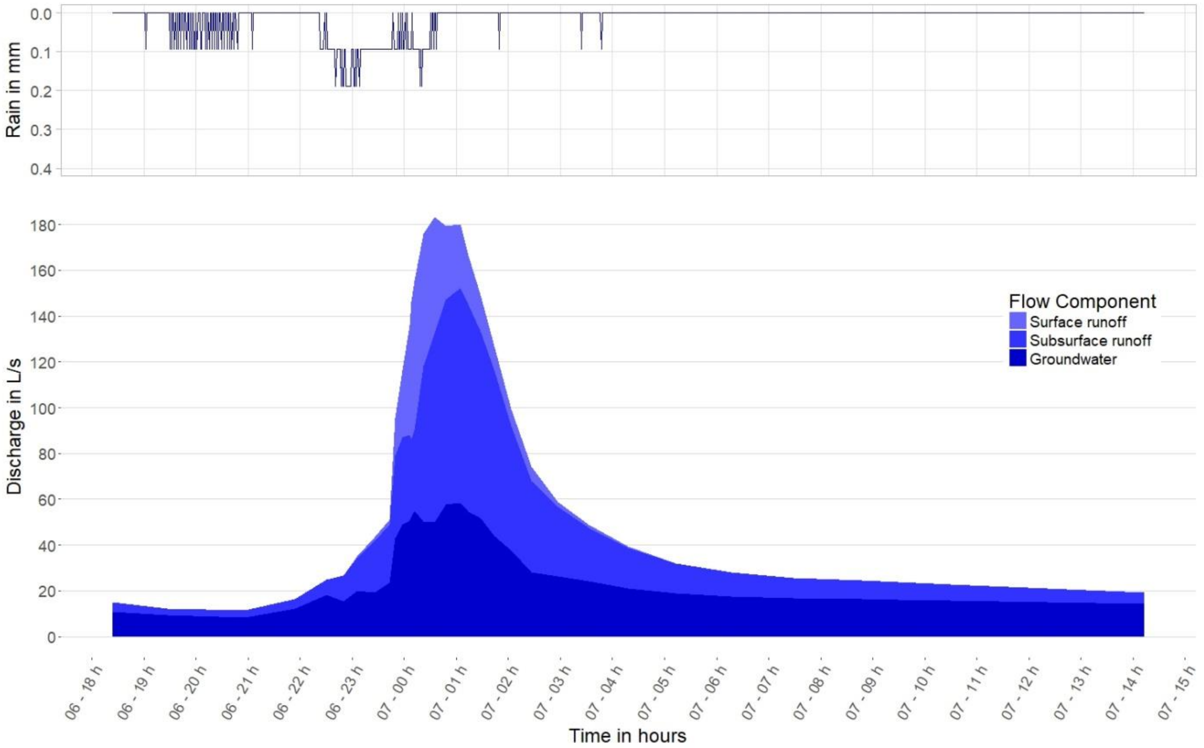

Figure 31 : Separation of hydrograph with predominant tracer: TSS and Strontium for the flood of 07/08/2007

It can be seen that unlike the graphical decomposition, the aquifer participates in the flow much faster than predicted by the graphical method. Regarding runoff, the use of

TSS as tracer may underestimate it. Indeed, the soil erodes very easily at the beginning of the rain event[22] loading the surface runoff in MES. However, the TSS concentration can drop quickly (Figure 23 and Figure 24) in runoff because of soil decrease in mobilizable particles and lead to an underestimation of surface runoff participation thereafter because we used an average concentration of TSS on the flood episode. We observe a low participation of runoff with this method: 6% for the episode of July 1 and 10% for the event of August 7 (Table 12). In general, the near-subsurface flow has lower concentrations[23] , this is particularly true for chosen tracers. As a result, subsurface is the buffering component to complete the system of equations, it is constrained by the other two components in the system (sum of flows = 1). It is therefore sometimes reduced at certain points of the hydrograph when the TSS are high, for example at the peak of flood.

However, subsurface peak discharge is shifted after the total discharge peak which is the same as the decomposition done in (El Azzi & Probst, 2016) and in the theoretical separated hydrograph where the subsurface runoff is also called “ interflow”.

TSS could be a good tracer of surface runoff if its concentration evolution in surface runoff during the flood was known. However, data are insufficient in order to perform such a separation of hydrograph and we have to respect the steady concentrations in the compartments.

6.3 End-Member Mixing Analysis

6.3.1 Available elements and data preparation

It is for metals and TSS that we have the most flood events; we will try to apply the EMMA method to metallic species of the Morcille basin retained after the considerations made in 5.2.3. We have aluminium, strontium, barium, uranium, lithium, rubidium, arsenic, copper and TSS.

6.3.2 Metallic trace elements combinations and Principal Components Analysis

It is necessary that any observation of stream water at the Versauds station has no missing concentration on selected elements. The incomplete or doubtful[24] observations have been removed.

Many combinations of tracers followed by a PCA were unsatisfying. An important number of metallic tracers results on a weak variance compression after the PCA (variance<80% on the first two components) which requires a number of End-Members higher than 3 to be correctly explained. Components provided by the different PCA have a very similar inertia which doesn’t give indication on the number of necessary End-Members (elbow criterion). One explanation could be that the mixture results from many different End-Members having a similar hydrogeological functioning. This is consistent with chapter 5.2.5 where we observed an important heterogeneity in concentrations of trace element from one groundwater to another for example.

---

[22] « first flush » phenomenon

[23] Except maybe for the aluminium

[24] Indicated by the operator

The combination of tracers being the most efficient was the aluminium/copper/strontium combination.
PCA has been applied on 357 observations of stream water from 2007 to 2012 including 182 coming from fractioned sampling in 2007 during floods.
PCA results are presented in the variables factor map Figure 32
The sum of the variance of the first two components is up to 89% which is a good compression. Here, it is clear that 3 End-Members are necessary to explain the mixture.

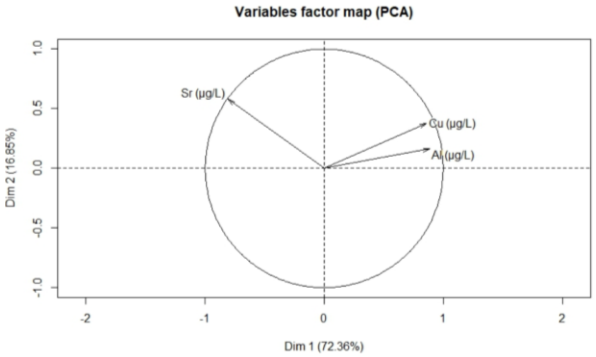

Figure 32: Variables representations (aluminium, strontium and copper concentrations) projected on the two first components after PCA (package FactoMineR)

6.3.3 Axis interpretations

The interpretation of the new variables (factorial axis) will be done using the individuals and variables contributing the most to the axis. We do not have much information on the individual observations on the watershed, except their position on the hydrograph and the date.
The individuals and variables participating to the two principal axis are presented Table 14.

Table 14: Interpretation of the first two components calculated by the PCA performed on the Morcille watershed

Axis	**Individuals observations and position on the hydrograph**		**Variables**	
	+	-	+	-
Axis 1	• Rising limb • Close to peak discharge	• Baseflow recession limb • Runoff recession limb	Al, Cu	Sr
Axis 2	• End of baseflow recession limb • Close to peak discharge • Rising limb	• Runoff recession limb (high time base events) • Beginning of the rising limb	Sr, Cu	

The first axe is a “water feeding” component, it opposes periods of stream feeding of the basin with high copper and aluminium concentrations(positively correlated with

discharge) and periods of stream depletion with higher strontium concentrations (negatively correlated with discharge) .
The second axis is more difficult to interpret; the positive contributions of individuals are observations:

- at the end of recession limb with high concentrations of strontium and copper due to evaporation of water in the stream mostly during summer
- during quick-floods on the rising limb and close to peak discharge with high concentration of Cu due to runoff

The negative contributions are observations with low concentrations on strontium and copper:

- On events with high time base, during runoff recession limb where surface runoff is more depleted on erosive elements.
- At the strict beginning of the rising limb when the intensity and the resulting surface runoff are not at their culmination.

As a result, the second axis seems to be a “chemical enhancement” component opposing stream observations with water rich in elements (concentrated water during recession, water fed by erosive surface runoff) and diluted water during floods .
The first axis identified the main factor explaining the chemistry of the watershed (discharge) which is the “identification of hydrological behaviour” performed in 5.2.3 with the same conclusion on strontium, aluminium and copper.
The PCA also indicated how much the two first axes described the variance in the water chemistry. The first axis had a variability of 72%, the second axis explained additive variability (17%) by specifying water degree of dilution which was not taken into account in 5.2.3.

6.3.4 End-Members projection and convexity criteria

According to the state of art in 3.2.4.3, the best end-members are the closest to U space after projection. Among potential experimental end-members presented in 5.2.4 the best one were the sample done in May 2017 :

- Groundwater from the piezometer 2P
- Surface runoff from Saint-Joseph
- Subsurface runoff taken on the trench at Ruyères

All others solutes such as waters from the wells or the piezometer upon the hill were very far away from the U-space indicating that waters from Dufour and Ducroux wells are not representative of the groundwater’s basin involved in the mixture or are not directly involved[25] in the mixture.

These 3 End-Members projected on U_1 and U_2 frame a big part of the observations as illustrated Figure 33.

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[25] Premixing and changes in water chemistry before mixing in the stream

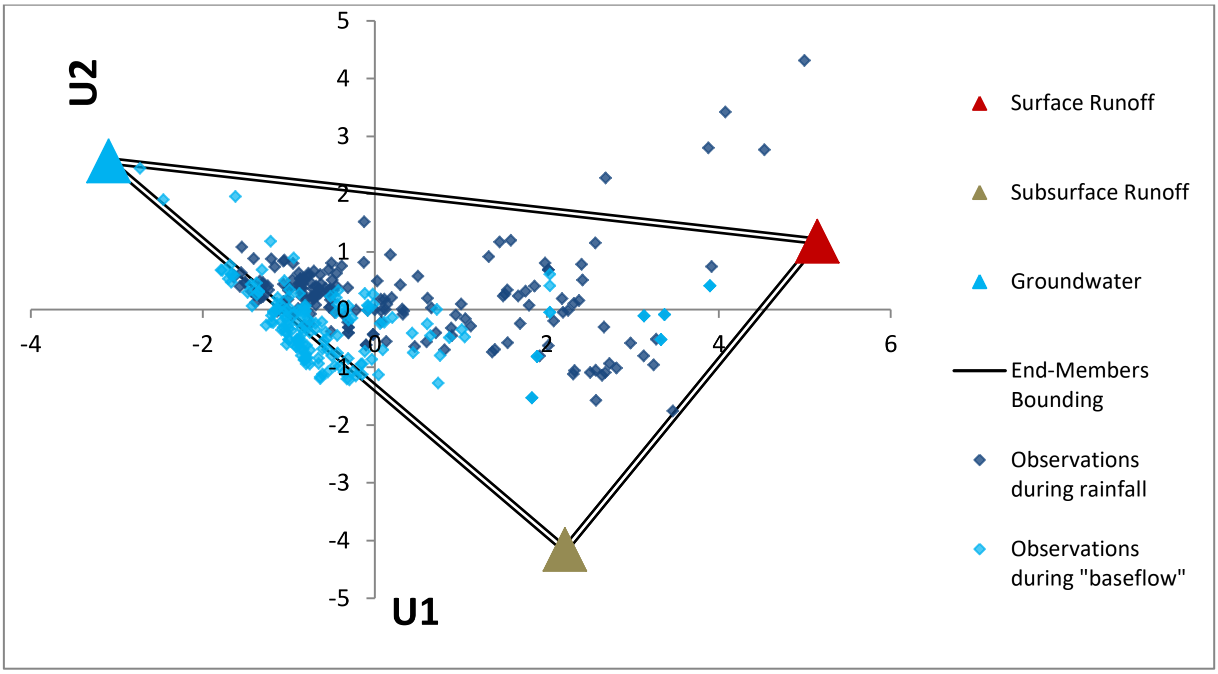

Figure 33 : Projection after PCA of observations on Morcille streamwater concentrations and projections of potential End-Members

End-Members projections are quite consistent:

The major part of the observations is bounded by the triangle formed by the End-Members or lies on the line between the groundwater and subsurface runoff.

These lying observations are mostly observations during baseflow while observations during flood are closer to the surface runoff end-Member.

The subsurface runoff End-Member is still a dilutive component (highest negative value on the “chemical enhancement axis”) while his positive value on the first axis confirms his “filling” role in the stream.

According to this mixing diagram, out of the flood events, water chemistry is the result of the mixing between groundwater and subsurface runoff in varying proportions. Two observations are very close to the groundwater End-Member, these are observations taken during a period of recession of the stream which shows that sometimes the stream in recession can be a “pure[26] End-Member” and the decision to take these observations as an End-Member (Pinder, 1969) can be accurate.

6.3.5 Goodness of fit

As presented in 3.2.4.3 it is possible to evaluate the relevance of the model by confronting the real observations and the predicted concentrations. It also allows to definitely precise end-members concentrations. These confrontations are presented Figure 34. The goodness of fit for these three elements is between 0.81 and 0.97 which is the same range of values than on the Panola Mountain for 6 elements and better than Birkenes with 3 elements (Christophersen & Hooper, 1992). The goodness of fit for strontium is presented Figure 34.

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[26] The water in the stream only comes from an unique End-Member. Here it’s the groundwater.

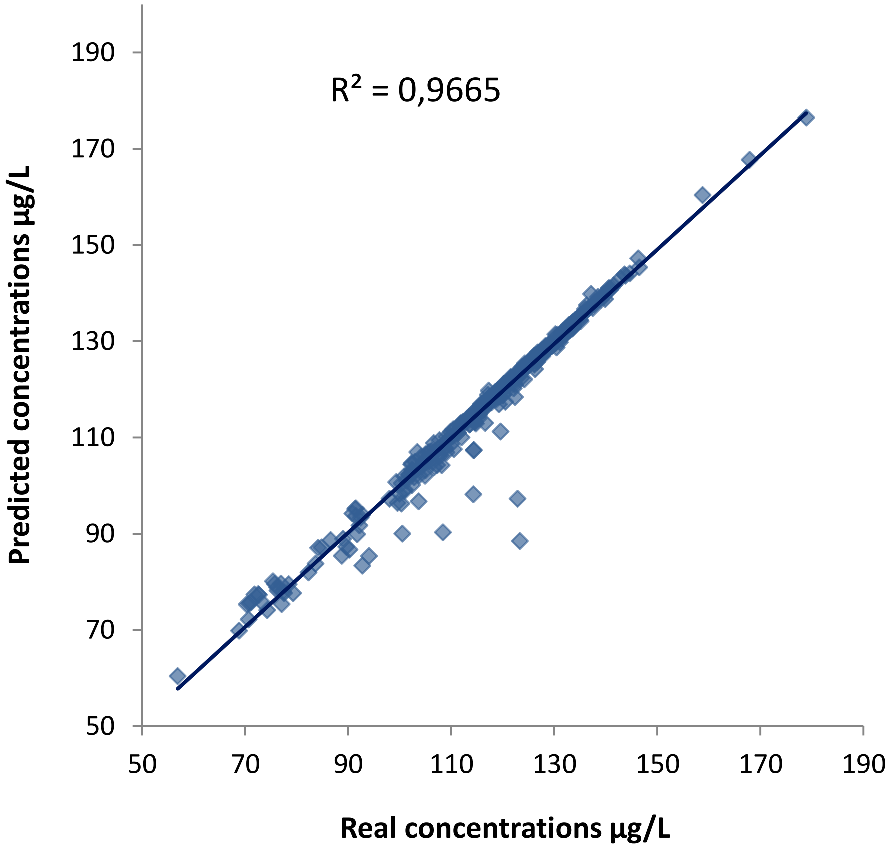

Figure 34: Strontium goodness of fit between real observations and back calculated concentrations by EMMA on 357 observations

The very good results on strontium confirm its good tracer properties in agreement with 5.2.6. The Table 15 compares the experimental chosen end-members with their orthogonal projections in order to precise their concentrations in the model.

Table 15: Confrontations between real observations and orthogonal projected concentrations for the 3 potentials End-Members

Flow components	**Groundwater**			**Subsurface runoff**			**Surface runoff**		
Tracers	**Sr**	**Cu**	**Al**	**Sr**	**Cu**	**Al**	**Sr**	**Cu**	**Al**
Initial Concentrations µg/L	184,3	1,45	0,82	36,4	5,83	17,4	69,5	48,0	26,5
Orthogonal Projected Concentrations µg/L	182,8	3,42	0,0	39,8	1,30	39,3	83,0	30,2	112,7
Difference	-0,81%	137%	0%	9,42%	-77,7%	126%	19,4%	-37,1%	326%

The groundwater end-member shows the smallest differences suggesting that Morcille's groundwaters seem to be very similar to groundwater on the Saint-Joseph site for natural elements such as strontium and aluminium. Overall, differences on strontium concentrations are small. Differences on groundwater copper concentrations could be explained by the increase downstream of cultivated parcels treated with a copper sulphate solution leading to a superior contamination of groundwater.

Concerning the aluminium, orthogonal projected concentrations on the surface and subsurface were substantially higher. These differences can be explained by the fact that these samples were taken in May during a rainfall event less intensive than usually on this basin (Orquevaux, 2010). Consequently, the aluminium release by surface and subsurface runoff could have been lower. This confirms the importance of sampling potential end-members during the flood-event as done in (Burns, et al., 2001). Overall, the orthogonal projected concentrations are plausible except for the copper concentration lower in the subsurface than in the aquifer. This is questioning because the subsurface being closer to the surface than the aquifer it should receive a bigger mass of copper from parcels.

Finally, as recommended by Christophersen, correcting the end-members using their orthogonal projections improved lightly the goodness of fit. The average determination coefficient (R^2) increased by 0,15.

6.3.6 Hydrograph separation

Now that all the observations including these taken during flood events are projected into the U-space they are all linear combination of the three End-Members and it is possible to decompose the hydrograph using the Mixing Model system of equations applied to U variables :

$$\begin{cases} \sum_{i=1}^{n} Q_i(t) = Q_{tot}(t) \\ \sum_{i}^{n} Q_i(t) * U_{1,i} = Q_{tot}(t) * U_1(t) \\ \qquad \dots \\ \sum_{i}^{n} Q_i(t) * U_{k,i} = Q_{tot}(t) * U_k(t) \end{cases}$$

Results of separation of hydrograph are presented Figure 35 and Figure 36.

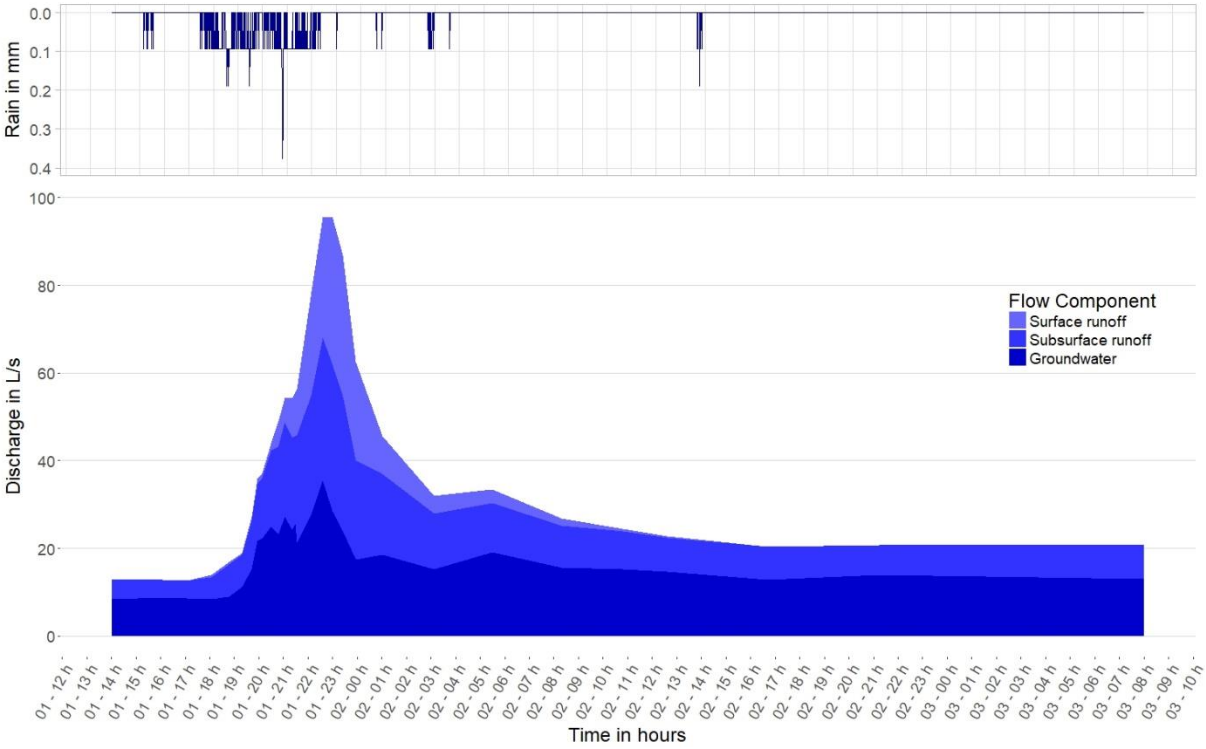

Figure 35 : Hydrograph decomposition by End-Member Mixing Analysis on Strontium Copper and Aluminium on the 01/07/2007 event

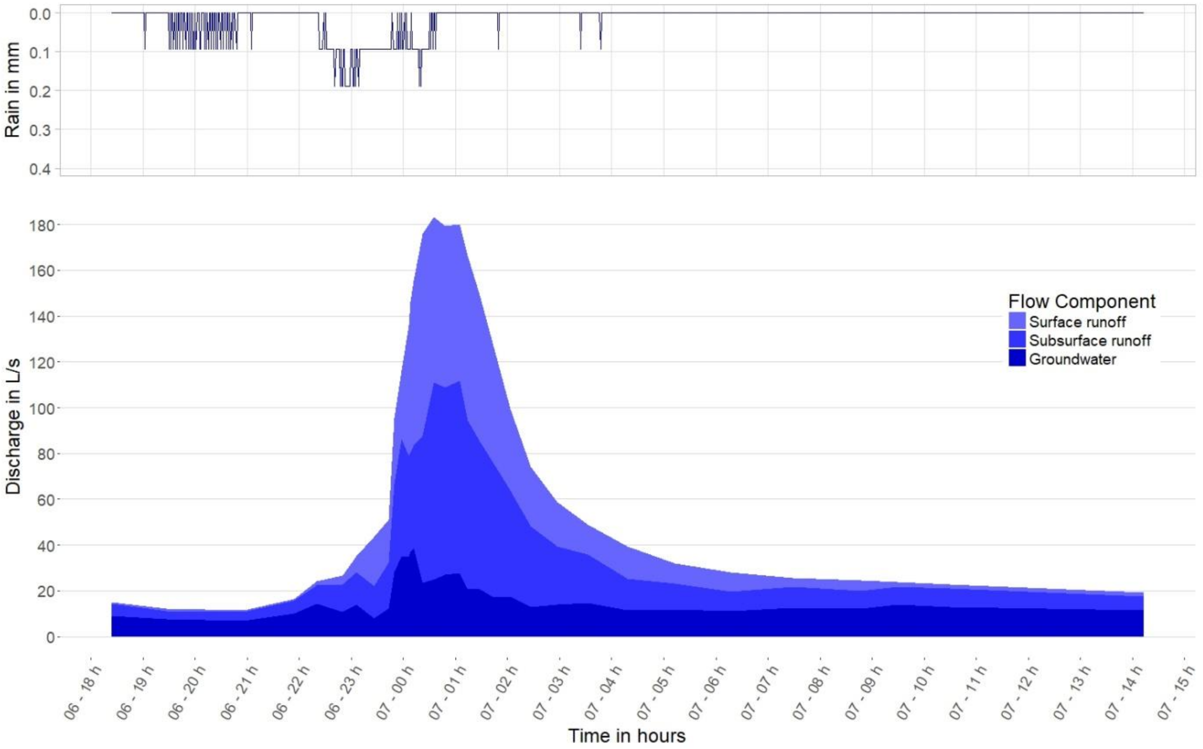

Figure 36 : Hydrograph decomposition by End-Member Mixing Analysis on Strontium Copper and Aluminium on the 07/08/2007 event

6.3.7 Observations on EMMA separation

We observe that the recessional parts are consistent for all the flow components but the variations of the flow components are more chaotic compared to the previous method due to compression by the PCA. The aquifer's response time seems to be very low in EMMA as observed in the first Mixing Model method. In addition groundwater decreased before peakflow in the second event, this is maybe due to a decrease in strontium concentration caused by the new water in the aquifer during the event. Data on piezometric level of groundwater could have given insights on groundwater's response time.

Differences on groundwater response time between the methods because could be explained by a chosen late groundwater initiation in the hydrological method which doesn't seem to be the case in this sandy basin with a shallow groundwater.

EMMA allows, thanks to a more complete chemical identity of the surface runoff, to mitigate the premature decay of surface runoff due to the depletion of TSS. On the opposite, there is maybe an overestimated surface runoff: in this method there is still 7% surface runoff in surface water eight hours after the peak discharge in the second event.

EMMA seems to be the best separation method being more objective on the analysis of data and being more flexible on degree of precision. Use of metallic trace elements is a key point for the decomposition because of their heterogeneities in concentrations. These heterogeneities can lead to a weak variable reduction by PCA and will explain the mixture in a multitude of "micro" and unknown end-members with close weights and a lot of data would be necessary to explain it. But this heterogeneity can be used to efficiently screen particular or uncommon end-members allowing specific decompositions. Here it seems that the provided EMMA model has the needed degree of precision with decent goodness of fit. These results will be applied in order to identify consequences for pesticides by performing a second deconvolution. However, end-members concentrations is likely to change from one event to another, a clue being the light heteroscedasticy on copper and aluminium concentrations. Highest observed stream concentrations in these elements cannot be simply explained by mixing. The more likely is that during high intensity events, with consequent runoffs, these flows are also more concentrated in these elements. Beyond statistics, a field example is the variation of TSS concentrations in surface runoff from one event to another observed by (Peyrard, 2016) As a result, new samples should be taken during each studied event as performed in (Burns, et al., 2001) and (Durand & Juan Torres, 1996) and could increase the model precision. Ideally, at least two samplings should be carried out for each end-member one at the beginning and one close to the peak discharge in order to evaluate the constant concentrations hypothesis.

7 Consequences for pesticides transfers

Eight pesticides are analised during floods : diuron (DIU), DCPMU (diuron main metabolite), dichloroaniline (<LQ), dimetomorphe (DMM), procymidone (PCM), tebuconazole (TBZ), carbendazime (CBZ), and azoxystrobine (AZS). Their Physicochemical properties and their periods of application are described in Table 18 in appendix 10.7. We will try to estimate their main paths.

Variations of these pesticides along with the river discharge are showed Figure 40 in appendix.

7.1 Correlations between pesticides concentrations and flow component mixing ratio

Correlations between the concentrations (above the limit of quantification) of the pesticides at the outlet have been calculated with the evolution of the mixing ratio of the different flow components. This approach is similar as (El Azzi & Probst, 2016) but we use the flow components mixing ratio instead of their discharges. According to the results, all the components discharges increased during floods, as a result a component's high discharge could still have a negligible impact on pesticides concentrations compared to the other discharges.

This analysis is presented Table 16 for the two studied events.

Table 16: Correlations between the concentrations of the pesticides at the outlet with respective flow components mixing ratios

01/07/2007	**DIU (n=31)**	**DCPMU (n=31)**	**AZS (n=17)**	**TBZ (n=33)**	**DMM (n=33)**	**CBZ (n=27)**	**PCM (n=26)**
Surface runoff	0,42	0,92	0,92	0,93	0,81	0,83	0,86
Subsurface runoff	0,13	0,06	-0,29	-0,01	-0,06	-0,01	0,16
Groundwater	-0,43	-0,90	-0,88	-0,89	-0,76	-0,80	-0,86
07/08/2007	**DIU (n=30)**	**DCPMU (n=28)**	**AZS (n=24)**	**TBZ (n=30)**	**DMM (n=29)**	**CBZ (n=16)**	**PCM (n=30)**
Surface runoff	0,93	0,91	0,89	0,93	0,87	0,65	0,63
Subsurface runoff	0,31	0,47	0,23	0,02	0,43	0,39	0,32
Groundwater	-0,91	-0,95	-0,85	-0,89	-0,91	-0,70	-0,68

From this it results that surface runoff is the main vector of pesticides (correlations >0.8) while groundwater seems to have a strong dilutive effect (correlations<-0.76). Correlations for these flows remained the same from one event to another except for diuron and procymidone. Correlations with subsurface contribution to total flow were not significant on the first event and low in the second event suggesting that subsurface dynamics differs depending on more or less triggering zones can be activated during a rainfall event as seen in 2.2.2.

However, the correlation analysis doesn't give much insight on pesticides mass flow from the different compartments

7.2 Deconvolution by least squares on an overdetermined system: Reverse Mixing Model

7.2.1 Deconvolution on observed concentrations by non-negative least squares

Thanks to the hydrograph decomposition we can develop a second Mixing Model with this system of n equations :

$$H_n = \beta_1 f_{1,n} + \beta_2 f_{2,n} + \beta_3 f_{3,n} + \varepsilon_n \qquad (17)$$

H_n being an observation n on the concentration of a pesticide at the outlet, $f_{i,n}$ the mixing ratio of a flow component i at time n, β_i the estimator (constant) for the component i and ε_n the residuals. In this case, β_i is the concentration in a flow component i.

There are nearly 30 available observations on pesticides concentrations for each flood and as a result, it's an overdetermined system with 30 equations. We studied 4 available pesticides: Diuron and its metabolite (DCPMU), dimetomorphe and tebuconazole because these pesticides have different solubilities, koc and are above the limit of quantification on more than 95% of the observations. The system was solved by using again the non-negative least squares:

$$\beta^* = HF^T(FF^T)^{-1} \qquad (18)$$

β being the vector of β_i estimators, H the pesticides concentrations vector and F the matrix of flow components mixing ratios.

A graphical study was done in order to evaluate the reliability of this reverse Mixing Model as first approach. A plot of residuals *(H-H*)* vs observed concentrations in DCPMU *H* for the 01/07/2007 event is presented Figure 37

The model is not really reliable in this state, we observed:

- Important residuals close to the observed concentrations itself
- heteroscedasticity in the residual's distribution (the cloud affects a shape in "funnel") (Grasland, 1998)
- discontinuities in the residual's distribution (two clouds)

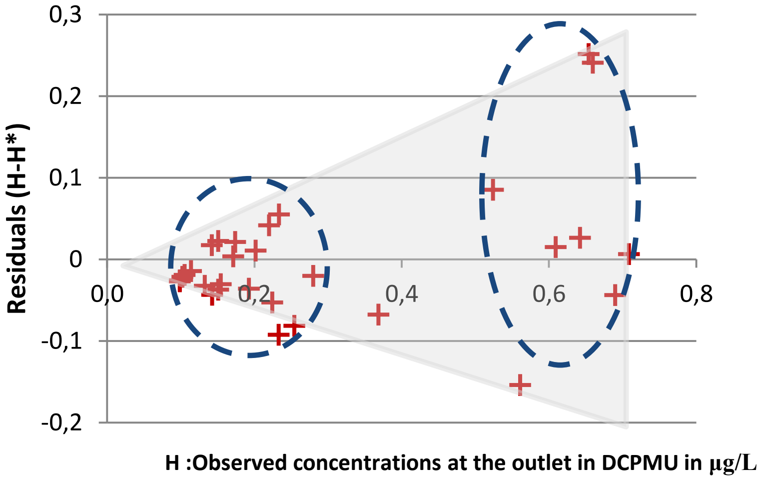

Figure 37 : Heteroscedasticity and discontinuities in residuals distribution for the multiple linear regression of DCPMU concentrations

7.2.2 Deconvolution on logarithmic observations by least squares

A light heteroscedasticity was already observed for copper and aluminium concentrations in EMMA. In the case of pesticides, this heteroscedasticity seems to be far more important. These problems can be attenuated by performing a logarithmic or semi-logarithmic transformation on the variable H (Grasland, 1998). We introduce the new variable $\mathrm{K_n}$:

$$K_n = ln(\frac{H_n}{H_1}) \qquad (19)$$

which is the logarithmical variation of concentration during the flood event at the observation n H_1 being the first observation before the flood. The system was solved using the least squares without constraints on positivity on β.

The new cloud of residuals is plotted Figure 38 :

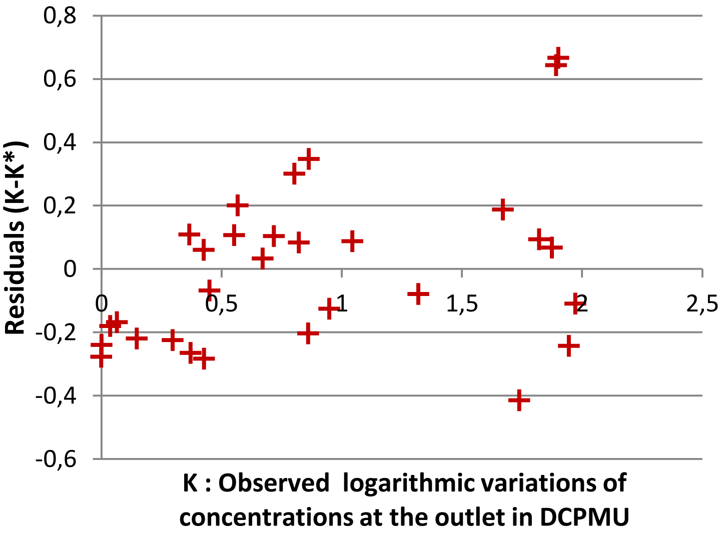

Figure 38 : residuals distribution for the multiple linear regression of DCPMU logarithmic variations of concentrations

After this transformation we note overall:

- lower residuals with a more casual distribution
- an increase of homoscedasticity

With this regression, there is no longer a third estimator due to linearity between the three flow components mixing ratios ($\sum_{i=1}^{3} f_n = 1$) coming from the first equation of Mixing Model (Equation 12). As a result, only 2 on three vectors are used for the regression.

The system will be described for each n equation as :

$$K_n = \beta_1 f_{1,n} + \beta_2 f_{2,n} + K_0 + \varepsilon_n \tag{20}$$

Where β_1 and $\beta_2$are the new estimators for the retained vectors and K_0 is the interception. We choose to retain surface and subsurface runoff vectors. Groundwater always provides water to the stream and as a result, interception K_0 has a physical meaning: it's the value of K_n when no surface and shallow subsurface flows occur, i.e. when the stream is only fed by groundwater. As it was providing a baseflow, groundwater also provides a "base concentration" by the way of K_0 which contains the information on its water quality. The largest the absolute difference between K_0 and the maximum value of K_n is, the more concentrated in pesticides are the surface and the shallow subsurface.

Also, $\beta_n$values allow to compare pesticides contaminations acuity in surface and subsurface runoffs on one event, and also the difference of exportations' dynamics from one event to another.

β_n estimators and K_0 for the studied pesticides on the two events along with indicators of fitting (F-test, t-test, R² and p-value) are listed Table 19 in Appendix.

Excepted for diuron, the R² are above 0.8

Fittings were significantly better for all pesticides studied on the 07/08/2007 event.

Overall, we observe a decrease of contaminations in surface and subsurface runoffs between the two events, except for dcpmu in subsurface with close ß (2.77 and 2.70) suggesting a persistence of this metabolite in the subsurface.
Except for diuron on the 01/07 event, surface runoff β_n estimators were the highest on all pesticides confirming its acuity in water contamination.
Assuming low residuals and the use of the exponential, equation (19) can be modified as :

$$H_n \cong H_1 exp(\beta_1 f_{1,n} + \beta_2 f_{2,n} + K_0)$$

By the property of the exponential function :

$$H_n \cong H_1\, exp\left(\beta_1 f_{1,n}\right) exp\left(\beta_2 f_{2,n}\right) exp(K_0)$$

Multiplying by the discharge and setting $\mathrm{W}_{1,\mathrm{n}} = \exp\left(\beta_1 \mathrm{f}_{1,\mathrm{n}}\right)$, $\mathrm{W}_{2,\mathrm{n}} = \exp\left(\beta_2 \mathrm{f}_{2,\mathrm{n}}\right)$ and $\mathrm{W}_3 = \exp(\mathrm{K}_0)$:

$$M_n \cong Q_n H_1 W_{1,n} W_{2,n} W_3 \qquad (21)$$

7.2.3 Results

By integrating the $W_{i,n}$, it is possible to esteem the relative contribution of each flow component in the total exported mass in streamwater. Estimated fluxes of studied pesticides in event I (01/07/2007) and event II (07/08/2007) are summarized in the diagram Figure 39.

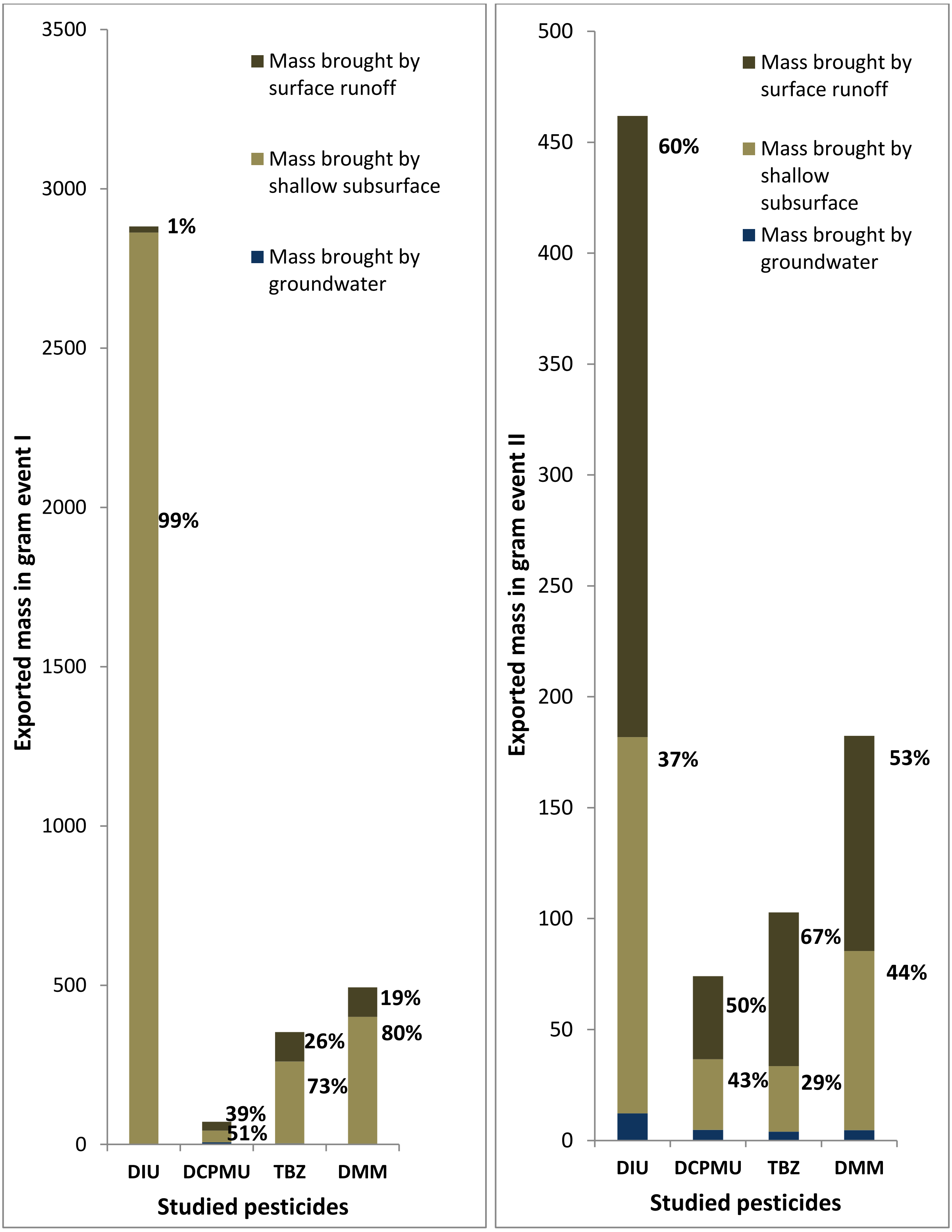

Figure 39 : Estimations based on Mixing Model of the exported masses of pesticides at the Morcille river during events I and II

On all events, for all studied pesticides groundwater was the last vector of contamination with participations under 10% to the total exported mass, the highest fraction was for DCPMU.

Exported masses were higher in event I, probably because they were closer to the pesticides' applications. Subsurface was the main vector of contamination in event I providing between 51 and 80 % of the total mass while surface runoff was the main vector in event II providing between 50 % and 67 %.

On the event I, the impact on subsurface runoff is quite consequent compared to surface runoff, even if surface runoff represented only 10% of the total water on this event. It can be also due to a substantially lower fitting for event I.

High koc pesticides such as tebuconazole were the most mobile in surface runoff while low koc pesticides such as dimetomorphe were the most mobile into the subsurface.

This is consistent with the results obtained on the Ruyères trench sampling, (Peyrard, 2016) : dimetomorphe was more likely to be stored in subsurface and remobilized than tebuconazole and as a rule, pesticides with low DT50 and high koc. These trends need to be confirmed on other flood events.

7.3 Limits of the Mixing Model “by layers”

Overall, a reduced model using a Mixing Model with flow components coming from differents depths provided interesting results. However, the Mixing Model failed to explain the concentrations in diuron on the 01/07:

- low correlations with all the flow components mixing ratios
- lowest R^2 in fitted values after the second deconvolution
- questionable physicochemical results (99% of mass coming from subsurface)

This is unfortunate because its concentration was the highest among all the studied pesticides. Sometimes a more pertinent mixing model could be needed to explain a concentration in a pesticide.

7.4 From the analyse of hydrograph to an efficient pesticides management on agricultural watersheds

The mixing analysis of hydrograph can give a raw estimation of water and pesticides flows on watersheds of different dimensions. It could be used, in a certain extent, to evaluate the reduction on pesticides transfers of corrective actions after their implementations.

Pesticide transfer is the result of an important interaction between molecules properties, agricultural practices, characteristics of the media and the climate. While climate being the least evident leverage, corrective solutions can be designed, for example on pesticides formulations[27], or by modifying more or less the catchment (INRA & Irstea, 2005).

For pulverized formulations (95% of application treatments), a fraction of pesticides is intercepted by the leaves while another fraction is intercepted by the soil aggregates[28]. We will briefly present the consequences of pesticides properties on their dynamics of exportation for these two fractions during floods and corrective solutions to prevent these transfers.

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[27] This includes the molecule of the active ingredient itself but also the adjuvant

[28] A last fraction is volatilized but we will focus on the transfers in aqueous phase

7.4.1 Leaching and lixiviation on the soil

Once the pesticide is intercepted by the soil, it can be absorbed. Adsorption mechanisms are already described in 3.2.3.1 a). According to the literature (Carluer, et al., 2017), and confirmed in 7.2.3, during rainfall, a part of the products present in the first centimetres can by mobilized by surface runoff. This mobilization can be either in solution (high solubility molecules) or adsorbed on suspended matter (high koc). Water which doesn't runs off infiltrates dragging pesticides molecules, mainly under dissolved phase. Again these can be adsorbed on soil aggregates (depending on the organic matter fraction) and/ or being degraded. The last part percolates and is susceptible to reach the groundwater by deep infiltration or surface water by lateral subsurface flow.

7.4.1.1 Influence of the physicochemical properties of the molecule

Overall, the more a molecule has a strong DT50 and solubility along with a low koc, the more this molecule is mobile in the environment and likely to trigger important contaminations of the streamwater.

7.4.1.2 Corrective actions to minimize the diffusion

a) Pesticides formulations

Molecules which meet all the criteria exposed in 7.4.1.1 such as diuron have shown an increased contamination on water according to 7.2.3. These molecules should have, a minima, increased restrictions on their use. Also, new generations of adjuvant, using nanoencapsulation for example, should be able to protect the most soluble molecules, allowing a slower release in the environment.

b) Landscape adjustments

Currently, on the Morcille watershed slopes, there are facilities such as concrete ditches which can court-circuit flows and enhance their concentrations in pesticides (Orquevaux, 2010). These court-circuits allow pesticides to join the streamwater without being degraded or retained and increase the contamination risk. As a result, any landscape management allowing an increased molecule residence time on the vineyard, with favourable conditions of their sorption (high fraction of clay or organic carbon) or degradation (exposition to sunlight or microbial activity) will promote their degradation (Carluer, et al., 2017).

Concretely, a possible management is the implementation of buffer zones. A buffer zone is an inter-plot zone roughly arranged and easy to maintain. Buffer zones can be dry (grass strips, faggots, slopes), wet (retention basins) or both depending on the hydrological conditions (permeable ditches). These elements have different functioning but their implementation aims to increase the favourable conditions above mentioned to pesticides dissipation (Carluer, et al., 2017). However, efficiency of these systems is unequal, and the consequences of an increased infiltration of pesticides on subsurface are not well known (Peyrard, 2016) for devices such as grass strip or permeable ditches.

A last solution could be changing the soil composition by adding organic amendments[29] into the soil which will increase the organic content of the soil, and as a result the increase of pesticides adsorption. In addition, the presence of organic matter stimulates

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[29] Compost of green waste

the microbial activity and enhances molecules degradation by co-metabolism (INRA & Irstea, 2005).

7.4.2 Leaching on plants

For pulverized formulations, between 10 and 70% of the active ingredient doesn't reach the plant and goes to the soil (INRA & Irstea, 2005). This is mainly due to the pluvioleaching on leaves. After direct pulverization on the plant, we observe pesticides residuals on leaves. These are constituted by a bounded fraction which penetrated in the leaf tissues. The free fraction, weakly bounded with the leaf surface, is susceptible to move with the fallen water intercepted by the leaf. This water, contaminated in pesticides, will then fall to the ground and pesticides will undergo the previously described mechanisms.

7.4.2.1 Influence of the physicochemical properties of the molecule

Free fraction for soluble molecules decreases exponentially after application. However the free fraction for lipophilic molecules remains constant. Overall, the velocity at which a pesticide reaches the leaf tissue determines its resistance to pluvioleaching. As a result, lipophilic molecules present less than 10% loss by pluvioleaching while polar molecules present a loss up to 80%. (INRA & Irstea, 2005).

7.4.2.2 Correctives actions to minimize the diffusion

The key here will be the minimization of the free fraction of pesticide on the leaf area.
This can be achieved by :

- A treatment by pulverization way before a rain event ensuring that a maximal fraction of the pesticide penetrated the leaf over time.
- Enhancing the adhesion and penetration potential of the molecule on the leaf tissues adding solvents, tensioactives or oils to the formulation. This is particularly efficient for leaves with an heavy cuticle. However, maintaining the molecules on the leaf exposes these to degradation product and volatilization likely to contaminate the atmosphere.

Let's not forget that only 1% of applied quantities moving through surface water is able to exceed the existent norme for drinking water of 0.1 μg/L for a phytopharmaceutical substance and 0.5 μg/L for the total of these substances.

8 Discussion and perspectives

The first objective of this study was to perform a deconvolution on the flood hydrograph of the Morcille river in order to estimate the different flow components to the flood discharge with different methods of hydrograph deconvolution and bring a critical analyse of these.

The hydrological method by recession analysis is not onerous in data and can be refined with data on the water table variations. It usually provides a reliable estimation of the global flow proportions during flood, but not always. Indeed, the rising part of the hydrograph is defined in a subjective manner. In addition, on some parcels ditches could short-circuit shallow subsurface runoff and account it as surface runoff leading to an overestimation of surface runoff and isn't reliable for water quality aims.

Physicochemical methods based on Mixing Model allow a more reliable decomposition. The use of simplified end-members by the way of a predominant tracer is licit if we're able to identify them. It supposes to verify that they are present in similar concentrations on different end-members with the same hydrological functioning and that they present substantial variations in their concentrations during floods.

Finally, the same thinking is behind the mathematical formalism of the EMMA method. Thanks to the PCA, it gives an indication on the number of end-members as well as their relevance to explain the mixture and finally how to precise them. Indications to precise end-members concentrations tell how the sampled water is representative of the end-member. This allows to precise the general water quality for different compartments at the catchment scale.

Concretely, EMMA is an iterative work consisting in using an increasing number of tracers while keeping a maximum of variability on a minimum of components, if the variability "moves" on additional components, the model is more precise but requires additional end-members to explain the mixture.

In this study, EMMA provided an hydrochemical model for the Morcille watershed based on three metallic trace elements; strontium, copper and aluminium.

EMMA results on studied events showed that, overall, all the flow components were quickly triggered. Shallow subsurface contribution to the stream total discharge was between 36 and 39% while groundwater flows contribution was between 31 and 54% during floods. This confirmed the high infiltrability of the watershed and maybe the presence of preferential flows. Despite this, surface runoff can contribute to the total discharge up to 30% on high intensity events.

All the methods showed a substantial contribution of the subsurface runoff to the streamwater confirming the importance of this component in exported water.

To improve the physicochemical methods of decomposition of the hydrograph it is necessary to follow in addition the major parameters during the floods because these elements are usually conservatives, such as Mg. Also, it could be an asset to take samples in the end-members preferably during the flood. This could help to verify the hypothesis of steady concentrations during an event and from one event to another.

The second objective was to assess the export potential of pesticides for these components. The first approach, as done in previous studies, was the study of correlations between mixing ratios of the flow components and pesticides variations of concentrations at the outlet. This gave a hierarchy on the potential of contamination for each flow component. The first vector of pollution was the surface runoff, followed by the subsurface runoff while groundwater provides a dilution on pesticides concentrations. However, this method didn't provide information on in the degree of contamination of each flow components.

A reversing of the Mixing Model by a second deconvolution performed directly on the observed pesticides concentrations at the outlet led has been applied. However, it led to important residuals and heteroscedasticity. A semi-logarithmic transformation of variables gave better results, particularly for the second event.

Finally, an estimated mass balance of pesticide was obtained based on these results.

The choice of the first filter, to decompose the hydrograph in flow components is crucial. Mixing model "by layer" failed to explain concentrations in diuron on the first event meaning that in some events there are bigger mechanics behind the exportation of a pesticide, possibly when its application is closer to the flood event.

Finally, an alternative would be to review in which components separate the hydrograph. Not by layers at different depths as performed in this study but rather by risky zones by using, in contrast, tracers of anthropic origin (copper) or tracers from different areas of the basin (Bélanger, et al., 1998). However, this would require additional data collection including subsurface flows and runoff in several areas of the basin.

The obtained mass balance showed that events with low surface runoff (event I) are still able to considerably damage the water quality. This contamination is partly due to subsurface runoff and severe concentrations in surface runoff when the event is close to vineyards treatments.

Important quantities of pesticides with low koc and high DT50 seem to be able to move through the shallow subsurface. Depending on their properties, they can be stored and being remobilized to the surface water with their eventual metabolites.

This confirms leverages such as:

- longest periods as possible between treatments and rainfall to reduce surface runoff acuity of concentrations
- Dimensioning buffer zones such as grass strip to block surface runoff which is generally the more concentrated component until late on the year
- Limit treatments after June, where events with high intensity and higher surface runoffs are more likely to happen
- Adding organic amendments to the soil in order to increase its retention potential

Above all, important limitations are needed on pesticides use. This is particularly true for molecules recalcitrant, mobile and precursors of dangerous metabolites such as diuron. For these molecules, grass strip are less effective and could ease their transfer to shallow subsurface enhancing its ability to export pesticides and their metabolites.

Obtention of a streamwater quality conform to the ECD includes an efficient watershed management and innovative pesticides formulations but these solutions only make sense if they are paired with a limited use of pesticides.

9 Bibliography

Barnes, B. S., 1939. *The structure of discharge-recession curves,* Tennessee: Reports and papers Hydrology.

Bélanger, Hendershot, N. & Bouchard, W., 1998. Identification des compartiments responsables de la qualité des eaux de surface d'un petit bassin versant du centre du Nouveau-Brunswick (Canada): application et analyse du modèle hydrochimique EMMA. *Journal of Water Science,* 11(1), pp. 117-137.

Biraud, Y., 1976. Les méthodes de déconvolution et leurs limites fondamentales. *Revue de physique appliquée,* 11(2), pp. 203-214.

Bossy, A., 2010. *Origines de l'arsenic dans les eaux, sols et sédiments du district aurifère de St-Yrieix-la-Perche (Limousin, France) : contribution du lessivage des phases porteuses d'arsenic ,* Limoges: s.n.

BRGM, 1971. *Application de l'analyse des hydrogrammes des cours d'eauà l'évaluation de l'écoulement souterrain,* Orléans: BRGM.

Burns, D., Mc Donnel, J. J. & Hooper, R. P., 2001. Quantifying contributions to storm runoff through end-membe rmixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia USA). *Hydrological Processes,* Issue 15.

Buttle, 1994. Isotope hydrograph separations and rapid delivery of pre-event from drainage basins. *Progress in Physical Geography,* 18(1), pp. 16-41.

Carluer, N., Catalogne, C., Dagès, C. & Tournebize, J., 2017. Aménager le territoire et gérer les aménagements : les zones tampons sèches et humides, les fossés pour lutter contre les pollutions diffuses par les produits phytosanitaires dans les aires de captage.. *Innovations agronomiques,* I(57).

Castany, G., 1967. *Traité pratique des eaux souterraines.* Paris: Dunod p 513-516.

Castany, G. & Margat, J., 1977. *Dictionnaire Français d'Hydrogéologie.* Orléans: BRGM.

Christophersen, N. et al., 1990. Modelling Streamwater Chemistry as a Mixture Of Soilwater End-Members_A Step Towards Second Generation Acidification Models. *Journal of Hydrology,* Issue 116, pp. 307-320.

Christophersen, N. & Hooper, R. P., 1992. Multivariate Analysis of Stream Water Chemical Data : The Use of Principal Components Analysis for the End-Member Mixing Problem. *Water Resources Research,* 28(1), pp. 99-107.

De Marsilly, .., 1981. *Hydrogéologie quantitative.* Paris: Masson.

Durand, P. & Juan Torres, J., 1996. Solute transfer in agricultural catchments : the interest and limits of mixing models. *Journal of Hydrology,* Issue 181, pp. 1-22.

El Azzi, D. & Probst, J. L., 2016. Trace Element and Pesticide Dynamics During a Flood Event in the Save Agricultural Watershed: Soil-River Transfer Pathways and Controlling Factors. *Water Air Soil Pollut,* Issue 442.

Grasland, C., 1998. *Initiation aux méthodes statistiques en sciences sociales.* [En ligne] [Accès le 1 Janvier 2018].

Hooper, R. & Schoemaker, C., 1986. A comparison of Chemical and Isotopic Hydrograph Separation. *Water resources research.*

Hubert, P., 1989. La séparation de l'hydrogramme. Apport des méthodes isotopiques.. *Hydrogéologie*, Issue 3.

INERIS, 2006. *Eléments traces métalliques,* s.l.: s.n.

INRA & Irstea, 2005. *Pesticides, agriculture et environnement,* s.l.: s.n.

Mul, M., Uhlenbrook, S. & Mutiibwa, R., 2008. Hydrograph separation using hydrochemical tracers in the Makanya catchment, Tanzania. *Physics and Chemistry of the Earth, Parts A/B/C,* Volume 33, pp. 151-156.

Nordstrom, D. K., 1985. *Toxic Element Composition Of Acid Mine Waters From Sulfide Ore Deposits,* Granada: International Mine Waters Association.

Orquevaux, M., 2010. *Etude du bassin-versant de la Morcille :synthèse de données et mise au point d'un schema de fonctionnement tenant compte des dynamiques de concentrationdes pesticides et des métaux,* Lyon: Cemagref.

Peyrard, X., 2016. *Transferts de produits phytosanitaires par les écoulements latéraux en proche surface dans le Beaujolais de coteaux,* Lyon: Ecole Doctorale de Chimie de l'Université de Lyon.

Pinder, G., 1969. Determination of the Ground-Water Component of Peak Discharge from the chemistry of Total Runoff. *Water Resources Research,* 5(2).

Rabiet, M. et al., 2015. *Environmental Sciences Pollution Research.*

Remenieras, 1965. *L'hydrologie de l'ingénieur.* Paris: Eyrolles p 355-373.

Renner, R., 1993. The Resolution of a Compositional Data Set into Mixtures of Fixed Source Compositions. *Journal of the Royal Statistical Society. Series C (applied statistics),* 42(4), pp. 615-631.

Roche, M., 1963. *Hydrologie de surface.* Paris: Gauthiers-Villars.

Sigg, L., Behra, P. & Stumm, W., 2000. *Chimie des milieux aquatiques.* Paris: Dunod.

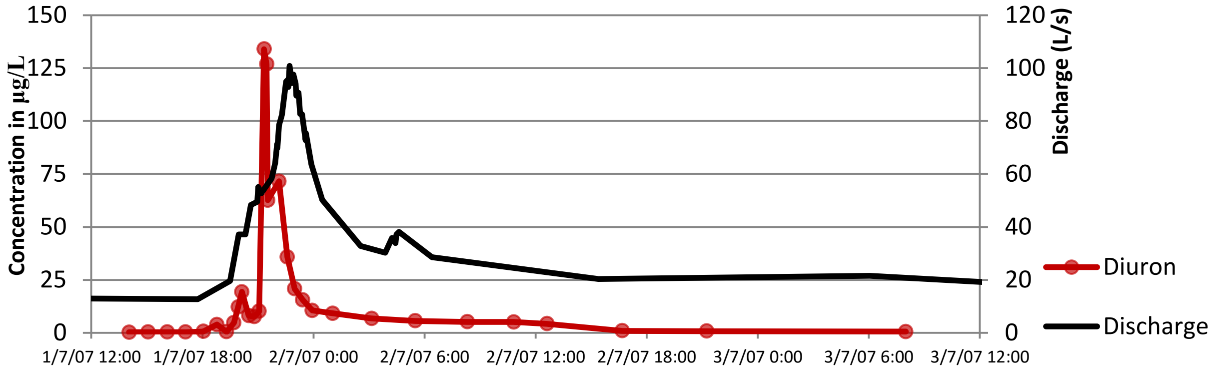
Takeno, N., 2003. *Intercomparison of thermodynamic databases,* Tokyo: National Institute of Advanced Industrial Science and Technology Research Center for Deep Geological Environments.

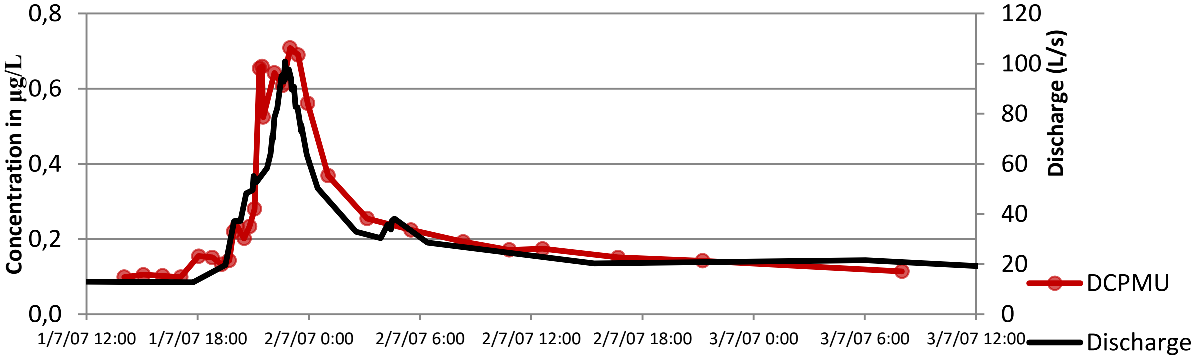
Tang, T., Stamm, C. & van Griensven, A., 2017. Hysteresis and parent-metabolite analyses unravel characteristic pesticide transport mechanisms in a mixed land use catchment. *Water research,* Issue 124, pp. 663-672.

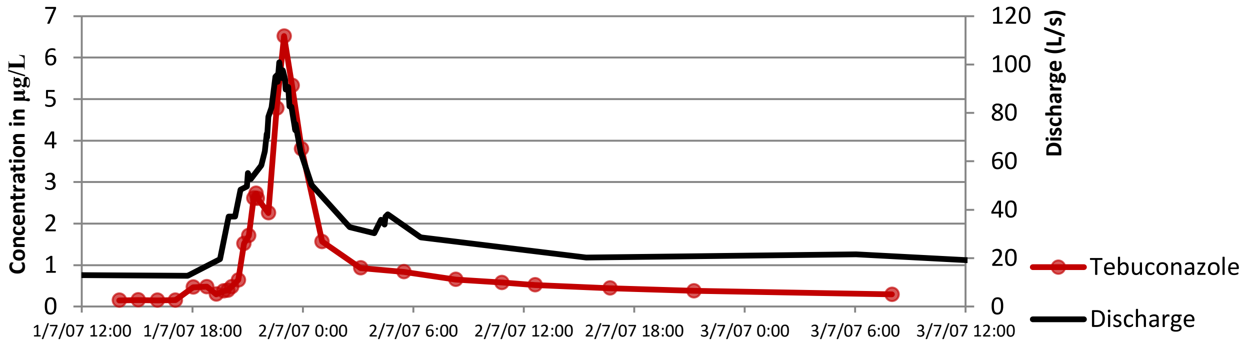
Tardy, Y., Mortatti, J. & Probst, J.-L., 1995. *Erosion chimique et mécanique dans le bassin de l'Amazone. Evaluation du ruissellement par la méthode dite des réservoirs à contribution variable mais à composition constante,* Paris: Académie des Sciences.

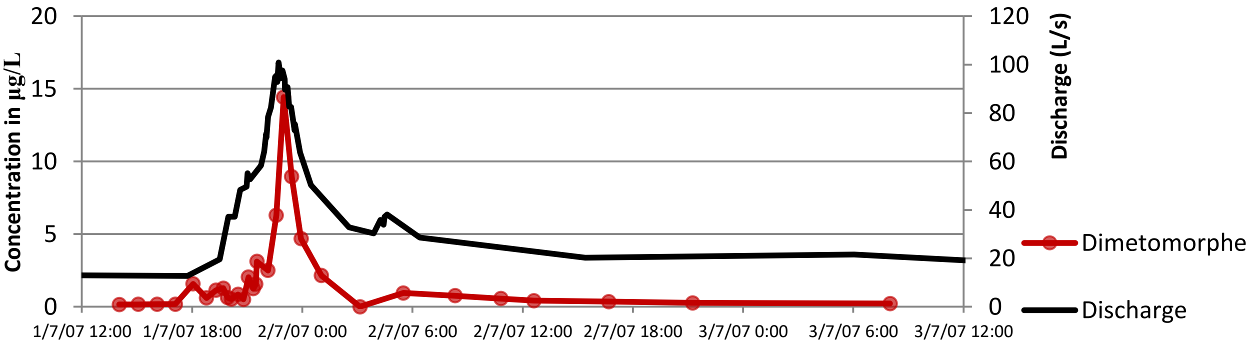
10 Appendix

10.1 Studied pesticides variations of concentrations









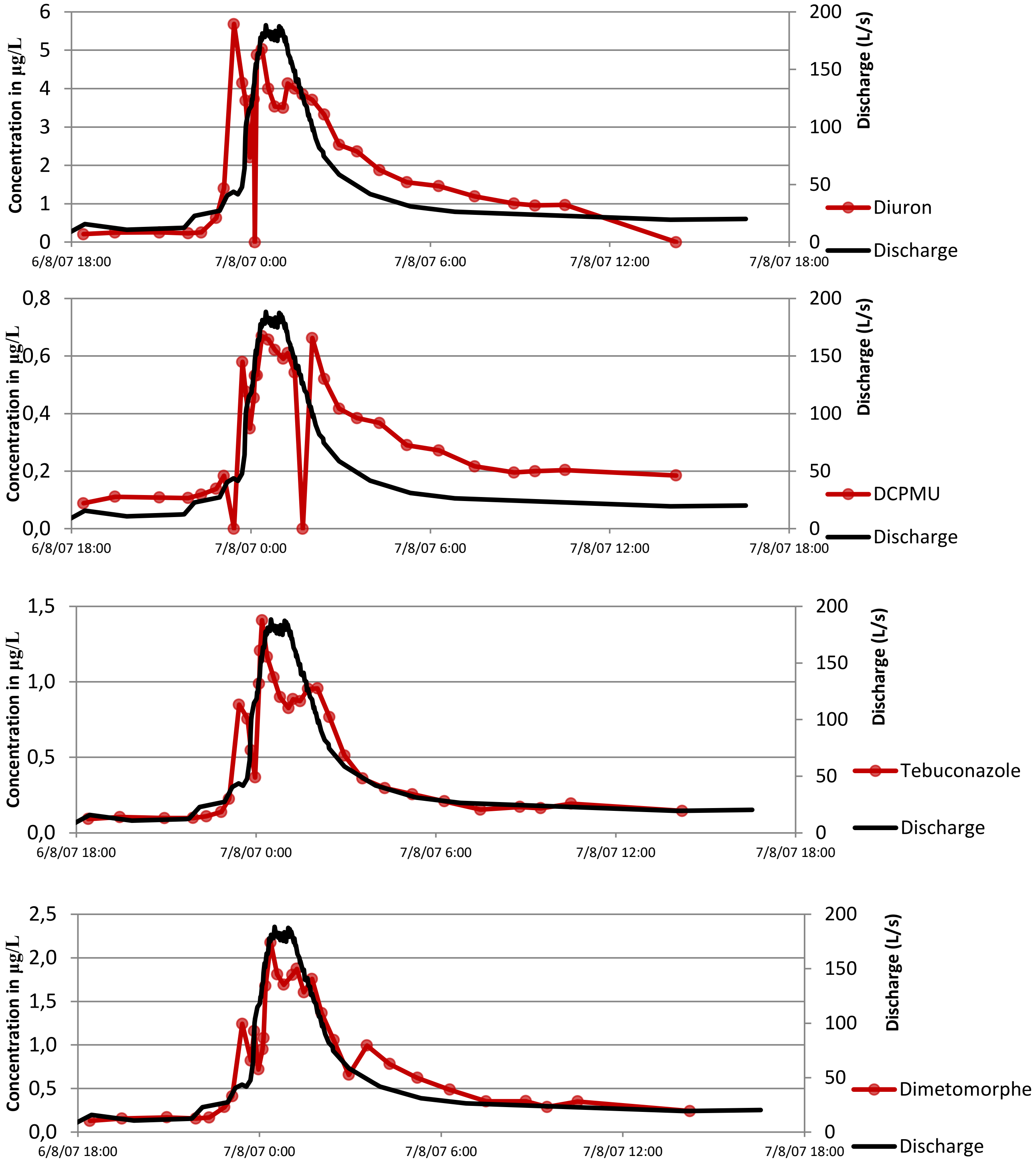


Figure 40: Variations of studied pesticides along with the discharge during floods

10.2 Literature review of simple mixing model

Table 17 : Non exhaustive list of studies and their contexts using the Mixing Model under its simplified form

Name of the study author(s) Journal Date of publication	Chemical elements or parameters used as tracers	Concerned flow(s)	Watershed characteristics (if indicated) : Area, topography, type of soil, climate and pluviometry
Determination of the Ground-Water component of Peak-Discharge from the chemistry of total Runoff *George F. Pinder and John f. Jones, Water resources research 1969*	Ca^{2+} Mg^{2+} Na^{+} Cl^{-} SO_4^{2-} HCO_3^{-}	Groundwater, two flow components model	3 sub-basins in Nova Scotia (continental climate, cold and wet) with trees between 3.5 and 8 km². Downhill between 100 and 280 meters. Generally clay shale base, sandstone, soil consisting of glacial sediments.
A Comparison of Chemical and Isotopic Hydrograph Separation *Richard P.Hooper and Christine A. Shoemaker, Water resources research 1986*	SiO_2 $^{\delta}D$	“Old water” Old and new water model	0.42 km² catchment in New-Hampshire (US). Bed of granite and metamorphic schists. Soil composed of very porous glacial sediments and a thin layer of organic matter on the surface. Heights between 2380 m and 1780 meters Rainfall of 1470 mm / year, 30% of which is snow
Hydrograph Separation : a Comparison of Geochemical and Isotopic Tracers *Christoph Wels., R. Jack Cornett and Bruce D. Lazerte, Journal of Hydrology, 1990*	$^{\delta}D$	Surface runoff , three flow components model	0.05 km² basin in the Muskoka Haliburton (South of the Canadian Shield). Downhill between 420 and 400 meters. Sandy Podzosol (63%, - 86%) with low clay content and low CEC, granitic gneiss bedrock. Large presence of forests. Rainfall of 1000 mm / year including 25% snow
	SiO_2 Mg^{2+}	Groundwater, three flow components model	
Erosion chimique et mécanique dans le bassin de l’Amazone. Evaluation du ruissellement par la méthode dite des réservoirs à contributions variables *Yves Tardy, Jefferson Mortatti and Jean-Luc Probst; Earth and Planetary Science, 1995*	Coarse/Fine fractions of Organic particular carbon and Total Suspended Solids (POCF/POCC, SSD/ SSC)	Surface runoff ; two component model	Amazon catchment.

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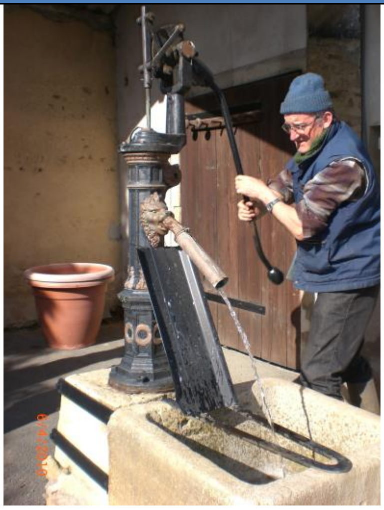
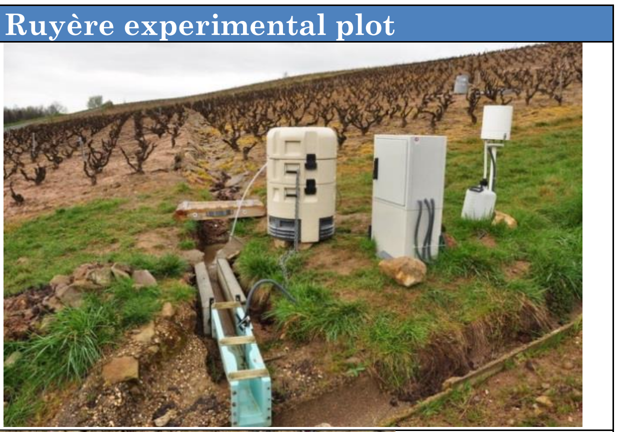
Four-Component Hydrograph Separation Using Isotopic and Chemical Determinations in an Agricultural Catchment in Western France *P. Merot, P. Durand and C. Morisson,* *Phys.Chim.Earth Vol 20 1995*	SO_4^{2-}	Subsurface runoff, four flow components model	North West France Coet Dan sub-basin of 4.9 km². Oceanic climate. Downhill between 65 and 137 meters. Base shale. Loess soil and shale debris (silt from wind erosion). Precipitation of 700 mm / year Intensive agriculture and pasture.
	Cl^-	Groundwater, four flow components model	
	^{18}O	Surface runoff, four flow components model	
	Rain (rain falling directly in the streamwater)		
Variation in stream water chemistry and hydrograph separation in a small drainage basin *Daniel Caissie, Tom L. Pollock, Richard A. Cunjak Journal of Hydrology, 1996*	Conductivity Ca^{2+} Na^+ Mg^{2+} K^+	Groundwater, two components model	Brook Catamaran Basin 52 km² in Canada. Soil made of glacial and fluvial sediments. Presence of forests, little urbanized. Rainfall 754 mm / year
Contribution of groundwater and overland flows to storm flow generation in a cultivated Mediterranean catchment. Quantification by natural chemical tracing *O. Ribolzi P. Andrieux, V. Valles, R. Bouzigues, T. Bariac, M. Voltz* *Journal of Hydrology, 2000*	Cl^-	Groundwater, three flow components model	Wine growing area of 0.91 km² in the South of France (Roujan). Mediterranean climate. Downhill of 50 meters. 80% occupied by vines. Limestone soil and lagoon deposits. Base of impervious marine sediments Rainfall of 650 mm / year
	NO_3^-	Subsurface runoff, three components models	
Hydrograph separation in a mountainous catchment —combining hydrochemical and isotopic tracers *S.Hoeg, S.Uhlenbrook and Ch. Leibungdut* *Hydrological Processes 2000*	$^{18}_{\delta}O$	Surface runoff , three flow components model	Basins of 18.4 km² and 40 km² in the Black Forest in Germany. Downhill of 900 meters: altitudes between 584 and 1493 meters. Permeable soil on gneiss. 75% of forests, 23% of pastures and urbanization less than 2%. Rainfall of 1700 mm / year
	SiO_2 Conductivity	Groundwater, three components model	
Hydrograph separations in a mesoscale mountainous basin atevent and seasonal timescales. *Stefan Uhlenbrook,1 Markus Frey,2 Christian Leibundgut,1 and Piotr*	Cl^- SiO_2 $^{18}_{\delta}O$(détermination du temps de résidence)	Groundwater, Three flow components model	
	K^+ $^{18}_{\delta}O$ (idem)	Subsurface runoff, three components	

Maloszewski *Water resources research* *2002*		model,	
Hydrograph separation using hydrochemical tracers in the Makanya catchment, Tanzania *Marloes L.Mul, Robert K.Mutiibwa, Stefan Uhlenbrook, Hubert H;G. Savenije, Physics and Chemistry of the Earth* *2008*	Conductivity Ca^{2+} Mg^{2+} Na^{+} Cl^{-} SO_4^{2-} HCO_3^{-} K^{+} F^{-}	Groundwater, two flow components model	2 sub-basins in semi-arid climate in Tanzania of 8.4 and 14.2 km². Downhill of 1300 meters: altitudes between 700 and 2000 meters. Season of short rains with an average duration of 2 months rainfall between 550 and 700 mm / year.
Trace Element and Pesticide Dynamics During a Flood Event in the Save Agricultural Watershed: Soil-River Transfer Pathways and Controlling Factors *D. El Azzi & J. L. Probst & R. Teisserenc & G. Merlina & D. Baqué & F. Julien & V. Payre-Suc & M. Guiress* *Water Air Soil Pollution* *2016*	PO_4^{3-}	Groundwater, three flow components model	Basin for agriculture (used at 90%) of the "Côteaux de Gascogne" (South-West of France) of 1110 km². Downhill of 500 meters: altitudes between 638 and 103 meters. Oceanic climate with a rainfall of 750 mm / year. Limestone-clay base. 90% of calcic soils composed of 50% clay. Strong erosion.
	TSS	Surface runoff, three flow components model	

10.3 “Key sites” of the Morcille watershed

“ Source Morcille “	well “ Ducroux “ (Site 1 : Saint Joseph)	well “ Dufour “ (Site 2 : les Versauds)
		

Saint Joseph experimental plot	Ruyère experimental plot
	
 *Figure 41 : Saint Joseph piezometer and canal with flowing runoff*	 *Figure 42 : Experimental trenchon Ruyères for subsurface runoff sampling automatic sampler*

10.4 Plotting of recession tangents of smaller events and resulting decompositions

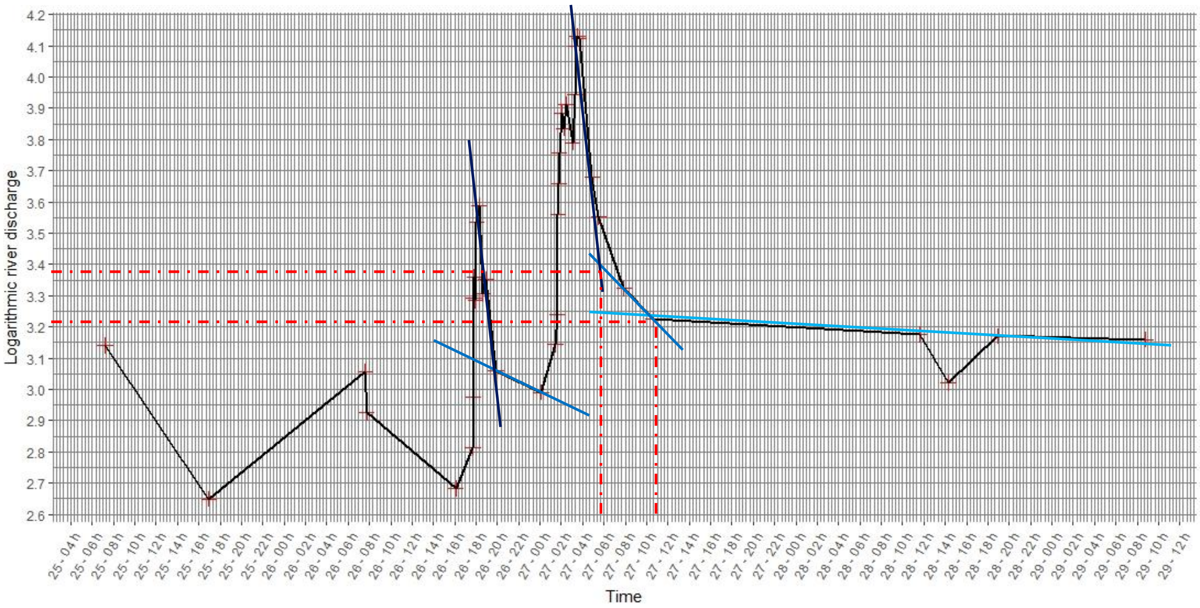


Figure 43 : Plotting of recession tangents and characteristic points of the hydrograph ln(discharge) of the 26 May 2007 event

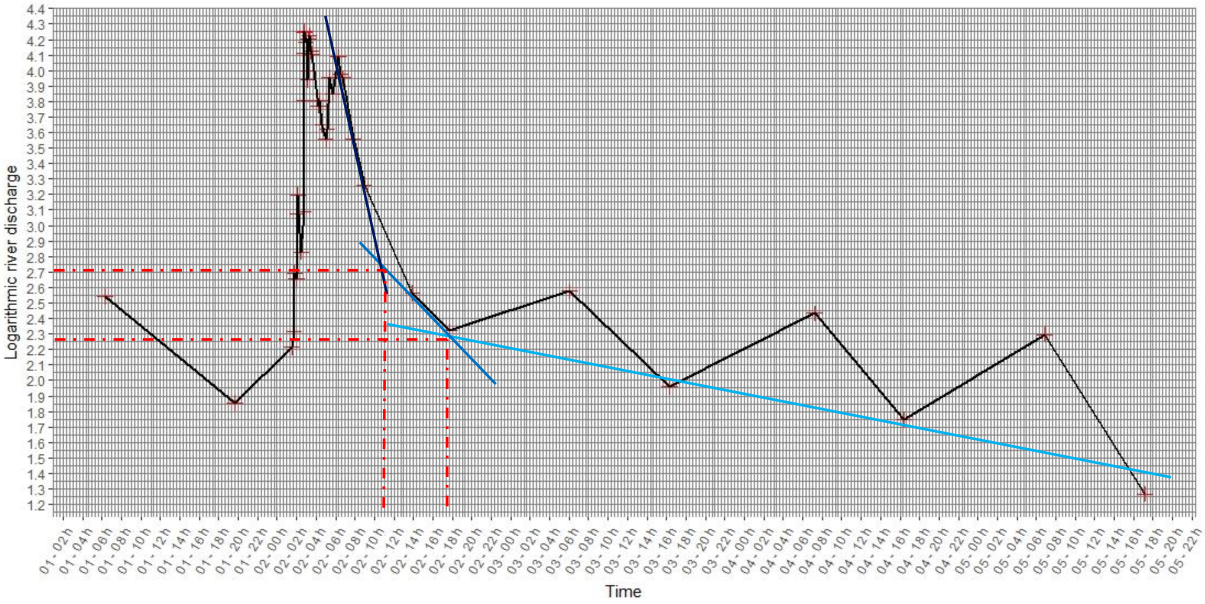


Figure 44 : Plotting of recession tangents and characteristic points of the hydrograph ln(discharge) of the 2 August 2007 event

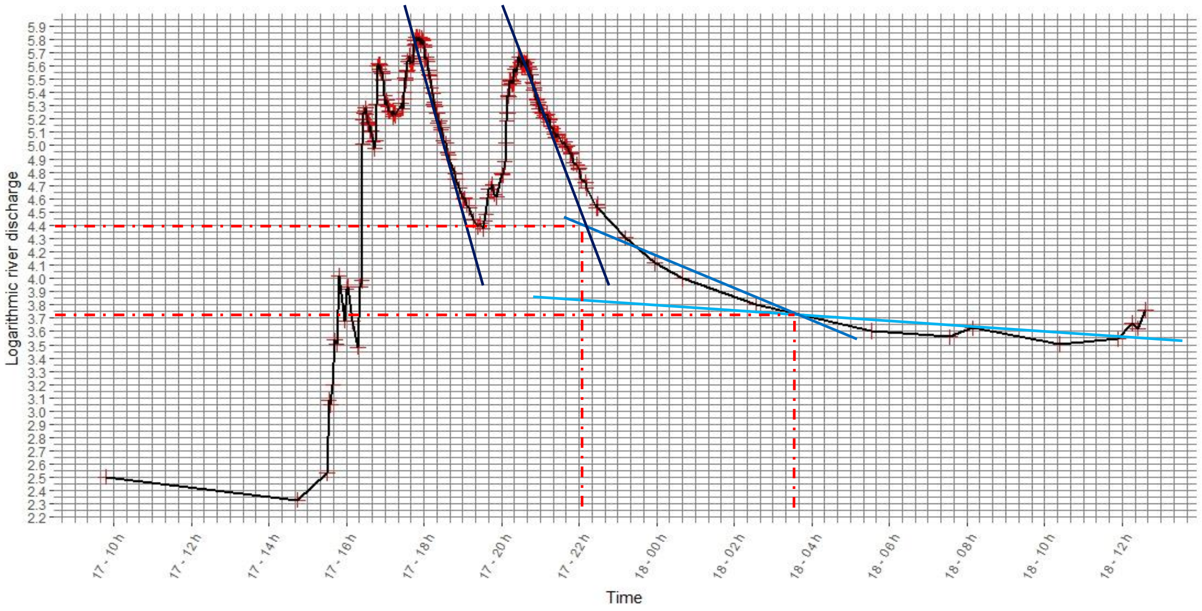


Figure 45 : Plotting of recession tangents and characteristic points of the hydrograph ln(discharge) of the 17 September 2007 event

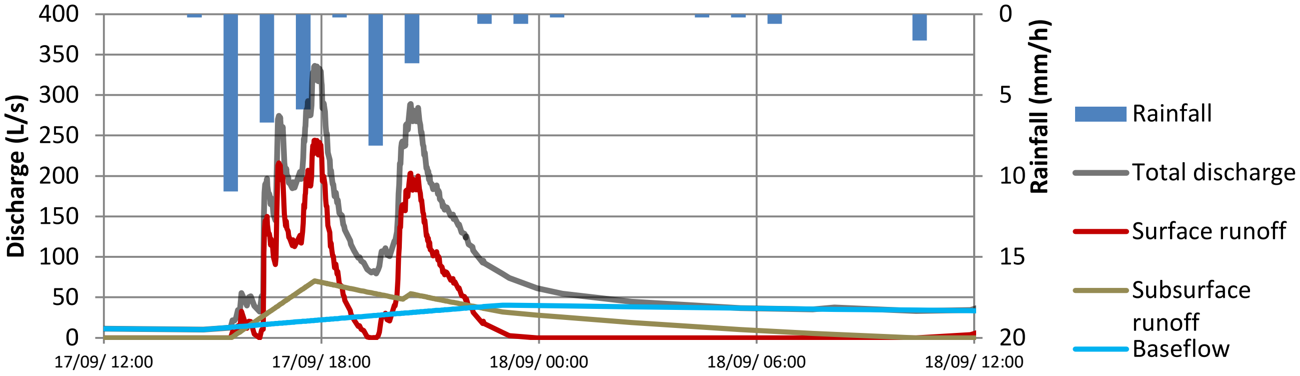


Figure 46 : Graphical decomposition of hydrograph by recession analysis 17/09/07event

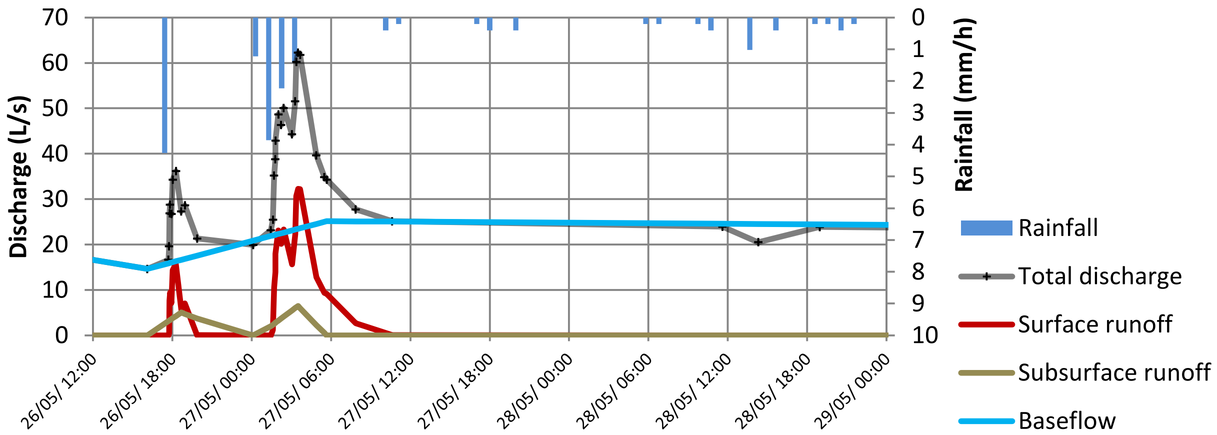


Figure 47 : Graphical decomposition of hydrograph by recession analysis 26/05/07event

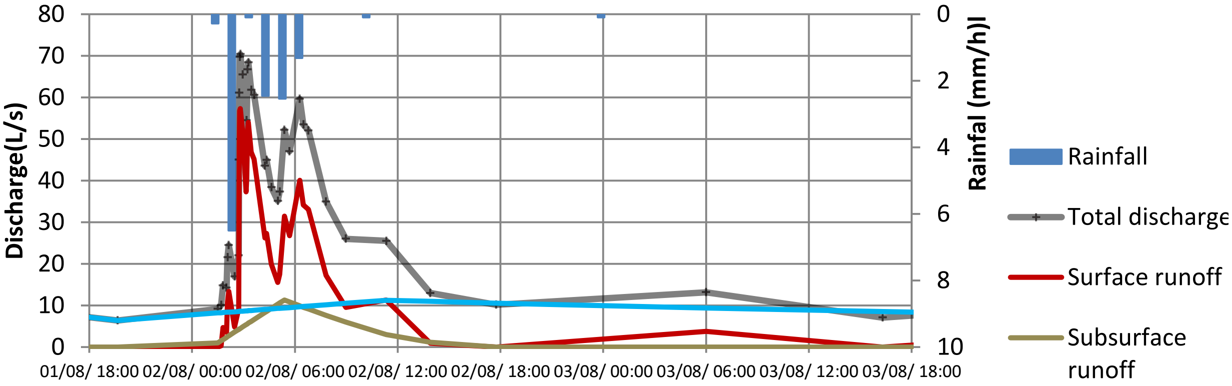


Figure 48 : Graphical decomposition of hydrograph by recession analysis 26/05/07event

10.5 Empirical curve of TSS concentration function of the « rain regularity »

Unlike the water table, setting a concentration for surface runoff is difficult because it is more or less concentrated in suspended matter from one event to another.

The Morcille basin is characterized by rainy events of three types according to the seasons: "Summer 1, Summer 2, Winter" (Orquevaux, 2010).

Samples of different surface runoffs during rainy events were made during a thesis taking place between 2013 and 2016.

The "Summer" type events were selected[30] and confronted with the volumes of rain that fell. The intense rains being generators of hortonian overland flow and thus potentially of TSS, the precipitated mm of rain were multiplied by a coefficient depending on the intensity with which they were precipitated then summed.

This new volume of falling rain was divided by the duration of the sampling. This coefficient of "regularity of rain" was compared with the average concentration of SS of each event (6) and an empirical relationship was found between the two.

By doing this same analysis on the volumes of rain falling from the events Summer of 2007 average concentrations of SS for runoff were calculated with the interpolation formula

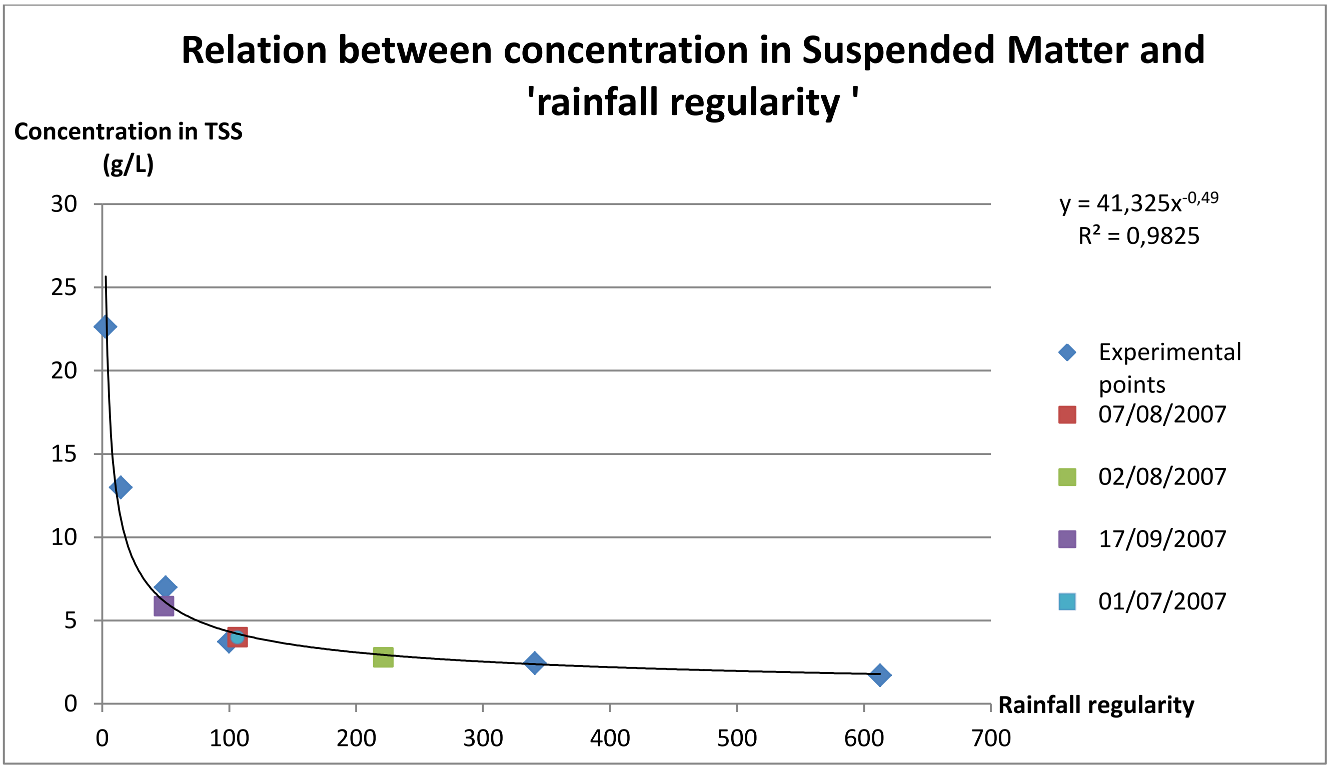


Figure 49 : Empiric relation between TSS concentration and pondered rainfall intensity

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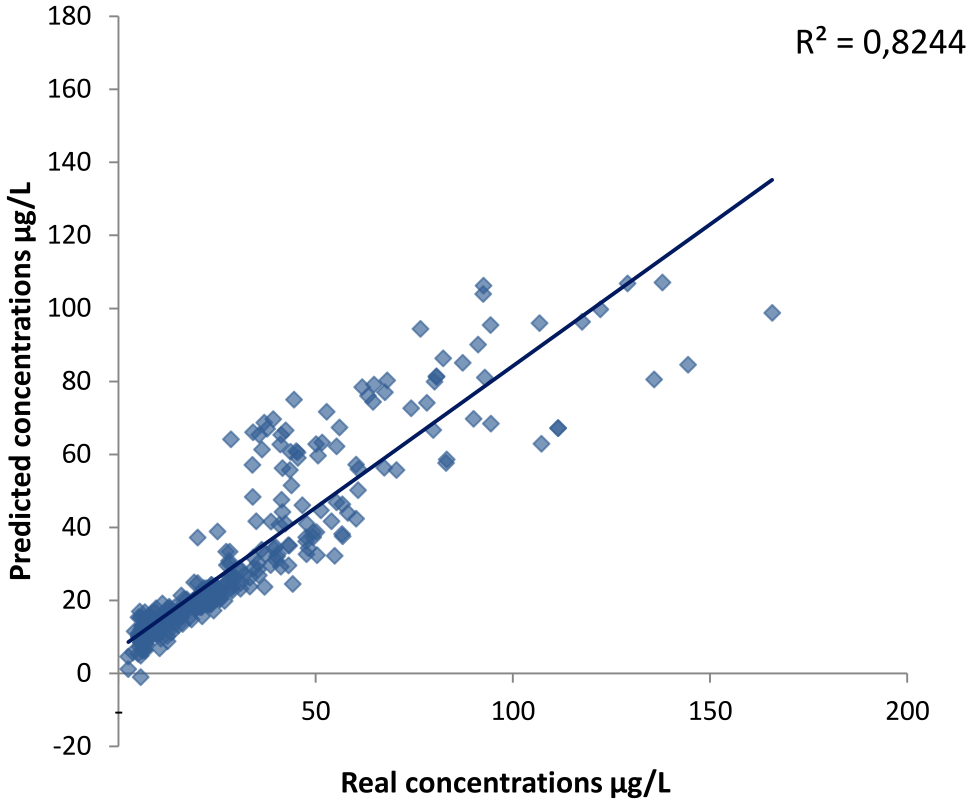
[30] We do not retain « winter events » (Orquevaux, 2010) because their TSS dynamic differ

10.6 Goodness of fit for copper and aluminium on EMMA



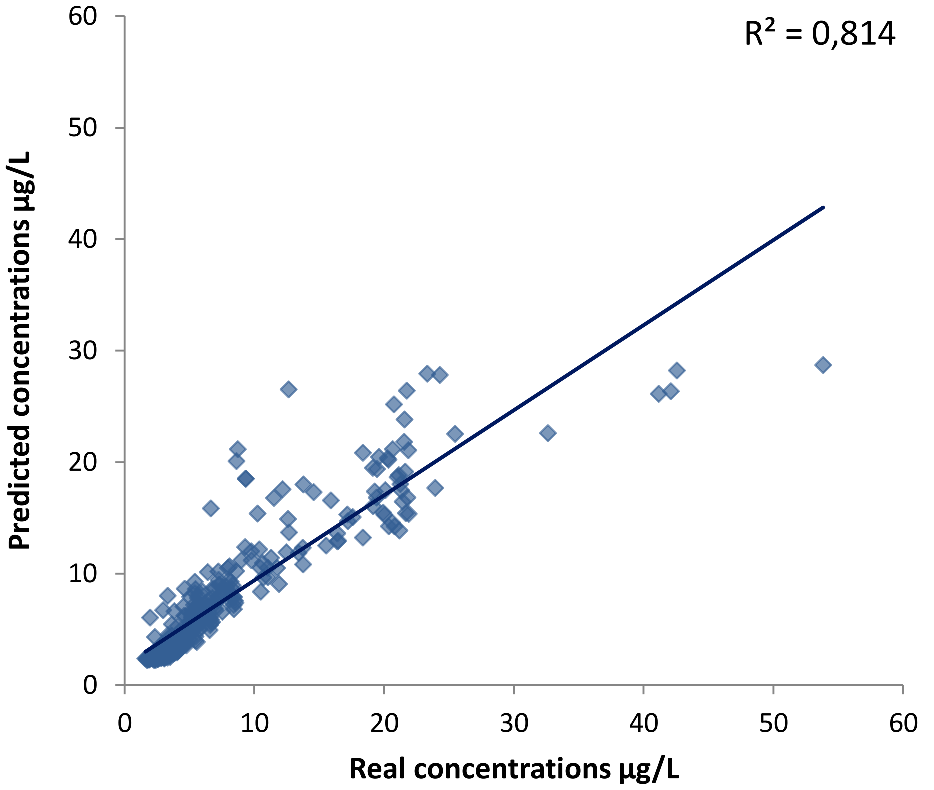
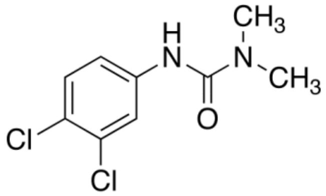
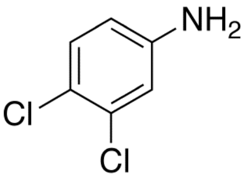
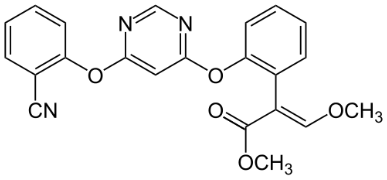
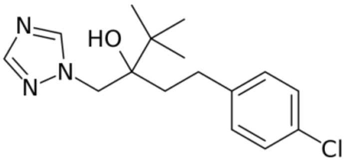
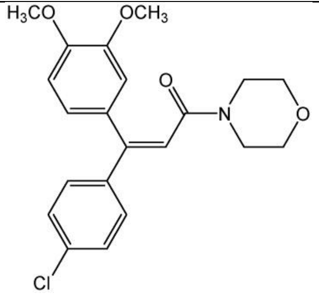
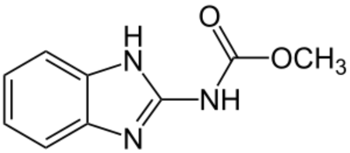
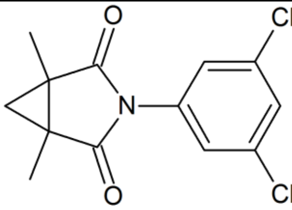


Figure 50 : Aluminium and copper goodness of fit between real observations and back calculated concentrations by EMMA on 357 observations

10.7 Studied pesticides on the Morcille surface water

Table 18: Studied pesticides on the Morcille surface water at the Versaud and Saint-Joseph station during the 2007 campaign

Formulation name	UICPA name	Developped formula	Use and period of application	Physicochemical characteristics
Diuron (DIU)	3-(3,4-dichlorophényl)-1,1-diméthyl-urée		Weedkiller March to May	DT 50 photolysis :173d DT 50 biodegradation : 372 d Koc :355 Solubilité :35,6 mg/L
Dichloroaniline (DCA)	1-amino-3,4-dichlorobenzene		Diuron metabolite	Koc :195 DT 50 photolyse :8 h DT50 biodegration:470 -1500 j
(DCPMU)	3-(3,’-dichlorophenyl)-1méthylurée		Diuron metabolite	DT50 : 28 days Koc :284 Solubilité :42 mg/L
Azoxystrobine (AZS)	Méthyl (E)-2-{2[6-(2-cyanophenoxy) pyrimidin-4-yloxy] phényl}-3-methoxyacrylate		Fungicide May to June/July	DT50 photolysis :18 d Koc : 423 Solubilité :6,7 mg/L
Tébuconazole (TBZ)	(RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)pentan-3-ol		Fungicide May to June/July	DT50 photolyse : 3d DT50 bio : 62 d Koc :992 Solubilité :29 mg/L
Diméthomorphe (DMM)	4-[3-(4-Chlorophényl)-3-(3,4-diméthoxyphényl)acryloyl]morpholine		Fungicide May to June/July	DT 50 photolyse : 28-107 d Koc :290-566 Solubilité :47,2 mg/L
Carbendazime (CBZ)	benzimidazole-2-ylcarbamate de méthyle		Fungicide May to June/July	DT50 (hydrolysis) :350 d a 22°C pH 7 Koc : 200-246 Solubilité : 80 mg/L
Procymidone (PCM)	3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.0]hexane-2,4-dione		Fungicide May to June/July	DT 50 (photolyse) : 8 d Koc : 199-513 Solubilité : 2,46 mg/L

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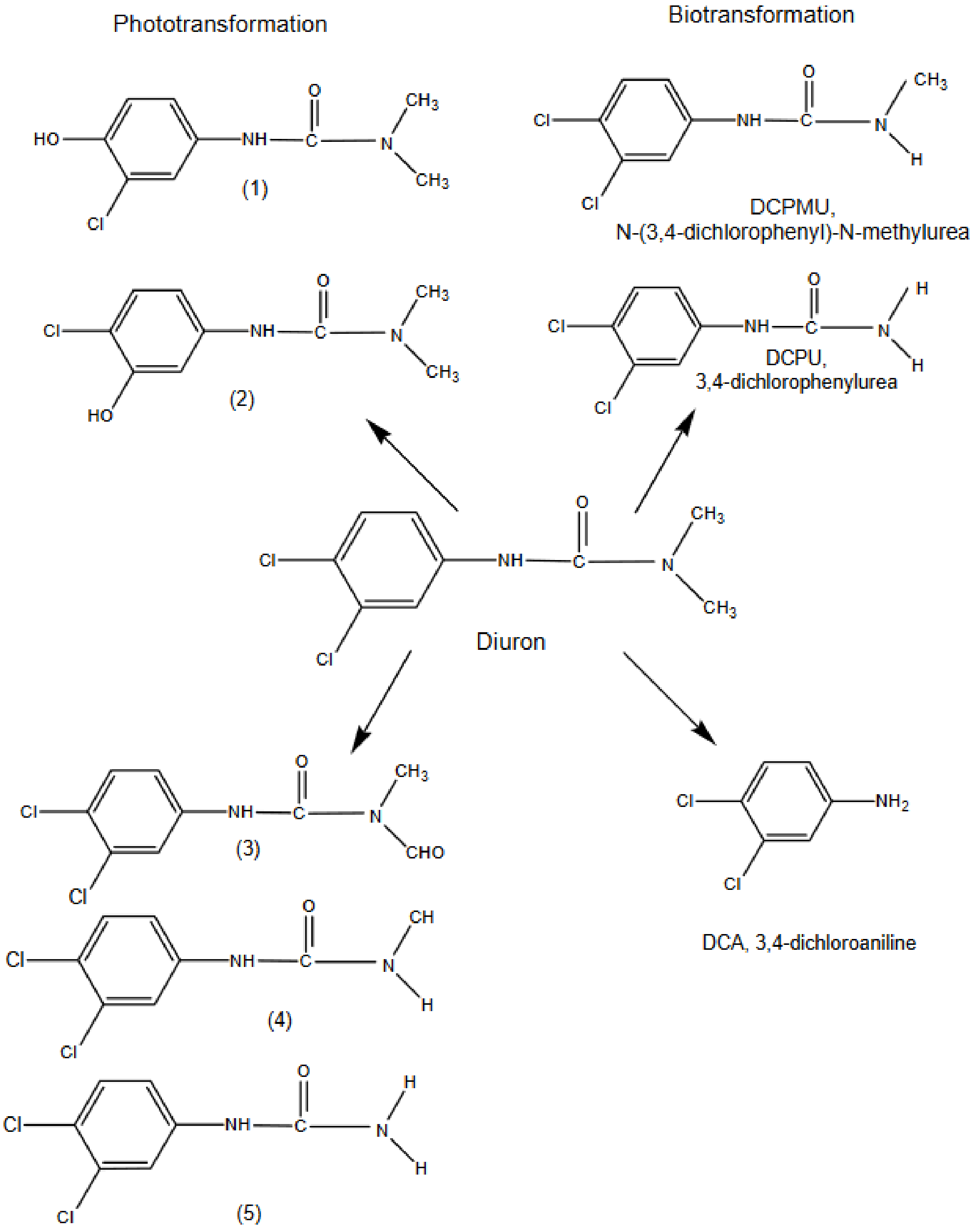

Figure 51 : General scheme of diuron photodegradation and bio-transformation (Bonnemoy et al, 2001)

10.8 B estimators of each flow component for studied pesticides

Table 19 :βestimators of each flow component for studied pesticides and indicators of fitting

Studied pesticide on 01/07/2007		**Diuron**	**DCPMU**	**Tebuconazole**	**Dimetomorphe**
$\boldsymbol{\beta}_{\textbf{Surface runoff}}$		10.204	5.04	8.44	8.68
$\boldsymbol{\beta}_{\textbf{Subsurface runoff}}$		19.014	2.77	7.04	8.525
$\boldsymbol{K_0}$		-5.12	-0.67	-1.80	-2.21
Pr(>|t|)[31]	$\beta_{\text{Surface runoff}}$	***	***	***	***
	$\beta_{\text{Subsurface runof}}$	*	■	**	*
	K_0	■	■■	■	■
F		17.2	76.2	98.1	61.51
R²		0.56	0.85	0.88	0.83
p-value		1.5×10^{-5}	7.8×10^{-13}	4.1×10^{-13}	1.4×10^{-10}

Studied pesticide on 07/08/2007		**Diuron**	**DCPMU**	**Tebuconazole**	**Dimetomorphe**
$\boldsymbol{\beta}_{\textbf{Surface runoff}}$		6.04	3.82	5.52	5.17
$\boldsymbol{\beta}_{\textbf{Subsurface runoff}}$		3.86	2.70	2.57	3.85
$\boldsymbol{K_0}$		-1.07	-0.80	-1.097	-1.30
Pr(>|t|)	$\beta_{\text{Surface runoff}}$	***	***	***	***
	$\beta_{\text{Subsurface runof}}$	**	***	**	***
	K_0	*	**	**	***
F		102.4	142.8	155.7	202.8
R²		0.87	0.91	0.91	0.93
p-value		1.3×10^{-13}	2.0×10^{-15}	2.2×10^{-16}	2.2×10^{-16}

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[31] Signification of the t test with t-value : 0 '***' 0.001 '**' 0.01 '*' 0.05 '■' 0.1 '■■ ' 1