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To my Divine Protector

To My Dear Parents

To My sisters

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Abstract

The mechanisms of pesticides transport to stream flow were studied in two agricultural nested catchments of different size in Gascogne region (South West of France): the Save river basin at Larra (1110 km^2) and the Montoussé experimental watershed at Auradé (3.28 km^2). The intensive agricultural practices used in this region lead to an important risk for water resources by pesticides, especially during storm events. This is why we have paid special attention on storm events when a large quantity of contaminant was transported during hydrological periods. Fourteen molecules of pesticides (herbicides and fungicides) were investigated during the study period. Both of these groups are widely used for agricultural purposed in these catchments.

The results achieved over the two years monitoring (2007-2009) enable us to emphasize the principal processes, implied in pesticide transfer on these agricultural catchments. The majority of compounds are detected during storm runoff events. And, the average concentrations of some pesticides are exceeded at the authorization limit of the European Union for pesticide concentrations in drinking water (0.1 $\mu g.L^{-1}$ for individual pesticides and 0.5 $\mu g.L^{-1}$ for total pesticides).

To better understand the mechanisms of pesticide transport hysteresis, patterns on the concentration-discharge relationship (result of different concentration of pesticides in rising and falling limb of storm) were studied. However, clockwise or anticlockwise hysteresis patterns could be observed for some molecules of pesticide and their controlling factors such as dissolved organic carbon (DOC), particulate organic carbon (POC) and total suspended matters (TSM) according to their transfer dynamic in the catchment. We proceeded with hydrograph separation of the main stormflow components (surface runoff, subsurface flow and groundwater) so that the main pesticide routing could be traced for its soil-river transfers. We also came to the conclusion that there is a positive relationship between riverine TSM, DOC and pesticide, concentrations and the discharges of surface or subsurface runoffs according to pesticide properties. Pesticide flux calculation shows between 60 to 90% of the molecule transport takes place during storm periods. Specific flux calculation also demonstrated the higher flux value in Save catchment than in Aurade with higher pesticide concentration for a given specific discharge. The latter result may be due to the more consumption of pesticide in Save catchment. The analyses of pesticides both in filtered and unfiltered water enabled us to estimate the distribution of pesticides into particulate and dissolved phases. Moreover, the pesticide flux values allow calculating average partition coefficients k_d between dissolved and particulate fractions which present good relationship with K_{ow} values (octanol-water) extracted from literature. The percentage of each pesticide transported as particulate forms is also well correlated to K_{ow}.

Keywords: Pesticides, hysteresis, hydrograph separation, DOC, POC, TSM, flux, K_d and K_{ow}

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Abbreviations

ACTA	Association to Coordination of Agricultural Technique
CACG	Compagnie d'Aménagement des Coteux de Gascogne
DAR	Desethylatrazine/Atrazine Ratio
DCM	Dichloromethane
DF	Detection Frequency
DL	Detection Limit
DOC	Dissolved organic carbon
DOM	Dissolved Organic Matter
EEC	European Economic Community
EU	European Union
FAO	Food and Agriculture Organization
G	Ground water
GC	Gas Choromatography
HPLC	High Performance Liquid Choromatography
K_d	Coefficient of distribution
K_{oc}	Organic carbon normalized soil solution partitioning constant (L/Kg OC)
K_{ow}	Octanol Water partitioning constant
LLE	Liquid Liquid Extraction
MEDD	Ministère de l'Ecology du Development Durable
MS	Mass Spectrometry
PF	Particulate Fraction
POC	Particulate Organic Carbon
S	Surface water
SIM	Specific Ions Monitoring
SPE	Solid Phase Extraction
SS	Subsurface water
SSC	Suspended Sediment Concentration
S_w	Solubility
TOC	Total Organic Carbon
TSM	Total Suspended Matter
VOC	Volatile Organic Carbon
WHO	World Health Organization

Scientific production and Awards

This Ph.D thesis has been partly published in peer reviewed journals or presented in national and international congresses.

Publications in JCR indexed Journals

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Boithias L. **Taghavi L.** , Oeurng C , Sauvage S, Polard T. Ferrant S. Jean S. Probst J.L. Merlina G. and Sanchez-Perez J.M., 2010. Modelling pesticide transfer during flood events in an agricultural catchment using the SWAT model. *Geophysical Research Abstract, Vol. 12, EGU2010*-8258-1, 2010. EGU General Assembly 2010. Vienne, Autriche, April 2010 (poster)

Taghavi L. Probst J.L. Merlina G., 2010. Contribution of the different stream flow components to the transfer of pesticides in an agricultural watershed (Save, south west of France). *Proceedings 6th European conference on pesticides and related organic micropollutants in the environments and 12th symposium on chemistry and fate of modern pesticide*, Matera, Italy, Sep 2010 (oral presentation)

Taghavi L. Probst J.L. Merlina G., 2010. Pesticide transfer dynamic in an agricultural watershed (Save-South west of France): contribution of the flood flows to the total fluxes. *Proceedings 6th European conference on pesticides and related organic micropollutants in the environments and 12th symposium on chemistry and fate of modern pesticide*, Matera, Italy Sep 2010 (poster)
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General Introduction

General Introduction

Pesticides are substances used to fight against pests of plants, animals and vegetal which pose serious problems to human activities, especially in agriculture (Gouy, 1993).

Herbicides are the main group of pesticides which are used frequently to maintain uncultivated soil, on the one hand and to protect the soil under cultivation in the early stage of growing crops, on the other hand. Fungicides fall into second category of pesticide in use in term of frequency to combat fungi. Substituted urea, s-triazine, toluidine, chloroacetamide and s-triazole are the pesticides used more frequently for corn, winter wheat, sunflower and colza in our study areas. As the consequence, a large quantity of the pesticides used enters into aquatic systems by rain, snow especially in spring and winter. As a matter of this fact investigation about the behaviour of these pesticide families is the purpose of our study.

The results of previous studies show many kinds of pesticides and their metabolites have been detected in various water bodies even under normal agricultural practices (Martin et al., 2003). Though their mechanisms remain unknown and it is highly necessary to conduct study on the transfer of pesticide in agricultural area (Louchart, 1999; Gouy et al., 2000).

Looking into pesticides' concentration and transport to water course especially during storm events by runoff have been studied by some investigators (Ng and Clegg, 1997 ; Borah et al., 2002 ; Holvoet et al., 2007; Rabiet et al., 2010). But none have really investigated course of storm events by runoff and therefore little is known about the main routs of pesticide transport. And consequently controlling the contribution of the different streamflow components (surface and subsurface runoff, groundwater) to this reverine transfers. Hydrograph separation has been used as a means to estimate the contribution of each stream component during every flood event. The relationship between some particulate and soluble elements with stream components was previously demonstrated (Probst, 1985; Kattan et al., 1986; Probst and Bazerbachi, 1986) but nothing as such for pesticides.

Natural water contains suspended matter, dissolved organic and inorganic matter and many kinds of biota. As a consequence, the interaction between natural water contents and pesticides' molecules is important to better understand pesticides transfers, particularly during storm events. In addition, in 1994 MC Bride pointed out that these interactions are influenced by the physico-chemical properties of the pesticides such as hydrophobicity (log K_{ow}) and pesticide distribution coefficient (K_d). Then, we have paid especial attention to prediction of pesticide distribution coefficient during storm events when there is a large quantity of particulate and soluble, TSM, POC and DOC, elements that serve as a vector on pesticides' transport (Mahler et al., 1999; Spark and Swift, 2002; Voice and Webber, 1993). Consequently, the distribution of pesticides in particulate and dissolved phase could be predicted by using the value of K_{ow} registered in literature. Since the distribution of pesticide in particulate or dissolved phases depends on organic fractions, therefore the extent of sorption is described in term of the organic-c-normalised partition coefficient, K_{oc} (Chiou et al., 1979). The relationship between K_{ow} and K_{oc} values has been found by several authors (Karickhoff, 1979; Kenaga and Goring, 1980; Lyman et al., 1982). Since the contribution of organic carbon is low in our study area we focus our attention on K_d calculation. Moreover, there is a lack of studies on the calculation of K_d based on the flux value during storm events.

The present study was realised in the Save watershed and its subbasin, Auradé, close to Toulouse. The agricultural zone is intensively cultivated with sunflower, wheat and corn. Storm events were centre of our attention during this research, whilst weekly sampling was also done out of the storm periods. Previous mesurements have shown that the concentration of some molecules such as aclonifen, isoproturon, linuron, chlorotuluron, metolachlor and tebuconazole recorded during these periods revealed values higher than the limit established by EU ($0.1 \mu g.L^{-1}$), particularly during flood periods.

Consequently, monitoring pesticides' displacements in surface water during flood periods carried out to pursue the following objectives:

- To determine pesticide levels in the different fractions (dissolved phase, suspended matter) and their variation during flood events.
- To understand the role of different controlling factors (flow, TSM, POC, DOC, pH, EC) on the transfer of pesticides and their distribution between different phases.
- To determine the relationship between concentration and discharge, in order to understand the principal processes of transport.
- To assess the contribution of different stream flows in exporting of pesticides into the river.

- To calculate the flux of each pesticide and their controlling factors during a whole period of study and estimate the contribution of storm and base flow to annual flux.
- To estimate the coefficient of distribution K_d (dissolved / particulate) for different molecules and verify its evolution based on the value of K_{ow} (listed in literature).

This thesis is divided into six parts

The first chapter is an introduction on pesticide and its interactions in environment.

The second chapter is dealt with the methodology, explaining how the field study and analysis were carried out.

Chapter three is the part where the spatial variation of pesticides during two sampling campaigns in Auradé catchment in the first and at the end of our observations is illustrated. Temporal variation of pesticides and their controlling factors in Save and Auradé watersheds are also demonstrated in this chapter.

The Fourth chapter presents the results of storm's hydrograph separation in the first part, then evolution of hysteresis pattern for controlling factors and molecule of pesticides was elaborated in the second part of this chapter. In the third part the relationship between different stream components with pesticides and their controlling factors was explained.

Chapter five is devoted to flux calculations during storm and base flow. Although, the value of flux only contributed to 4 storm periods in Auradé catchment. The result of specific flux to comparing between Save and Auradé watersheds was also investigated in this chapter. Finally to better understand the partitioning of the molecules in dissolved or particulate phase, the relationship between coefficient of distribution (K_d) and Octanol/Water coefficient (K_{ow}) was established.

Introduction Générale

Les pesticides sont des substances utilisées pour lutter contre les ravageurs des plantes, animaux, insectes ou champignons et contre les végétaux concurrentiels des cultures qui posent de sérieux problèmes aux activités humaines, en particulier dans l'agriculture (Gouy, 1993). Les herbicides sont le principal groupe de pesticides qui sont utilisés fréquemment pour conserver l'état du sol et protéger les cultures en place dans la phase initiale de leur développement. Les fongicides constituent la deuxième catégorie de pesticides utilisés en terme de fréquence pour lutter contre les champignons. Les phénylurées substituées, les s-triazines, les anilides, les chloroacétamides et les s-triazoles constituent les familles de pesticides les plus fréquemment utilisées dans la zone d'étude (Sud Ouest de la France) sur le maïs, le blé d'hiver, le tournesol et le colza. Ainsi, une grande quantité de pesticides utilisés peut entrer dans les systèmes aquatiques par les apports d'eau dus à la pluie ou à la neige et plus particulièrement en hiver et au printemps. Cette étude porte donc sur le comportement de ces familles de pesticides dans deux types de bassins versants du sud ouest de la France.

Les résultats des études précédentes ont montré que de nombreux types de pesticides et de métabolites de ceux-ci ont été détectés dans divers compartiments aquatiques, même pour des pratiques agricoles normales (Martin et al., 2003). Dans ces conditions d'usage, le mécanisme de leur transport et l'impact de ces activités agricoles restent mal connus (Louchart, 1999; Gouy et al., 2000). La concentration des pesticides et le transport de ceux-ci dans les cours d'eau, en particulier par les eaux de ruissellement en période de crue ont été étudiés par quelques chercheurs (Ng and Clegg, 1997 ; Borah et al., 2002 ; Holvoet et al., 2007; Rabiet et al., 2010). Cependant, aucun n'a vraiment étudié le phénomène en fonction des débits caractéristiques de la crue et donc on connaît peu l'itinéraire principal des produits pesticides dans ce transfert du champ au cours d'eau et par conséquance la contribution des differants écoulements (ruissellement, écoulement hypoderemique et nappe) au transfert fluvial. La décomposition de l'hydrogramme de crue est utilisée comme un moyen d'estimer la contribution de chaque composante durant chaque événement. Des relations ont déjà été mises en évidence antérieurement entre certaines phases particulaires ou les éléments solubles et les différentes composantes de l'écoulement fluvial (Probst, 1985; Kattan et al., 1986; Probst et Bazerbachi, 1986), mais aucune jusqu'à présent sur les pesticides.

Les eaux naturelles contiennent des matières en suspension, des matières organiques dissoutes et inorganiques ainsi que de nombreux élements biogènes. En conséquence, les interactions entre les teneurs en ces constituants et les molécules de pesticides présentes sont importantes pour mieux comprendre le transfert des pesticides, en particulier ces interactions sont controlées notamment par les propriétés physico-chimiques des pesticides tels que l'hydrophobicité (log K_{ow}) et le coefficient de distribution des pesticides entre differentes phases (coefficients K_d, Mc Bride 1994). Une attention particulière est accordée à l'estimation de ces coefficients de distribution des pesticides en période de crue lorsqu'une grande quantité d'élements dissous et particulaire, TSM, POC et DOC, éléments vecteurs pour le transport des pesticides est présente (Mahler et al., 1999; Spark et Swift, 2002; Voice et Webber, 1993; Thouvenin et al., 2007). Ainsi, la distribution des pesticides dans la phase particulaire et la phase dissoute peut être évaluée en utilisant les valeurs de K_{ow} de la littérature. Comme cette distribution de pesticides entre les phases particulaires et dissoutes dépend des fractions organiques respectives, la différence de sorption peut être aussi décrite en terme de partition organique représentée par le coefficient C-normalisé K_{oc} (Chiou et al., 1979). Une relation entre les valeurs de K_{ow} et de K_{oc} a sauvent été établie par differents auteurs (Karickhoff, 1979; Kenaga and Goring, 1980; Lyman et al., 1982). Quand la contribution du carbone organique est faible comme c'est le cas dans notre zone d'étude, l'approche de la répartition du pesticide entre les deux phases peut être ramenée au calcul du K_d pour l'épisode de crue par une valeur basée sur les différents flux permettant une nouvelle représentation de ce phénomène, plus réaliste et plus proche de la réalité hydrologique.

La présente étude a été réalisée dans le bassin hydrographique de la Save et un de ses sous-bassins, i.e., le Montoussé à Auradé, près de Toulouse. C'est une zone de culture intensive de tournesol / blé en rotation et de maïs en monoculture. L'objectif est ici d'étudier les périodes de crues, même si un échantillonnage hebdomadaire est fait en dehors de ces périodes. Les premieres mesures des concentrations de certaines molécules telles que l'aclonifène, l'isoproturon, le linuron, le chlorotuluron, le métolachlore et le tébuconazole enregistrées durant ces périodes ont révélées des valeurs supérieures aux limites établies par l'Union européenne ($0.1 \mu g.L^{-1}$) notament en periode de crue. Ainsi le suivi de l'évolution du transfert des pesticides vers les eaux de surface au cours de ces périodes de crue devrait nous permettre de :

- Déterminer le niveau de concentration de pesticides dans les différentes fractions (phase dissoute, les matières en suspension) et leur variation pendant la période de crue.
- Comprendre le rôle des différents facteurs de contrôle (débit, TSM, POC, DOC, pH, CE) sur le transfert des pesticides et leur répartition entre les différentes phases.
- Déterminer la relation entre les concentrations et les débits, afin de comprendre les principaux processus de transfert des pesticides.
- Evaluer la contribution des différentes composantes de l'écoulement fluvial dans l'exportation des pesticides dans la rivière.
- Calculer le flux de chaque pesticide et des facteurs de contrôle sur la période d'étude et estimer la contribution des périodes de crue et de débit de base au flux total annuel.
- Estimer le coefficient de distribution K_d (dissous / particulaire) pour les différentes molécules et mettre en évidence sa relation avec le paramètre K_{ow} caractérisant l'hypophilie de ces molécules.

Ce travail de Thèse est divisé en six parties.

Le premier chapitre est une introduction sur les pesticides et sur leurs interactions avec l'environnement. Le second chapitre est consacré à la méthodologie concernant l'étude sur le terrain et les analyses. Le chapitre trois est la partie traitant de la variation spatiale des pesticides durant deux campagnes sur le site d'Auradé effectuées en début et fin d'étude. On aborde aussi dans ce même chapitre la variation temporelle des pesticides et les facteurs de contrôle pour les bassins versants de la Save et d'Auradé. Le quatrième chapitre est divisé en3parties : dans la première partie on présent les résultats sur la séparation des hydrogrammes de crue. Dans la deuxième partie, on montre les résultats sur l'évolution des facteurs de contrôle et des molécules de pesticides. La troisième partie est consacrée à l'explication des relations entre des débits des differentes composantes de l'écoulement et les molécules de pesticides et leurs facteurs de contrôle. Le cinquieme chapitre est consacré au calcul des flux durant les crues et le régime de base. Bien que la valeur du flux soit basée sur 4 périodes de crues sur Auradé, les résultats des flux spécifiques ont été comparés entre les bassins versants de la Save et d'Auradé dans ce chapitre. A la fin de ce chapitre on aborde la relation entre K_d et K_{ow} tiré de la littérature pour mieux comprendre le transfert et apporter des éléments pour une modelisation ultérieurement dans l'équipe.

Chapter I

Pesticides in the environment

(Literature review)

Chapter I

Pesticides in the environment (Literature review)

Introduction

The first part of this chapter out lines in brief, the definition of pesticides suggested by some official organizations. In the second part, history of pesticides use is adumbrated. Moreover, classification and market status of pesticides will be highlighted. In the following part pesticide's life cycle and the main factors such as runoff and stormwater, playing undeniable roles in pesticide's fate and behavior in the environment, will be of our interest.

I: Pesticide history, classification, market and use

1 General knowledge

1.1 Pesticides' definitions

The name of pesticide is derived from the Latin words *pestis* (pestilence, plague) and, *caedere* (to kill). According to the definition used in the Joint FAO/ WHO food standards programme a pesticide is:

"*any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport (FAO, 2002)*".

According to Directive 91/414/EEC of 15 July 1991 (EEC, 1991) pesticide is one or more active substances which are designed to:

- protect plants against all harmful organisms or to prevent them from harmful actions,
- influence the life processes of plants,
- conserve the plants,
- destroy parts of plants, check or prevent undesired growth.

In 2002 ACTA the French Association to Coordination of Agricultural Technique has denoted the pesticides are substance that apply to fight against pests, pest control and protection, under different names, are used to identify chemicals and minerals and sometimes a majority in the form of synthetic organic compounds that applied to plants growth.

The term «**pesticide residues**» describes the surplus substance present in the environment or in products following the use of a pesticide. This term covers both the compound and its degradation products.

1.2 Historical context of pesticide use

Humans battling to eradicate pests and protecting crops date back to the twentieth century. Sulfur is known to be the very first chemical used in Mesopotamia some 4500 years ago.

No noticeable progress in using and discovering new substance was traced in history until 15th century when the campaign against harmful pests gained momentum. By then till 17th century number of toxic chemicals such as arsenic, mercury and lead were used to safeguard crops from harmful pests. Nicotine, a substance contained in tobacco, was employed as an insecticide, for the first time in the 17th century. Some more natural pesticides such as pyrethrum, rotenone were introduced to combat harmful pests in the 19th century (Miller, 2002). The mid-twenty century appears to make something of turning point in the compaigns against harmful pests. Arsenic derived pesticides were, until 1950, the most commonly used of all chemicals (Ritter, 2009). DDT was recognized to be a highly effective insecticide. And, organochlorines were dominant chemical substances in use in the U.S. from mid 1970s, organophosphates and carbamates and their derived substances like pyrethrin compounds were among the dominant insecticide used in the U.S. Herbicide utilizations have become widespread in 1960s. However, in 1962 the Silent Spring, written by Rachel Carson, was published. Carson’s book focused public attention on the problem of pesticide and other chemical pollution. Table I, presents a chronology of pesticides development suggested by Stephenson and Solomon (1993).

Table I- Chronology of pesticides development by Stephenson and Solomon (1993).

Period / year	**Uses of pesticides**
1500 BC	Egyptians produced insecticides against lice, fleas and wasps.
1000 BC	The Greek poet Homer referred to a pest-averting sulphur.
200 BC	The Roman writer Cato advises vineyard farmers to burn bitumen to remove insects.
Early 1700s	John Parkinson, author of Paradisus, the Ordering of the Orchard' recommended a concoction of vinegar, cow dun and urine to be put on trees with canker.
1711	In England, the foul smelling herb rue was boiled and sprayed on trees to remove cantharid flies.
1763	In Marseilles, a mixture of water, slaked lime and bad tobacco was a remedy for plant lice.
1821	London Horticultural Society advised that sulphur is the remedy for mildew on peaches.
1867	The beginning of modern pesticide use. Colorado beetle invade US potatoes crops and arsenic is applied.
Late 1800s	French vineyard growers have the idea of selective weed killers.
1892	The first synthetic pesticide, potassium dinitro-2-cresylate, marketed in Germany.
Early 1900s	Insecticides, fungicides and herbicides have all been discovered. Inorganic substances introduced.
1932	Products to control house hold pests marketed.
1939	Muller discovered the powerful insecticides properties of DDT.
1945	After the Second World War, farming intensity intensified production.
1950s	Geigy introduces the carbamates.

Generally, producing pesticides capable of distorting pest without harming plants in the environment has always been a challenge for the manufactures.

New pesticides are being developed, including biological and botanical derivative and alternative that are thought to reduce health hazard and environmental risks. In addition, applications are being encouraged to consider alternative controls and adopt methods that reduce the use of chemical pesticides.

Today, environmentally friendly pesticides can be manufactured so that to target a specific pest's life cycle only.

1.3 Pesticides classification

The pesticides on the market today are characterized by a multiplicity of chemical structures, functions and activities that making their classification difficult. In general, pesticides are classified based on different criteria such as:

- Chemical structure
- Active substances
- Specific use of the pesticide

1.3.1 Classification based on chemical structure: inorganic, organic and botanical

- **Inorganic pesticide**

Some pesticides do not have carbon in their formulae. These compounds usually have relatively low molecular weight and often contain less than 10 atoms.

These types of pesticides are derived from mineral deposit and chemical compounds which are very stable in the nature. A few inorganic pesticides have been used for more than 1000 years but their use increased dramatically from 1850 to 1950. The popularity of many inorganic pesticides declined after the development of more effective and less persistent organic pesticides. In the past, people were quick to adopt any treatment that would control pests and increase food supply. These inorganic pesticides containing lead-mercury- arsenic have been banned, on the grounds that they will harm the environment. And they now constitute only small part of the pesticides in use. Examples of inorganic pesticides are:

- Arsenical pesticides (Paris green)
- Fluoride insecticides (Cryptile)
- Inorganic herbicides (Borax)
- Inorganic fungicides (Bordeaux mixture)

- **Organic pesticide**

Organic pesticides include a wide rang of pesticides in use today. They have carbon atoms and may contain other elements such as oxygen, hydrogen, phosphorus, sulphur and many more. Some of these pesticides are extracted from plants however most of them are synthetically produced.

- **Botanicals**

The botanical pesticides are the pesticides which are extracted from various parts of the plants as stems, seeds, roots, … . Many of botanical pesticides act as stomach poisons, and some of the botanical insecticides have a short residual activity and do not accumulate in the environment. Some of the examples of this category are nicotine, rotenone.

1.3.2 Classification and active chemicals

According to the active substances used in the chemical formula pesticides can be classified as:

- organochlorine (DDT, dieldrin,…)
- organophosphates (parathion, malathion,)
- carbamate (carbaryl, aldicarb, …)
- phenoxyacetic acid herbicides: (2.4-D, MCPA,)
- substitute urea: (chlorotoluron, isoproturon, …)
- triazine herbicides: (simazine, atrazine,…)
- pyridinium herbicides: (paraquat, Diquat,…)

Existence of a wide rang of pesticide families some of which contain several active substances to combat two or more group of parasites, make their classification a real challenging task.

1.3.3 Classification and pesticide -specifity

The growth and reproduction of parasites can be suppressed by applying specific pesticides. The three main families of pesticides are: herbicides, fungicides and insecticides.

Herbicides are the most widely used pesticides in the world. They are intended for elimination of grass that competing with the crops. Herbicides act on plants in a variety of ways. For example they can inhibit : photosynthesis (atrazine, terbuthylazine, isoproturon), cell division (trifluralin, pendimethalin), lipid synthesis (family of cyclohexanediones , like cycloxydime), cellulose synthesis (chlorotiamide), amino acid synthesis (glyphosate) (Record, 1965 ; Gunsolus et al., 1999).

Fungicides fight the spread of plant disease caused by fungus or bacteria. Like herbicides, fungicides act on plants in different ways. They can inhibit: respiration (transfer inhibiter of ATP, like silthiofam), cell division (benomyl), biosynthesis of amino acids or proteins (it is essentially the family of anilinepyrimidines like, cyprodinil), disturb the metabolism of carbohydrates (fludioxinil) (Fairbanks et al., 2002; Dane and Dalgic, 2005).

Insecticides are used to protect plants and animals from harmful insects by eliminating them or preventing them from reproducing. There are various types including: neurotoxins (i.e. sodium channel blocking, like oxadiazines family (indoxacarbe), growth regulators (teflubenzuron), cell respiration inhibitors (inhibit of oxidative phosphorylation like tha accaricide family as cyhexatin), (Aamlid et al., 2007; James et al., 2008; Demicco et al., 2010).

Apart from these main pesticide families, some others can be included in table II:

Table II- The most common classification scheme based on the pest group control.

Pesticide Group	**Pest controlled**
Acaricide	Mites, ticks, spiders
Avicide	Birds
Bactericide	Bacteria
Fungicide	Fungi
Herbicide	Weeds
Insecticide	Insects
Miticide	Mites
Molluscicide	Snails, sluge
Nematicide	Nematodes
Piscicide	Fish
Predacide	Vertebrate
Rodenticide	Rodents

1.4 The Market for pesticides (Current Status)

Today, pesticides are conclusively identified as the main source of surface and groundwater contamination and have become a major environmental preoccupation in Western Europe (Albanis et al. 1998). In sum, market of pesticides was 33 390 billion dollars in 2007. The contribution of each continent is: Europe (10 568), Africa (1 330), Latin America (6 170), North America (7 507), Asia (7 815) in billion dollars. And the market of different category of pesticides is: herbicides (16 115), Fungicides (8 105), insecticides (8 016) and others (1 154) in billion dollars, the percentage value was demonstrated in figure 1.

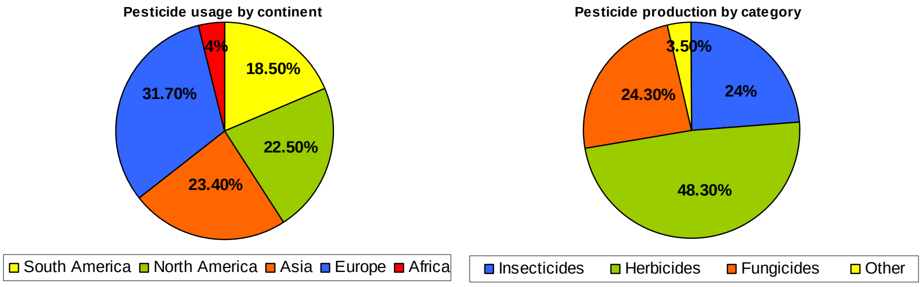


Figure 1- Current status of pesticide's market by continent and by category of pesticides in billion euros.
((U.I.P.P.http://http://www.uipp.org/var/uipp/storage/original/application/eac46ae8e554ec913d206818f33e57c0.pdf).

Of the total amount of pesticides used in the world the quantity of herbicides accounted for the largest part, followed by insecticides, fungicides and other pesticides. In fact, pesticides are among the substances liable to harm both human health and the environment. This problem is all the more pressing in France, as it is the world's third largest utilizer of pesticide products, behind the United States and Japan. France, due to the vast agricultural area which represents more than half of its territory, is the largest European consumer of pesticides followed by Germany and Italy (figure 2).

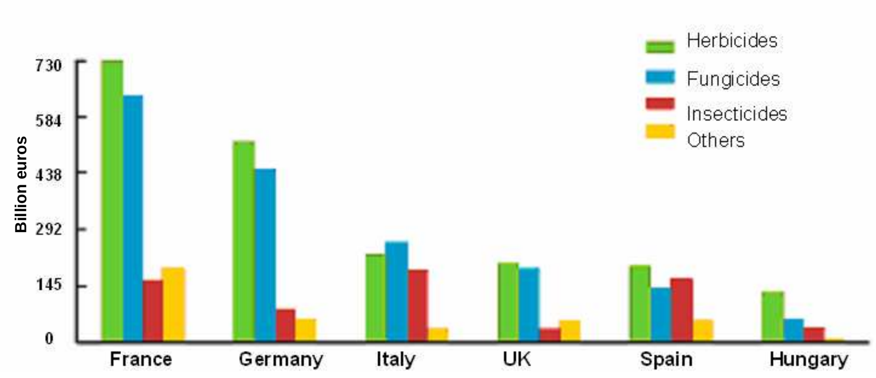


Figure 2- Distribution of pesticide market (billion euros) in Europe in 2006.
(U.I.P.P.http://http://www.uipp.org/var/uipp/storage/original/application/eac46ae8e554ec913d206818f33e57c0.pdf).

1.5 Pesticide usage and consumption

1.5.1 General context

Over the past 10 years there has been an increasing awareness about nonpoint source pollution and the potential linkage to agriculture. According to the status list of active substances available commercially in the EU, more than 1.100 pesticide substances to combat harmful organisms (pests) are currently registered (Huskova et al. 2008). However, reliable data on the usage of pesticides in any country is not easily available as manufacturers are reluctant to disclose such information. In developing countries, data is even sparser since records are often incomplete and there is little government control on the use of pesticides (Wilson and Tisdell, 2001). Observations of pesticide occurrence in streams and lakes adjacent to agricultural fields have prompted much discussion about whether to ban or greatly restrict agricultural activities that would potentially impair water quality.

1.5.2 National context

France ranks 3rd after the USA and Japan in the use of pesticide with around 110, 000 tonnes of active substances consumption annually. In agriculture, there are more than 6000 varieties of pesticides produced from 800 different active substances. 400 of these active substances are used to manufacturing pesticides in France (IFEN, 2006).

France is also the first agriculture producer in Europe (21.7% of the total production in Europe) and it is the top corn producer, and very big herbicide utilizer (42.7% of the total production in Europe) (Miquel and Revol, 2003). The quantities consumed in France are nonetheless equivalent to average European countries per hectare, that is to say 4.4 $kg.ha^{-1}$. Which is quite a considerable amount comparing to Portugal which does not consume more than 1.9 $kg.ha^{-1}$ whereas the Netherlands is the bad European fellow utilizing 17.5 $kg.ha^{-1}$.

The quantity used in France is hence important and consequently we find these quantities in aquatic ecosystem accordingly; and this is why the French Ministry of Ecology and Sustainable Development (Ministère de l'Ecology et du Development Durable (MEDD)) asserts in a recent report that pesticide contamination will be a major problem in terms of pollution of the natural waters in the years to come (MEDD, 2003).

1.5.3 Regional context

The Garonne is the most important river of southwestern France and its watershed covers 57 000 km^2. In fact, there is a long history of agricultural development in this catchment

(Fortuné, 1988). Forest area was gradually replaced by agricultural land in the Garonne river valley along with its main tributaries in the eighteenth and nineteenth centuries (Chauvet and Décamps 1989). In sum, the Garonne watershed undergoes permanent agricultural activities which make the degree of pesticides contamination in this region high (figure 3). The major tributaries of Garonne are the Ariege, Tarn and Lot on the rightside of Garonne, and the Gascogne rivers (Gers, Baïse, Save) on the leftside.

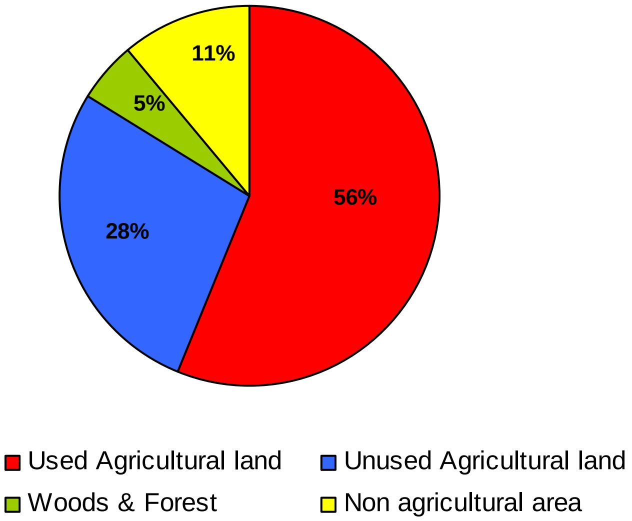


Figure 3- Distribution of land use in Garonne watershed.
(Agreste- Statistique agricole annuelle, 2007).

Among these cultivated land:

30% Cereals/ Wheat, Corn…

10% Proteaginous and Oleaginous plant: Sunflower, Rapeseed…

II: Pesticide's Movement

2 Transfer of Pesticide

2.1 Pesticide life cycle

Pesticides are active substances that are directly released to the environment during and after the use phase of their life cycle. During application, the mechanism for off-target movement is primarily direct aerial drift and volatilization. After deposition within the target site, numerous biological, physical and chemical processes determine the fate of the chemical (figure 4). Certain combination of soil properties and chemical characteristics (e.g. high infiltration) promote vertical movement in the soil profile, increasing the chance of movement to groundwater, but decreasing surface runoff potential. Similarly, when the physical characteristics of the site promote surface runoff (e.g., heavy soil with low infiltration), overland surface transport of the chemical becomes more likely. During runoff, pesticides may be transported in either water or soil phase or both but this significantly depends on the characteristic of pesticides. Insoluble, hydrophobic chemicals with a solubility < $1 mg.L^{-1}$ are tightly bound to soil, and most or all loss occurs in the particulate phase. Off-target movement of chemicals is both an ecological and human health concern. Sensitive ecosystems are often adjacent to agricultural lands and minimization of pesticide runoff is needed for the protection of such resources. There are several factors and processes playing important role in the fate and movement of pesticide that pointed out in table III.

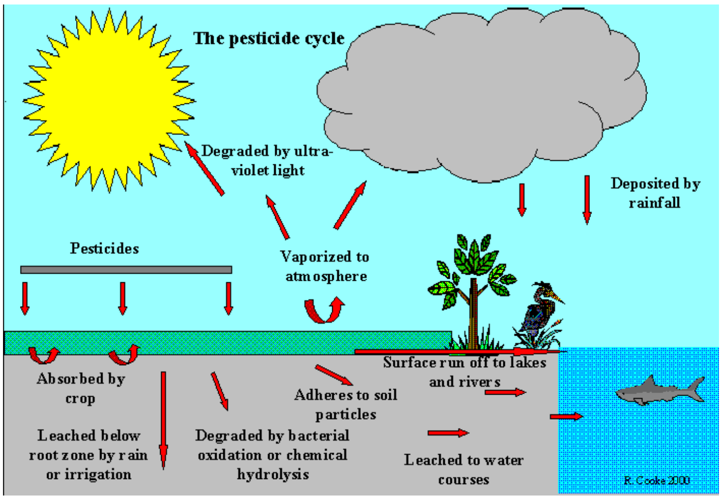


Figure 4- Cycle of pesticide in the environment.
(http://www.bestchoicemall.com/howtomakecompostguide/pesticide%20cycle.gif)

2.2 Behavior and fate of a pesticide in the environment

The behavior, transport and fate of an organic chemical in environment are controlled by the properties of the chemical and the environmental conditions. The structure of the organic chemical determines its physical, chemical and biological properties.

The environmental processes that control an organic chemical's behavior and fate of the pesticides can be classified into three types in figure 5 according to Cheng (1990):

- transformation processes which change its chemical structure
- transport processes which move it away from its initial point of introduction to the environment and throughout the surface water system
- retention

2.2.1 Transformation processes

The transformation of a pesticide results in changes in its chemical structure. Producing one or more new chemicals would lead to the disappearance of the original pesticide. These new chemicals can be organic or inorganic molecules and ions.

Microbial breakdown is the breakdown of chemicals by microorganisms such as fungi and bacteria. Biodegradation or microbial breakdown is the only transformation processes able to completely mineralize the pesticide (Alexander, 1981). Microbial breakdown tends to increase when: temperature is high, soil pH is favorable, soil moisture and oxygen are adequate and soil fertility is good.

Chemical breakdown is the breakdown of pesticides by chemical reactions in the soil and can cause structural changes in an organic chemical. The rate of change and type of chemical reaction that occur are influenced by the binding of pesticides to the soil, soil temperatures, pH levels and moisture.

Photodegradation is the breakdown of pesticides by sunlight. All pesticides are susceptible to photodegradation to some extent. The rate of breakdown is influenced by the intensity and spectrum of sunlight, length to exposure and the properties of the pesticides. Immediately after application, pesticides will undergo biotic and abiotic processes that lead to their, more or less complete degradation. The major physical transformation is the photodecomposition by ultraviolet radiation. The majority of the pesticides have the maximum absorption between 200 and 400 nm.

2.2.2 *Transport processes*

In fact the environmental behavior of a pesticide is affected by the natural affinity of the chemical of one of four environmental compartments (Calamari and Barg, 1993): solid matter (mineral matter and particulate organic carbon), liquid (solubility in surface and soil water), gaseous form (volatilization), and biota. This behavior is often referred to as «Partitioning» and involves, respectively, the determination of the soil sorption coefficient (K_{OC}), solubility (S_W), Henry's Constant (H), and the n-octanol/water partition coefficient (K_{OW}). These parameters are well known and enable us to predict the environmental fate of the pesticide.

Pesticides, like other chemicals can be affected just as they can affect the environment depending on the type of pesticide and the conditions of the environment. Generally, the changes can be classified as physical and non-physical reactions that determine the fate of pesticide. Usually pesticides are transferred from one environment to another without any change if the factors causing the movement are physical, such as drift, volatilization, …. . However, through non physical processes such as photochemical, microbial, and chemical and metabolism, pesticides will be degraded.

2.2.3 *Retention*

The term «retention» is most frequently equal with adsorption or simply sorption. And the term adsorption reffered to attraction of a chemical on the surface for a longer or shorter period of time depending on the affinity of the chemical to the surface. As an example, Hamalker and Thompson, (1972) have paied especial attention to the retention processes on pesticides in soil system.

Thus, a set of such physical and biochemical processes is determined the final environment fate of a pesticide.

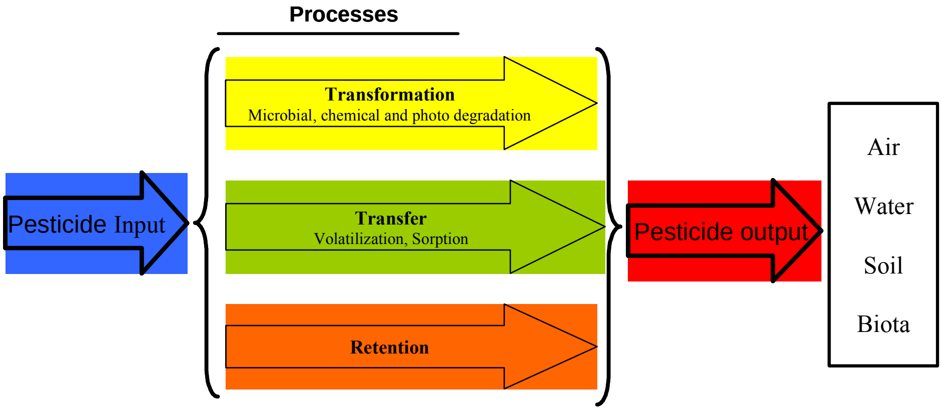


Figure 5- Behavior and fate of a pesticide in the environment.

Table III- Transfer and degradation processes controlling the movement and fate of organic chemicals like pesticide.
(Source: Marathon-Agricultural and environmental consulting, Inc.1992. Video cassettes-Fate of pesticides in the Environment, box 6969, Las Cruces, NM 88006).

Process	Consequence	Factors
Transfer (processes that relocate organic chemicals without altering their structure		
Physical drift	Movement of organic chemical due to wind action	Wind speed, size of droplet
Volatilization	Loss of organic chemical due to evaporation from soil, plant or aquatic ecosystems	Vapour pressure, wind speed, temperature
Adsorption	Removal of organic chemical by interacting with plant , soils, and sediment	Clay and organic matter content, clay type, moisture
Absorption	Uptake of organic chemical by plant roots or animal ingestion	Cell membrane transport, contact time
Leaching	Translocation of organic chemical either laterally of downward through soils.	Water content, macropores, soil texture, clay and organic matter
Erosion	Movement of organic chemical by water or wind action	Rainfall, wind speed, size of clay and organic matter particles with adsorbed organic chemicals
Degradation (processes that alter the organic chemical structure)		
Photochemical	Breakdown of organic chemicals due to the absorption of sunlight	Structure of organic chemical intensity and duration of sunlight exposure
Microbial	Degradation of organic chemicals by microorganisms	Environmental factors (pH, moisture, temperature) nutrient status
Chemical	Alteration of organic chemical by chemical processes such as hydrolysis, and redox reaction	High and low pH, same factors as for microbial degradation
Metabolism	Chemical transformation of organic chemical after being absorbed by plants or animals	Ability to be absorbed, organism metabolism, interactions within the organism

Vryzas et al. (2007) and Arias-Estévez et al. (2008), have reported that the mobility of pesticides in soil, and hence their bioavailability and transfer to other environmental compartments, depend on a variety of complex dynamic of physicochemical and biological processes, including sorption-desorption, volatilization, chemical and biological degradation, uptake by plants, runoff and leaching. However, catchment's variables influencing runoff include the gradient of the land on which pesticides have been sprayed, crop type, organic carbon in the soil, the size of the cropped area and the vegetation type and density of buffer strips that lie between agricultural land and water body. It is also dependent on the application and physicochemical properties (such as solubility) of the pesticides.

Himel et al. (1990) pointed out the essential characteristics to study the fate and transport of pesticides in environment are:

- **in physical level**
    - saturation vapor pressure
    - solubility in water (in mg.L^{-1} in special temperature)
    - distribution coefficient (k_d)
- **in chemical level**
    - ionic states (cationic, anionic, basic and acidic)
    - hydrophilic and hydrophobic characters
    - chemical, photochemical and biological reactivity

2.3 Most important factors playing a major role in the fate of pesticides in detail

As it is mentioned before survival and movement of pesticides in water depend on factors such as soil and geologic properties, climate, and also properties of the pesticides. By studying these factors one can determine the best strategy to tackle pest problems in the water.

2.3.1 Pesticides properties

- **Physical properties**

Pesticides are found in groundwater or surface water. Properties such as adsorption capacity, persistence, solubility and volatilization will determine whether pesticides can leach through layers of the soil and get into groundwater or they can stay on the surface and get into runoff.

- **Adsorption property of pesticides**

This process takes place when pesticides sprayed on the soil surface adhering to the soil particles and organic matters. The degree of soil adsorption depends on the characteristics of the latter. A fine soil enjoys a higher degree of adsorption due to its higher specific surface area than a course soil. A pesticide that is strongly adsorbed is lost mostly with sediment during runoff and is less apt to leach to ground water. Pesticides that are moderately or weakly adsorbed are lost mainly in surface runoff water and more likely to leach. Absorption may be the most important chemical characteristic determining environmental fate.

- **Solubility property of pesticides**

This process shows the capacity of a pesticide or a chemical to dissolve in water. Solubility is often expressed in milligrams per liter ($mg.L^{-1}$) or parts per million (ppm). Pesticides with high degree of solubility enjoy greater tendency to pass through the soil and reach to groundwater. Others with solubility of less than 1.0 $mg.L^{-1}$ are normally strongly adsorbed or attached to sediment and loss to surface waters via soil erosion and is the primary environmental concern. There is another limit for this classification proposed by Wauchope (1978) who estimates that pesticides having water solubility (S_w) greater than 10 $mg.L^{-1}$ are lost mainly (>50%) in the water phase of runoff, and those with smaller S_w come off of fields in runoff mainly adsorbed to sediment. Water solubilities of pesticides are among the most important physical properties controlling the transport and fate of the chemicals in aquatic systems (Chlou et al., 1986).

- **Persistence property of pesticide**

Persistence is the property of pesticides through which it is determine how long they can survive in the environment. The degree of persistence determines by the length of time a pesticide can survive in the environment and also its effective durability in combating the target pests. Persistence can be expressed in terms of half-life, or the time required for one-half of the pesticide to discompose to products other molecule than the original pesticide. Pesticides with long degradation half-lifes will typically have greater annual pesticide losses in runoff than pesticides with smaller half-lifes due to the longer «key period» where significant amount of pesticides and precipitation occur (Leonard, 1990).

- **Volatilization property of pesticide**

Volatilization takes place when a pesticide vaporizes into the air. This gas is usually not a direct threat to water supplies, although pesticide volatilization may harm off-target plants or contribute to pesticides in rain water. Volatilization can reduce the total amount of chemicals available for movement to ground or surface water.

The rate of volatilization is related to the size of the molecules, i.e. as measured by the molecular weight. Usually volatilization is described as an equilibrium transfer between the gas phase and water phase. The ratio of the chemical concentration in the gas phase and in the water phase is formulated by Henry's constant (Schnoor, 1996).

2.3.2 Chemical properties

Chemical structure of a pesticide plays an important role in their survival and movement in the environment. Pesticides can be divided into the following chemical categories:

- **Hydrophilic and hydrophobic pesticides**

Hydrophilic compounds have an affinity to water and are usually charged or have polar side groups to their structure that will attract water, while hydrophobic compounds are repelled by water.

These two characters play a major role in adsorption and desorption of pesticides in water. The n-octanol/water partition coefficient (k_{ow}) is an index to determine the hydrophilic or hydrophobic characteristic of the organic molecules like pesticide. This parameter describes the equilibrium partitioning of a chemical between octanol and water phases.

Octanol/Water coefficient (k_{ow}) gives us a measure of the hydrophobicity of an organic molecule, Bacci et al. (1994). Bacci in 1994 has reported that all those chemicals having a k_{ow} greater than 3 are hydrophobic. This parameter is also used to describe the intensity of pesticide sorption reaction. In other words, the octanol–water partition coefficient is used to estimate bioconcentration in aquatic organisms, concentration ratios for transfer between soil and plants, transfer factors between animal feed and animal products (meat and milk) and other physical parameters. High K_{ow} values are usually related to significant bioconcentration effects where organisms accumulate significant quantities of a compound in their tissue.

- **Ionizable pesticides**

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. Ionizable pesticides comprise a significant proportion of both existing and new active substances registered for use in agriculture worldwide. This group of pesticides includes chemicals that are frequently found in groundwater and surface waters in many different countries. Despite this, approaches to predict the influence of soil properties on the behavior of ionizable pesticides in soils are poorly developed.

2.3.3 Climatic factors

In addition to properties of pesticide, environmental factors also affect the life and movement of pesticide and are important in determining the amount of pesticide loss to surface or ground water (Leonard, 1990).

- **Rainfall duration / amount**

The amount and duration of rainfall influence the total volume of runoff and percolation and they also determine the quantity of chemical washed off the plant surfaces. The greater the rainfall amount and duration is the greater the potential runoff of a pesticide will be.

- **Rainfall intensity**

As rainfall intensity increases, runoff rate is increased and more pesticide is detached from the soil surface into runoff. Lower intensity storms may move the pesticide into the soil before runoff begins. The amount of soil water present prior to rainfall will affect the amount of pesticide moved by runoff. The amount of pesticides loss caused by runoff is greater when the runoff gets momentum during a storm event.

- **Rainfall timing**

The closer the rainfall events take place following application of the pesticide, the greater the potential for leaching or runoff.

2.3.4 Soil and geologic properties

The movement of pesticides to surface or groundwater is depending on the characteristic of a site. The site characteristics include: hydrologic soil group, soil permeability, organic matter, soil erodibility, soil texture, soil pH, flooding potential and the nature of the geological formations and depth to ground water.

According to hydrologic soil group, soils are categorized into four hydrologic groups (A, B, C, and D).

- **Soil permeability**

Permeability is a physical characteristic of a soil and is a measure of the ability of the soil to let the water pass under saturated conditions and through the natural voids that exist in the soil. Permeability is a function of soil texture, mineral and organic composition. In contrast 《porosity》 is the measure of the amount of void space in a soil; However, permeability refers to the extent to which the porosity is made up of interconnecting voids that allow water to pass through the soil. Soils that are less permeable have greater potential runoff compared to highly permeable. Kalkhoff et al. (2003) pointed out that soil permeability may influence the delivery of water and pesticides to streams and affects runoff and base flow conditions.

- **Soil erodibility**

Soil erodibility is an indicator of a soil's susceptibility to raindrop impact, runoff, and other erosive processes. Practices that reduce soil erosion and sediment transport will reduce the amount of pesticide loss if the pesticides in question enjoy high degree of adsorption to soil particles.

- **Soil texture**

Soil texture is used to describe the relative proportion of different grain sizes of mineral particles in a soil. Particles are grouped according to their sizes into what are called soil textures. These separates are typically named clay, silt, and sand. Soil texture classification is based on the fractions of soil separates present in a soil. The soil texture triangle is a diagram often used to figure out soil textures. Soil texture plays an important role in leaching or runoff of pesticide phenomenon. A soil with high clay content will have higher potential for runoff and less potential for leaching compared to a coarse textured, sandy soil. On the other hand, soil with fine particles (silts and clays) has the most surface area.

- **Soil pH**

Soil pH will affect the electrical charge of certain pesticides. The electrical charge will determine the type and degree of adsorption. Soil pH can also affect the chemical and/or microbial degradation.

- **Organic matter**

The most important factor affecting pesticide adsorption in soil and water is organic matter. A soil with higher organic matter content will have more pesticide adsorbed to the soil, thus reducing detachment and leaching, but may have a higher runoff potential because more of the chemical is retained in the surface zone of the soil. Soil with high organic matter content may need higher application rates of some pesticides for best control. Organic matter content of soils may be increased by the addition of manure and incorporation of crop residues. In our study we paid special attention to this parameter and we will explain it in detail later.

2.4 Pesticide transfer in surface water

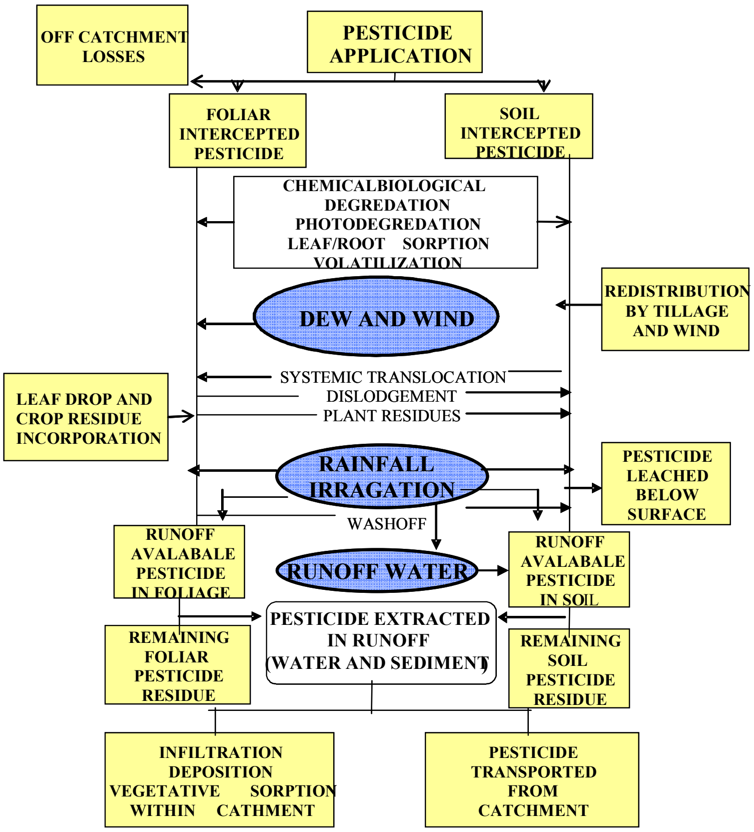


Figure 6- Processes involved in the dispersion of a pesticide in the interaction zone with stream flow according to (Leonard, 1990).

The complexity of processes involved in the fate of pesticides in the environment was illustrated in figure 6. Understanding the fate of a pesticide in the surface area is the first step to study the transfer of the pesticide by runoff.

Following application, pesticides can be moved from the target field and transferred by rainfall/ irrigation that introduced runoff and erosion into an adjacent river, stream, or lake which cause a great potential for contamination of surface water bodies. Three critical processes are included in this place:

- transfer of the dissolved pesticides from soil solution to the runoff water
- move of the pesticides sorbed onto the eroded soil particles
- transport of both dissolved and adsorbed pesticides in the stream flow from application fields to the outlet

Although the transfer of pesticides to surface water depends on many factors, such as climatic conditions, soil's characteristics, practices and management like the frequency of application, vegetated buffer zones and also the characteristic of molecules, etc; (Wauchope, 1978; Leonard et al., 1979; Leonard, 1990; Cessna et al., 1994; Pantone et al., 1996; Ng and Clegg, 1997). But two principal parameters to enter of pesticide in surface water are: ***runoff and stormwater.***

2.4.1 Runoff

There are several definitions of runoff in literature; Horton (1933) pointed out that surface "runoff is overwhelmed by overland water after failing to infiltrate". Leonard (1990) stated "Runoff is the water and any dissolved or suspended matters it contains that leaves a plot, or small single cover watershed in surface drainage". Another definition that proposed by Postel et al. (1997) is: "Runoff containing mixtures of nutrient, sediments, industrial chemicals, and pesticides have contributed to a variety of significant impact on aquatic system and it's around environment specially during stormwater when we supposed to have a large quantity of pollution".

Kookana et al. (1998) pointed out "Runoff considered worldwide as a key processes for pesticide contamination of surface water".

Wu et al. (1983) reported runoff has been shown to be a major non point source of pesticide to surface water in agricultural areas.

Ahuja (1986) and Roth and Helming (1992) have pointed out rainstorm events immediately after pesticide application lead to high losses of pesticides in runoff due to high surface water flux, high losses of sediment and high concentration in the runoff compartments. Guo et al. (2003) have reported that pesticide displacement by runoff during rainfall events is one of the major pathways for transporting pesticides from the field to the surface runoff. Franks et al. (1982) identified runoff as a predominant mechanism for the entrance of pesticide into surface water from investigation of 11 watersheds in Ontario. Bach et al. (2001) showed that surface runoff is considered to be a major source of diffuse pesticide input in Germany.

Generally speaking, in runoff water, both the dissolved and particle-bound pesticides are considered as mobile fractions. However, they may have different transport pathways. For the lateral transport, pesticides bound to particles of different sizes differ in their settling velocity and therefore their transport distances (Krein and Schorer, 2000; Walker, 2001). For the vertical transport, the water-soluble pesticides are assumed to be most mobile. However, pesticides attached to colloidal particles can also have a rapid transport pathway due to a size exclusion effect (Seta and Karzthanasis, 1997; Celis and Koskinen, 1999; Kretzschmar et al., 1999). Pesticides could also be dissolved into the runoff water either by instantaneous dissolution (depending on its solubility properties) or desorption from transported soil particles once these are in the water.

Particle transports of pesticides depend to a great extent on the affinity of pesticides to suspended particles, the release of suspended matter from the soil matrix, and the mobility of suspended particles.

The affinity of a pesticide to suspended material is closely related to the hydrophobicity of the pesticide and the content of organic matter in the suspended material. The release of suspended material is dependent on soil erodibility, water flow, water chemistry, soil management practices, and vegetation cover. The mobility of the suspended particles is mainly determined by their particle size, their stability in water and flow velocity.

2.4.2 Stormwater

Refers to an atmospheric disturbance characterized by a heavy rainfall and sometimes accompanied by snow, sleet and hail. The amount of rainfall cannot all be absorbed by the vegetation and soil. Some quantities of the rainwater stands on the leaves of the vegetation and some feed trees and plants and ultimately a part of this rainwater evaporated into the air. The remaining water runs fast under the law of gravitation and before eventually percolate into the ground and replenish the groundwater supply (ULI, 1979). In fact the accumulation of runoff in any given area is called stormwater. Storm water is capable of causing great damage and carries out lots of pollution (Makepeace et al., 1995; Lehner et al., 1999; USEPA, 2000). As an example, Frank and Sirons (1979) have reported the highest losses (60%) of the atrazine (and its metabolite) were caused by stormwater and particularly in January to April period.

Stormwater pollution has been the subject of investigation for some decades in the United States. It was in mid 1960s when the US government related agencies diagnosed stormwater discharge as a major pollution source of waterways in the country. In a report presented to Congress in 1990, National Water Quality stated that 30% of identified cases of water impurity are attributed to stormwater discharge or non point source pollution (USEPA, 1990). Recipient of stormwater may be inflicted by detrimental toxic and/or erosion effect. This harmful effect of stormwater pollution on the waterways and the need for treatment was also recognized in the 1960s by Muschak (1990).

The contaminant transport during a single storm event is often characterised by higher load in the beginning of the runoff event. This mass transport phenomenon is known as first flash (Berteand-Krajewski et al., 1998; Urbonas and Stahre, 1993). The first flush phenomenon can be described as the initial period of stormwater runoff during which the concentration of pollutants is substantially higher than those in the later stages of the storm event (Lee et al., 2002; Deletic and Maksumovic, 1998). Characteristics of the first flush are influenced by a number of factors including intensity and duration of the rainfall event, catchment size, catchment land usage and antecedent rainfall (Wanielista and Yousef, 1993). Lee and Bang (2000) have shown during the first flush, enormous quantities of pollutants are often entering into receiving water. Previous studies have also shown that the first flush phenomenon is a leading cause of degradation of the water quality (Lee, et al., 2002).

2.5 Principal parameters in pesticide’s transfer

2.5.1 Organic matters

2.5.1.1 Organic carbon pathways in streams

Total organic carbon (TOC) occurs in the form of dissolved organic carbon (DOC), particulate organic carbon (POC) and volatile organic carbon (VOC). But, the dominant form of organic carbon in the waters is the dissolved form, i.e. DOC (Dunalska et al., 2004), and considerably smaller part of TOC in water comprises POC. In fact organic matters are a very complex mixture of substances from all biological processes that occur in the watershed (Artemyev, 1996); and they will be identifiable molecules (carbohydrates, amino acids, hydrocarbons, fatty acids et phenols) and other natural macro molecules (humic substances) also phytoplankton and other plant debris (Meybeck, 1993; Hope et al., 1994; Tipping et al., 1997).

The composition of the material transported by rivers is the result of the complex interaction between various physical, chemical and biological processes that took place both in the drainage basin and the river (Hedges et al., 1986; Cummins et al., 1993).

Most of the organic material is of fluviatile origin or allochthonous includes debris leaves, wood, grasses, and the product derived from agricultural activity, also compound that enter in aquatic system by the leaching of soil (Bilby and Likens, 1979; Thurman, 1985a; Hedges et al., 1986; Hope et al., 1994; Hedges et al., 1997). Organic matter can also be produced «in situ» by physico-chemical or biological process (Sempéré, 1991). The autochthonous fraction, generally less important, is composed of products from local plankton, and presents a more labile character (Hedges et al., 1997).

2.5.1.2 Dissolved and particulate organic matter

Organic carbon in rivers and streams can be divided into two main categories (Wotton, 1994):

- Particulate Organic Carbon or POC which includes:
    - Coarse Particulate Organic Carbon or CPOC (diameter>1mm)
    - Fine Particulate Organic Carbon or FPOC (0.45 µm or micron to 1 mm)
- Dissolved Organic Carbon or DOC (<0.45 micron)

This classification of the organic matter is very often used in convenital studies in ecological river (Cummins, 1974; Cushing et al., 1993; Webster and Meyer, 1997).

The DOC is generally defined as the organic carbon passing through 0.45µm silver or glass filter and it is frequently used in the study of organic carbon (Thurman, 1985b; Hope et al., 1994). In the dissolved material, we can make subdivisions between dissolved and colloidal material, although the boundary between these two categories is difficult to establish. Colloids would aggregates with molecules grouped humic acids, organo-metalic complexes, complex mineral and organic matter.

The colloidal fraction can represent approximately 10% of the dissolved organic matter (Thurman, 1985b). The concentration of dissolved organic matter or more commonly dissolved organic carbon is highly variable and mainly depending on the geographical location of the river, its discharge, and regional climate or season of the year, the slope of the cachment and characteristics of the soil near the watershed (Spitzy and Leenheer, 1990; Nelson et al., 1993). Thurman (1985b) suggested the different rang of the concentration of DOC in mg.L^{-1} according to the climatic zone of the planet: small arctic and alpine rivers (1-5), taiga (8-25), in cold temperature climatic (2-8), temperature (3-15), arid (2-10), tropical moist (2-15), marshes and flooded areas (5-60).

The particulate organic carbon (POC) is the organic carbon retained on a 0.45µm glass fibre filter and is essentially identical to suspended organic carbon; however nominal pore sizes of filters used for particulate analysis are not accurate (Sheldon 1972). The major sources of CPOC are fallen leaves, woody debris from the catchment and water plants (Maltby, 1992; Walker et al., 1992; Allan, 1995). FPOC includes the products of CPOC breakdown, and aggregation of DOC (Meybeck, 1982; Ward et al., 1994; Robertson et al., 1996).

The concentration of particulate organic carbon may vary considerably between different rivers, and the intensity of the mechanical erosion processes have an important role and can be the orgine of particulate organic carbon (Ludwig et al., 1996). Other factors that contribute to the POC concentration in the river basin is physical characteristics (slope, geology) vegetation cover and the local animal population in the watershed (Sabater et al., 1990).

CPOC and FPOC can be consolidated into Particulate Organic Carbon (POC). The total pool of in-stream organic carbon (TOC) therefore consists of POC and DOC. This consolidated poll (TOC=POC+DOC) contains organic carbon from autochthonous (in-stream) sources and allochthonous (off-stream) sources (Robertson et al., 1996). An input of carbon through land or allochthonous sources is usually greater in amount than the input of organic carbon generated through aquatic plants within the stream channel (Bunn, 1986; Cummins, 1993; Lovett and Price, 1999). The concentration of DOC and POC will increase when discharge increases (Moore 1989, Collier et al. 1989). A large quantity of DOC and POC is displaced as precipitation increases; the above researched paper asserts. Table IV presents a summary of the concentration of DOC and POC in several rivers with different sizes worldwide.

Table IV- Summary of the concentration of DOC and POC in several rivers with different sizes worldwide.

River	DOC (mg.L^{-1})	POC (mg.L^{-1})	source
Clearwater Creek (Australie)	3.8	-	(Nelson et al., 1993)
Parana (Brésil)	1.7-4.5	1.7	(Eyrolle et al., 1993)
Mackenzie (USA)	4.5	3.2	(Telang et al., 1991)
Rhone (France)	1.7	0.8	(Kempe et al 1991)
Lena (Russia)	3.6-7.2	0.1-1.4	(Cauwet and Sidorov, 1996)

2.5.2 Suspended matters

According to EEA (European Environment Agency), suspended matter is made up of fine particles. Some are present naturally in river water, such as plankton, fine plant debris and minerals, while others stem from human activity (organic and inorganic matter). Suspended matter can make water more turbid, which has a negative impact on river and stream biology.

There are quite a number of studies that indicate the role of suspended sediment in transport of pesticide. For instance, Tanimoto and Hoshika (1997) have suggested that pesticide can be adsorbed onto eroded particle and transported in the river water by the suspended matter. Bergamschi et al. (1997) showed a large amount of suspended sediment is transported during first flash phenomenon and a considerable amount of pesticide entrance into estuaries with this fraction. Zhou and Rowlland (1997) pointed out that hydrophobic pollutants (HOP$_s$) such as pesticides with low solubility have a tendency to adsorb on suspended particle in water.

It is therefore important to underline the significant role of total suspended matter and dissolved and particulate organic carbon in transfering pesticides. Gao et al. (1997) and Worrall et al. (1999), have suggested DOC and TSM are two very widely known parameters to control pesticide concentrations.

2.6 Interaction between organic and suspended matters with pesticide

The retention and mobility of a pesticide in soil and water is determined by the extent and strength of sorption reactions which are governed by the chemical and physical properties of the environment in which they are found. The sorption interactions of pesticides in the soil and water compartment may involve either the mineral or organic components, or both. For soils that have higher organic matter levels (>5%) , the mobility of pesticides is related to the total organic matter content, but the nature of the organic matter has little apparent influence on sorption processes (Bailey and White, 1964; Hayes, 1970; Arienzo and Buondonno, 1993; Riise et al., 1994; Jenks et al., 1998; Bekbolet et al., 1999).

For soils with low organic matter content, the mobility of pesticides is often related to the active components of the inorganic fraction, which is predominantly the clay sized fraction. An increase in the clay content leads to decreasing mobility of pesticides. However, the composition of the clay is also an important ingredient (Baskaran et al., 1996).

I must add that many organic matters (humus) are made up of a series of organic polymers and generally consist of two systems: a hydrophilic (water-loving) surface and a hydrophobic (water hating) interior. Pesticides that are water soluble tend to remain at the surface of soil organic matter, while those that are insoluble will penetrate to the hydrophobic interior.

The amount of pesticide sorbed is largely a function of the total amount of organic matter in the soil and water. DOC concentration increases in stream is very important because it can complicate and make water treatment costly. It is also a vector for micropollutants such as heavy metal or pesticides (Reuter and Perdue, 1977; Campbell et al., 1992; Miskimmin et al., 1992). Sorption to clay mineral particles also occurs but usually is less significant than sorption to organic matter in determining environmental fate, unless the soil has very low organic matter content.

The mechanism of adsorption/desorption or partitioning of chemicals between particulate matter and the dissolved phase plays two important roles in elimination processes: (i) sorption of the chemical onto the suspended or sediment and Particulate Organic Carbon (POC) reduces the aqueous phase concentration and thereby, reduces the bioavailability for microbial biodegradation (Stuijfzand, 2000); (ii) the sorbed phase can be removed from bulk of water due to sedimentation of POC and thereby, reduces the concentration of pesticides in the water column.

Some examples of interaction between pesticide and dissolved and particulate organic carbon are presented by Worrall et al. (1996) for isoproturon, Gao et al. (1998) and Ling et al. (2006) for atrazine, Thevenot et al. (2009) for diuron and Wu et al. (2004) for propiconazole.

2.7 Partitioning between dissolved and particulate phases (K_d)

The distribution of pesticide in dissolved and particulate fractions depends on the characteristic of molecules and also physical and chemical characteristic of water and suspended matters.

Thus, K_d partition coefficient is an index for distribution of molecules between dissolved and particulate phases. k_d (in $g.L^{-1}$) of each molecule was calculated as the concentration ratio between dissolved ($\mu g.L^{-1}$) and particulate ($\mu g.g^{-1}$) fractions:

$$\mathbf{K_d\ (g.L^{-1}) = C_{dissolved}(\mu g.L^{-1}) / C_{particulate}\ (\mu g.g^{-1})} \qquad \textbf{Eq.1}$$

Where:

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

$$C_{particulate}(\mu g.g^{-1}) = [C_{unfilterd}(\mu g.L^{-1}) - C_{filtered}\ (\mu g.L^{-1})]/TSM(g.L^{-1})$$

In fact the adsorption coefficients like k_f, k_d, k_{oc} are correlated with characteristic of molecules (Briggs, 1981; Green and Karickhhoff, 1990; Baum, 1998; Gramatica et al., 2000; Calvet et al., 2005). The principal characteristics of molecules are solubility and octanol/water partition coefficient. However, relationship between adsorption coefficients and property of the soil such as carbon content, the amount of clay minerals as well as pH attract a considerable attention in literature (Barriuso and Calvet, 1992; Coquet and Barriuso, 2002; Weber et al., 2004; Calvet et al., 2005).

3 Occurrence of pesticides in water

Increasing environmental awareness has generated concerns regarding the impact of pesticides on aquatic ecosystems. Palma et al. (2004) and Comoretto and Chiron (2005) have stated that in surface water of many countries in all over the world pesticide can be detected in high concentration.

To protect aquatic organisms and human health, almost every country and some official organizations determine upper limit of concentration of pesticides in water. For instance, the «Directive concerning the quality of water intended for human consumption of European Union, foresees standards for pesticides residue in drinking water at 0.1 $\mu g.L^{-1}$ for each active ingredient (the parametric value for aldrin-dieldrine, heptachlor oxide being 0.03$\mu g.L^{-1}$) and 0.5 $\mu g.L^{-1}$ for the sum of all pesticides» (EEC, 1980- EEC, 1991).

Despite the negative impact of pesticides they have been and will continue to be an integral part of modern crop protection in intensive agricultural activities for satisfying consumption needs and food supply for the increasing world's human population (Streibig and Kudsk 1993). Compared to other xenobiotics, pesticides are unique compounds that placed into the environment in large amounts. As we have said earlier pesticides are divided into groups based on their target pests, e.g. herbicides, insecticides, fungicides. Among them herbicides are more present in the environment. Konstantinou et al. (2006) provide the most comprehensive review on contamination of rivers in Europe by the large variety of herbicides in use between 1988 and 2000. Muller et al. (2006) pointed out traces of herbicides and mixtures of them are frequently detected in aquatic ecosystems in agricultural landscapes.

Readman et al. (1993) have shown that several Mediterranean rivers (Ebre, Rhône, Pô, Nile and five small rivers of Greece) are significantly contaminated by herbicides (alachlor, atrazine, metolachlor, molinate, simazine), sometimes above 1 $\mu g.L^{-1}$. In particular, pesticides of s-triazine and the phenylurea families are often occurring in surface water and groundwater in European countries (Thurman et al., 1994; Schiavon et al., 1995; Lemieux et al., 1995). And Pantone et al. (1992) have emphasized the importance of these pesticide families due to their high water solubility leading to a high mobility which enhance the risk of aquatic environment contamination.

In river Humber (Estuary in north east of England, 64 Km), House et al. (1997) found more than 8.7 $\mu g.L^{-1}$ of diuron in 1995, Cerejerira et al. (2003) reporting 4.8 $\mu g.L^{-1}$ in Sado in 1999, Griffini et al. (1997) registered 3.68 $\mu g.L^{-1}$ of metolachlor in Arno in 1995. Garmouma et al. (1998) have investigated the concentration of trazine and phenylurea in four subbasins of the Marne river (France) in 1992 and 1993, according to their investigation the concentration peak of atrazine, simazine and isoproturon occurred between March and July. And in all of the study area, the concentration peak was in relation with the herbicide application period and with important rainfalls.

Albanis et al. (1995) showed that in Greece, small coastal rivers that are Louros and Arachthos (with annual average flows between 5-30 $m^3.s^{-1}$) can occasionally present levels of herbicides particularly important. During application period, until 4.1 $\mu g.L^{-1}$ for atrazine, 1.65 $\mu g.L^{-1}$ for alachlor, 1.45 $\mu g.L^{-1}$ for simazine and 1.12 $\mu g.L^{-1}$ for metolachlor were detected in estuarine part of these two rivers. In Norway, Poland, Italy, Germany and France, several studies indicate contamination by pesticides precipitation (Lode et al., 1995; Dörfler and Scheunert, 1997; Huskes and Levsen, 1997; Grynkiewicz et al., 1998; Polkowska et al, 2000; Lacoste et al., 2004), sometimes far from their spreading sites.

Pesticides in non-agricultural areas have been detected in a significant quantity and proved to be widespread. Quite a number of studies measuring the concentration of pesticides in urban catchments, in golf courses, roads, have also been conducted (Leonard, 1990; Lee et al., 2000; Guidotti et al., 2000; Ramwell et al 2002; Muller et al., 2002; Phillips and Bode, 2004; Irace-Guigand et al., 2004, Leu et al., 2004).

Estimates indicate that the average herbicide loss is around 1% of the applied volume (Wauchope 1978, Kreuger 1998, Carter 2000). Senseman et al. (1997) have estimated that from 0.01 up to 5 % of pesticides applied on field are lost in runoff events. Riise et al. (2004) pointed out substantial amounts (0.1-0.5%) of pesticides might be lost from the application field to the surface water via runoff and drainage. However, a number of field studies showed the rang of loss between 0.01- 0.5 % (Traub-Eberhard et al., 1994; Brown et al., 1995), also in a study conducted by Louchart et al. (2001) it is illustrated that the rate of losing for diroun and simazine are 0.52% and 0.24% respectively. Studies on filed plots and watershed scales indicate that losses of herbicides are approximately 1-4% depending on the soil types, tillage practice and slope of the fields (Hall, 1974; Buttle, 1990).

France, a major user of pesticides in Europe, is particularly concerned by this problematic. Careful and regular observations made by IFEN in 2005 highlighted the overall state and quality of water courses and groundwater (IFEN, 2005).

The results show that pesticides were detected at 91% of the measurement points for water courses and at 55 % of points for groundwater. Contamination levels are significant: 36% of surface water measurement points indicated quality that was moderate to very poor, 25% of groundwater points indicated poor to very poor quality.

Devault et al. (2007) have indicated that the average of pesticide concentration in some tributary of Garonne watershed was close to 1.17 $\mu g.L^{-1}$. Whereas in some stations the herbicide’s concentration was higher than the allowable threshold set by European directive.

Summary

Pesticides are chemicals using to control pests that harm food production, health and environment. There are mainly three types of pesticides: herbicide, insecticide and fungicide. During a long time pesticides are used to suppress the various pests. Before 1960, attention was primarily focused on contamination by organochlorin insecticides such as DDT. In reality the use of pesticides in agriculture has progressively increased since World War II with a concomitant increase in world food production. However, agricultural pesticides residues in surface waters have been a growing concern ever since the 1940s (Butler, 1966; Richards and Baker 1993).

We are all exposed worldwide to an overwhelming number of chemical contaminants in our air, water and food. Modern agriculture is highly dependent on the use of pesticides. Herbicides accounted for the largest portion (48.30%) followed by insecticides (24.30%) fungicides (24%) and other pesticides (3.5%). The trio, USA, Japon and Franch are part of the world using pesticides the most. Pesticides can move in ecosystems according to their properties such as half-life time, vapour pressure etc, Wania et al. (1998); the environmental conditions, and their application modes Hansen et al. (2001), soil properties Lecomte et al. (1999), hydrological regimes Nash et al. (2002), atmospheric transport or air-surface exchange of pesticide Bidleman, (1999), are the other parameters that play an important role in transportiong of pesticides.

In fact the transport of pesticides in surface waters depends on the form in which the compounds exist in the water and the hydrodynamics of the system. A pesticide molecules can exist either in the dissolved phase or it can be associated with a particle or colloid. In the dissolved phase, transport of the pesticide will be governed essentially by water flow while in the associated phase; transport will be governed by the movement of the particle or colloid. Transport of pesticide associated with dissolved organic matter or colloids is primarily governed by water flow, similar to that of dissolved pesticides. However, it is worth mentioning that rapid flow processes such as preferential flow or surface runoff can drastically reduce the time available for physical as well as chemical reactions such as sorption or degradation and can lead to direct transfer of pesticides from the soil and plant surface into surface water, Muller et al. (2003). Leonard (1990) has reported the amount of pesticides lost from fields and transported to surface waters depends on several factors. These factors are soil characteristics, topography, weather, agricultural management practices, and the chemical and environmental properties of individual pesticides.

Underestanding the mechanisms of pesticides displacement from soil into water, specially during storm runoff, requires an accurate knowledge of controlling factors such as dissolved organic carbon (DOC) , particulate organic carbon (POC) and total suspended matters (TSM) of the environment.

Chapter II

Materials and Methods

Chapter II

Materials and Methods

Introduction

The aim of this part is to elucidate the analytical method and also explain the experimental procedures that were utilized in order to achieve the objectives set in our research. This chapter describes firstly the environmental feature of the Auradé and Save catchments where a large case study of environmental research was carried out. the processes used and laboratory experiments such as the sample preparation, pre-concentration and quantification procedures are also delineated in this part.

1 Experimental Study

1.1 Study areas (Locations and characteristics)

Our research area lies in the South- Western part of France where the Garonne, the most important river in this region, flows throughout the area.

The hydrological regime of Garonne, i.e., distribution of its waters on the surface and underground and the cycle of its evaporation does not follow a regular pattern and this is due to high precipitation in spring and much reduced rate of rainfall in August and September.

The existence of quite a significant amount of data bank in the study area and observation of frequent trace of pesticides in surface water and sediment in this river have attracted our attention to Save catchment and its subcatchment, Auradé, which is one of the left tributary of the Garonne river.

The Save catchment, located in the «Coteaux de Gascogne», area is an agricultural catchment with an area of 1110 km^2 (figure 7). A river of about 140 km length, which gets its source in the piedmont zone of the Pyrénées Mountains (south-west of France) at an altitude of 600 m, runs through this catchment. The upstream part of the Save catchment is a hilly agricultural area mainly covered with forest and pasture while the lower part is flat and devoted to intensive agricultural activities mostly wheat, corn and sunflower which make the use of pesticides indispensable.

The experimental area, Montoussé catchment at Auradé, is located in the Midi-Pyrenees province (south west of France), 35 km west of Toulouse (Figure 7). The study area is a hillside of the "Coteaux de Gascogne" with an altitude of approximately 300 m. The Montoussé drains an area of some 3.28 km^2, with a river length of 5 km. 90 % of this catchment is devoted to agricultural activities on highly fertile land with calcareous (around pH=8) and clayey (36%) soils. The main cultures are winter wheat (20%) and durum wheat (31%) in rotation with sunflower (47%).

The land use in the Save catchment for the year (2005) was mapped, supported by photos of aerial surveys by cemagref Bordeaux. The information gained was digitalized with geographic information system, which showed that about 44% of the land was used for crop productions, with 44% also for pastures, and 12% forest and 0.6 % urban and snowmelt. As a matter of fact pasture occupies 44% of the watershed, but the contribution of herbicides losses is considered negligible. And, this is also what putforward by some authors like Fox and Wilcock (1988), Wilcoke and Costley (1991).

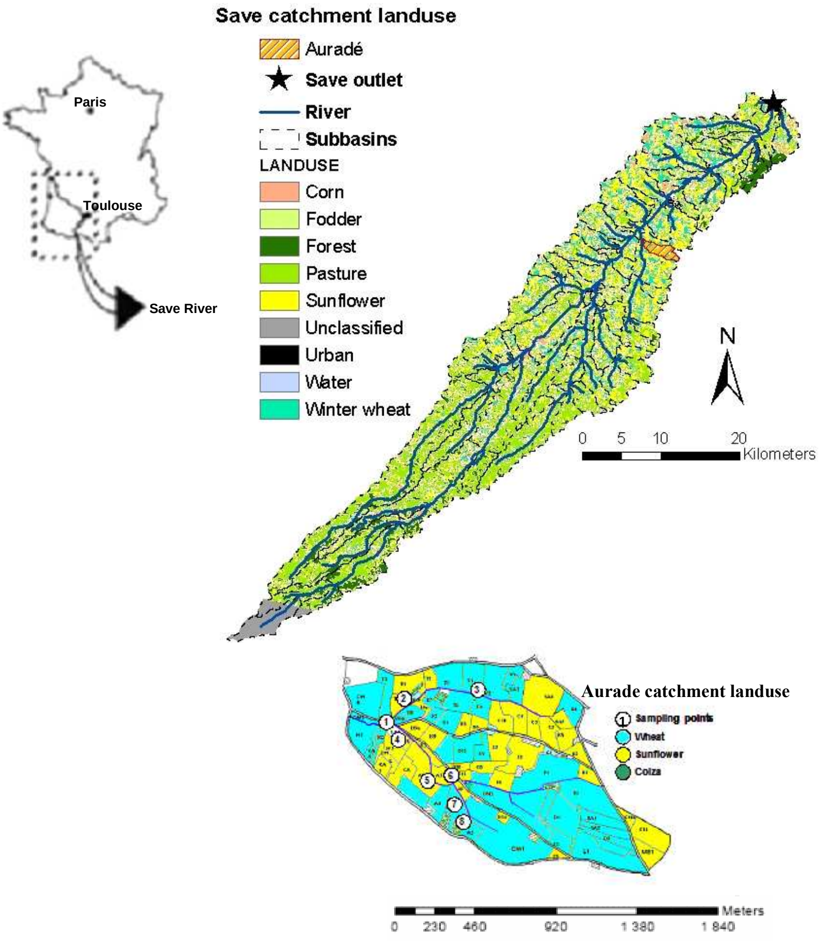


Figure 7- illustrates the occupation of soil and the location of Save and its subbasin, Auradé in catchment.

For Auradé catchment, the contribution of landuse is collected with «Association des Agriculteurs d’Auradé» for the whole study period from the inquiry and field observation. The results show 86% of the catchment is contributed to crops (winter wheat and sunflower) and the remaining, i.e. 14 % to pasture, forest, urban and grass strip together.

1.2 Climate and Hydrology

The climate of Auradé and Save areas is characterized as oceanic because the influence of the Atlantic-ocean plays an important role in regulating temperature variation and therefore determining climate conditions. The average annual precipitation is about 700mm to 800mm, mostly in the form of rain, which is the main hydrological source of supply for surface and subsurface run-offs. The wet period runs from October to May with the highest rate of discharge in February while the water flows more slowly from June to September (Ribeyeix – Claret, 2001).

The bulk of annual rainfall occurs, in the form of thunderstorms, from November through December and April to May. The average water evaportranspiration from the soil/vegetation system is very high and stands, from west to east, at 500mm to 600mm.

For Auradé catchment hydroclimatological data, we relied on the statisticals data of precipitation and discharge measured by Ecolab laboratory. And at Save station the data of hourly discharge made available to us by the hydrological monitoring unit of the Compagnie d’Aménagement des Coteaux de Gascogne (CACG in Tarbes). Rainfall data was recuperated from five meteorological station in the catchment that managed by Meteo France.

1.3 Geological substratum and soil characteristic

The geological substratum is a Miocene molasse resulting from the erosion of the Pyrénées Mountains and the subsequent sediment deposition in the Gascogne fan at the end of the tertiary. This molasse consists in a mixing of sands, clays, limestones and calcareous sediments. The study area is characterized by a fairly impermeable substratum due to its widely extended clay content.

Two principal types of soil have developed on this impermeable substrate (Cavaille, 1969; Revel, 1982): (i) the «terreforts» by dominance of clay–silt, characterized by a compact texture, with the low degree of permeability and thus, very sensible to surface runoff. The «boulbenes» (soil of alluvial terraces), represent less than 10% of the soil in this area, which is siliceous soil or light soils and characterized by a relative permeability.

As the result of this sedimentation, river discharge is mostly supplied by surface and subsurface runoffs. Groundwater reservoirs are very limited and during the summer dry period the stream discharge is very low and sometimes the creek is dried. The land slopes of Auradé catchment varying to the north between 0% to 20% and are drained by a system of river flowing to the North into the Save catchment with an average slope of 3.6% which is a main fluvial axis of south west of France, the Garonne River.

1.4 River water composition

The characteristic of pH of water in this region is alkaline pH (7.47-8.11). This value is in accordance with the category of carbonate water established by Meybeck (1986) for the water stream that flow on detritus carbonate bedrock. Bicarbonate (HCO^-_3) and Calcium are the principal anions in water, whereas, K^+, NO^-_3 and SO_4 are the elements less abundant.

1.5 Selection of pesticide

First, the most frequently detected herbicides and fungicides in the Gascogne catchment where determined, based on historical data of the Agence de l'Eau, and also by the study performed by Institutional networks. And the selection of five families of pesticides was then further based on the study and the availability of data of a 4-year lasting project by Devault et al. (2007).

In this project, five families of pesticides (14 molecules) were measured weekly during two years in the Auradé catchment and one year in Save catchment especially during storm events. Glyphosat is not included in this study because no technique was available for this herbicide in our laboratory. The fungicides were also selected according to their application. The application period of different pesticides under study was given by the Association des Agriculture d'Auradé and the chemical properties of molecules are schematically shown in table V.

Table V- Chemical formula, Type of pesticides (H for herbicide, F for fungicide), application periods and chemical and physical characteristic of molecules was listed.

Pesticide	Formula	Type	Culture	Application period	S_w ($mg.L^{-1}$)	log K_{ow}
atrazin	$C_8H_{14}ClN_5$	H	Corn	Apr-May	30*	2.75*
DEA	$C_6H_{10}ClN_5$	H	Corn	metabolite	2.700*	1.3*
metolachlor	$C_{15}H_{22}ClNO_2$	H	Corn	Apr-May	488	2.9
isoproturon	$C_{12}H_{18}N_2O$	H	Winter Wheat	Oct-Feb	65	2.5
linuron	$C_9H_{10}Cl_2N_2O_2$	H	Corn Sunflower	Apr-May	63.8	3
chlorotuloron	$C_{10}H_{13}ClN_2O$	H	Winter Wheat	Oct-Feb	74	2.5
alachlor	$C_{14}H_{20}ClNO_2$	H	Corn	Apr-May	240	3.09
aclonifen	$C_{12}H_9ClN_2O_3$	H	Sunflower	Aprl-May	1.4	4.37
trifluralin	$C_{13}H_{16}F_3N_3O_4$	H	Sunflower	Apr-May	0.221	4.83
fenpromiroph	$C_{20}H_{33}NO$	F	Cereals	May-June	4.32	4.1
flusilazole	$C_{16}H_{15}F_2N_3Si$	F	Wheat	May-June	45	3.74
cyproconazole	$C_{15}H_{18}ClN_3O$	F	Cereals	May-June	93	3.1
tebuconazole	$C_{16}H_{22}ClN_3O$	F	Cereals	May-June	36	3.7
epoxiconazole	$C_{17}H_{13}ClFN_3O$	F	Cereals	May-June	6.63×10^{-4}	3.44

* Mackay, et al., 1997.

1.6 Pesticide families

Five families of pesticides (as follows) were center of our attention in this study (figure 8).

- **s-triazine**

  Compounds include many pesticides of widespread use in agriculture. s-triazines are characterized by a symmetrical hexagonal ring consisting of alternating carbon and nitrogen atoms.

- **N-phenyl substituted ureas**

  A phenyl group is the functional group C_6H_5. The term phenyl is used when a benzene ring is connected to a chain of six or more carbon atoms. If there are fewer than six carbon atoms in the chain, the compound is named as substituted benzene. The phenyl group is abbreviated in chemical structure as Ph or sometimes as Φ. Various pesticides such as the phenylureas contain phenyl ring.

- **toluidine**

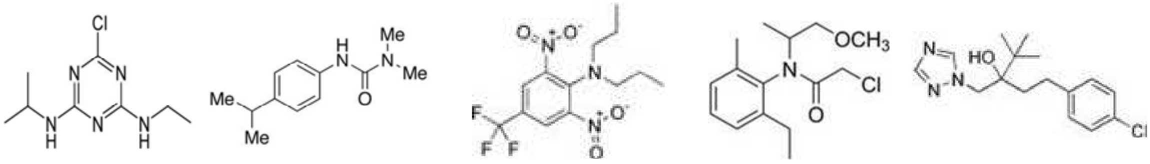
  Toluidine is an organic compound family with the formula C_7H_9N. The chemical properties of toluidines are quite similar to those of aniline.

- **chloroacetamide**

  Refers to the molecules with chemical formula (C_2H_4INO) and derivative of aniline group. Chloroacetamide family substances are used world-wide as a pre-emergent herbicide to control grasses.

- **triazole**

  Refers to either one of a pair of isomeric chemical compounds with molecular formula $C_2H_3N_3$, having a five-member ring of two carbon atoms and three nitrogen atoms.



s-triazine substituted urea toluidine cloroacetamide triazole

Figure 8- Chemical formula of different families of pesticides.

1.7 Sampling

Water sampling for our research started in June 2007 and continued until June 2009 for the Auradé catchment and one year from March 2008 to March 2009 for the Save catchment. In two watersheds the sampling was done in out-let at which all surface drainage from a basin comes together. The main sampling months were February to June during the period of raining. Out of the raining-period water samples were collected manually each week. However, Robertson and Roerish study in 1999 states that the most effective sampling strategy depends on the length of the study. For one year observations, fixed-point monthly sampling supplement storm chasing, (i.e. collecting additional samples during storm events) was the most effective strategy. For a longer period of observation, fixed-period semimonthly sampling result is not only the least biased but also the most precise loads.

For the Auradé catchment during the raining period an automatic sampler (Model: ecotech® AWS 2002) with a capacity of 8 glass bottles was used. Water was pumped through a plastic tube whose inlet was submerged in the water, and the other end of the tube was connected to the sampler. The automatic sampler was programmed for 30 min interval sampling and all composite samples were stored at +4°C during the collection period in a sampler refrigerator. After transportation to the laboratory, samples were stored in refragrator and extraction was done only a few days after the sampling took place.

Prior to any sampling procedure, all the equipment (glasses, bottles) are carefully cleaned and decontamination procedure was carried out according to the protocols described below.

The water sampling carried out in glass bottles previously cleaned with Decon® (a blend of amphoteric surface active agents, non-phosphate detergent builders, alkalis and sequestering agents, in an aqueous base) and then rinsed with ultrapure water, for residue analysis of pesticides.

As part of a manual sampling, each bottle was cleaned according to the procedure explained earlier. Then in the field they were rinsed three times to ensure representative of the samples. The sampling was done in an area where there was a current, i.e., a steady and continuous flowing of the river. Sampling was under the complete immersion so that to limit the presence of air and minimizing the contamination on the one hand and the evolution in samples (change in the sample or to avoid an alteration in the sample) on the other hand. For unfiltered water, dichloromethane was added in the field to the bottles to inhibit microbial degradation of the pesticide (Kreuger, 1998 and Devault, 2007).

The water sample was filtered by applying vacuum. The filter used to filtration was a nitro cellulose ester filter (Millipore, 0.45 µm) according to Namiesnik et al. (1997). Each filter was rinsed with MilliQ water before filtration.

Before filtration, each sample was homogenized in order to recover all particles in suspension. Filtration should be made as soon as possible after sampling to avoid any process of dissolution, precipitation and sorption to avoid any possible change or transformation in the sample properties.

2 Technical methods

2.1 Extraction of pesticide residues

2.1.1 *Principle in the Liquid-liquid extraction*

Liquid- liquid extraction (LLE) is a classical method for matrix removal and pre-concentration of metal and organic compounds like pesticides (Ong and Hites, 1995).

LLE also known as solvent extraction and partitioning, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. This is a common method frequently used for determination of organic pollutants in water (Tan, 1992). Solvent selection for the extraction of environmental samples has been described in many reviews or in official methods, and is related to the nature of the pesticides (Kaufman and Clower, 1991). The large choice of available pure solvent, which provide a wide range of solubility and selective properties, is often claimed as an inherent advantage of LLE technique. In fact, each solvent is specific for a given class of compounds and LLE is mainly used for the wide spectrum of compounds extracted. Hexane and cyclohexane are tyipical solvents for extracting non-polar compounds such as organochlorinated or some organophosphorus pesticides (Meulenberg et al. 1995). Dichloromethane and chloroform are certainly the most common for extracting non polar to medium polarity pesticides (Marco et al., 1995). Many solvents like n-hexane, petroleum ether, petroleum ether-methylene chloride and acetone or ethylacetate were used as extraction solvents over the past few years.

In our study extraction of water sample performed by using shaker flask (3-4 L with Teflon key) as a means and dichloromethane as a solvent for phase exchange (figure 9). The total solvent/water ratio noted as 1:6, V/V. Once the extraction (after vigorously shaken for three times) performed, dichloromethane (DCM) was dried on 50 g anhydrous sodium sulphate (to remove the moisture in organic phase), and the remaining organic phase was evaporated under vacuum to dryness and the dry residue was re-dissolved in 2 ml of hexane.

2.1.2 Advantages and drawbacks

The main advantage of LLE is twofold: (i) its simplicity and (ii) its requirement of simple and inexpensive equipment. However, it is not always easy to compare recoveries obtained by different laboratories due to dissimilarity of the condition of extraction (pH, phase ratio, number and time length of extractions, salinity, etc). Another disadvantage of this procedure is unfavorable phase-ratio which may render low extraction efficiencies, and the requirement that the extracting solvent should be completely immiscible with the water sample, which is difficult to achieve with the more polar solvents that will dissolved in the sample (Van der Hoff and Zoonen, 1999). Also, the procedure of LLE is tedious, time consuming and high level of solvent consumption in this method.

The argument often cited in favor of LLE technique is that it can be used both for the extraction from filtered and non filtered waters. In contrast, only organic compounds dissolved in water are analyzed using Solid Phase Extraction (SPE) techniques, because surface water is generally filtered before percolation to avoid plugging of the SPE cartridge.

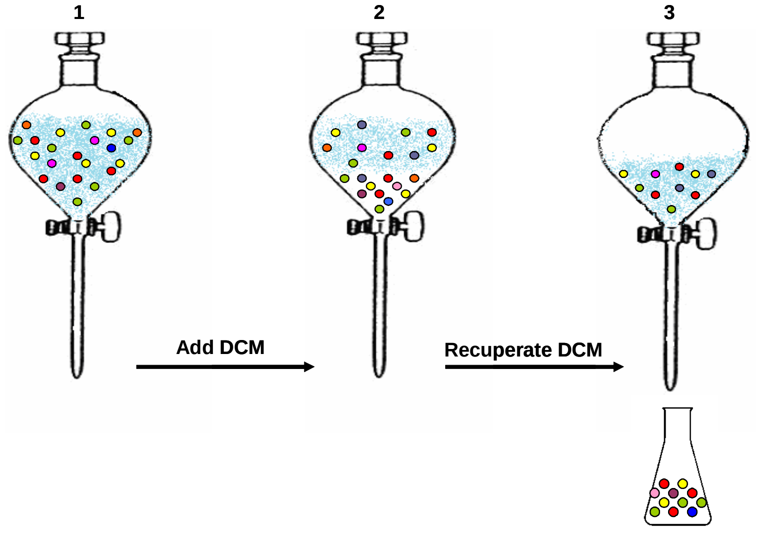


Figure 9- Principle of liquid liquid extraction method (1- row water, 2- add DCM as an organic solvent 3- recuperated DCM in an erlen as an organic phase).

2.2 Methods of analysis

2.2.1 Multiresidue analysis

Many pesticides have similar physical and chemical properties and it is true not only for pesticides of the same chemical families but also for pesticides of different families having similar functional properties, solubility, adsorption characteristics, vapour pressure, etc. These similarities allow the analysis of relatively large group of pesticides using the same analytical method.

Multiresidue methods rely on chromatographic techniques to (i) separate pesticide residues (ii) to determine an analyses' identity on the basis of retention time and (iii) to quantify responses from a specific detector. To this end, two chromatographic techniques are most common: gas chromatography (GC) and high performance liquid chromatography (HPLC). In our study we utilize the GC and we will explain it in detail as hereafter.

2.2.2 GC and MS techniques

Gas chromatography is perhaps the single most important advancement in analytical chemistry in making trace of pesticides residues testing possible. Many review articles address GC techniques and GC application for pesticides residues analysis (Zweig et al., 1972; Claver et al., 2006; Togola and Budzinski, 2008; Menezes et al., 2010). The gas chromatography has become the primary instrument for pesticide residue screening because the physical and chemical properties of many common pesticides (~ 560) are ideally suited to the GC technique (Giarrocco, 1997). These pesticides are semi-volatile with different vapour pressures, relatively stable to high temperature, and soluble in organic solvents. In Gas chromatography, the sample is vaporized and injected onto the head of chromatography column. Elution is brought about by the flow of an inert gaseous mobile phase.

The combination of Gas chromatography for separation and mass spectrometry (MS) for detection and identification of a mixture of compounds is rapidly becoming the definitive analytical tool in the laboratory (McMaster and McMaster, 1998).

In fact GC and MS together create a power analytical technique which can be used for many different purposes. The great quality of GC, first described in 1956 by James, and Martin, is its advantage in separating the volatile components of any mixture. This technicality soon after 1956 was recognized as an indispensible tool for the analysis of organic compounds.

- **The principle of GC**

Identifying pesticides' residue covering fruit, vegetales and polluting the current water requires an appropriate method of investigation. Gas chromatography (GC), together with electron capture detector (ECD), Nitrogen Phosphorus Detector (NPD), Flame Photometeric Detector (FPD), and Mass Spectrometric (MS) are the most common techniques to trace pesticides' remaining (Luke et al. 1981; Anderson and Ohlins, 1986). In fact GC is a popular, powerful, reasonably inexpensive and easy-to use analytical technique. Mixture or sample to be analyzed are injected via an injector port (a septum port on top of the GC) using a graduated capillary syringe. Helium, which served as a carrier gas, is used to sweep the injected sample onto and down the column where the separation occurs, then out into the mass spectrometer interface.

- **The principle of MS**

Mass spectrometry is recognized as a highly sensible and specific technique that can be used for environmental organic analysis. In fact Mass Spectrometry (MS) is an instrument used for measuring fragments molecular weight. A sample in a molecular or atomic state is transformed into ionic particles. It is a highly sensitive, versatile and appropriate analytical technique in use.

In molecular Mass Spectrometry, sample is vaporized and bombarded with a stream of electrons that lead to the loss of an electron and the molecular ion M^+ is formed as shown below:

$$M + e^- \longrightarrow M^+ + 2e^-$$

The M^+ stands for the molecular ion, which is a radical ion with the same molecular weight as the molecule collision between electrons and analyte molecules usually transfer sufficient energy to the molecules to leave them in a «stormy» state. «Stormy» state eases off by the fragmentation of molecular ion and produces ions of lower masses.

The most usual Mass Spectrometer consists of four components: (i) an inlet system, (ii) an ion source, (iii) a mass analyser and (iv) a detector. Figure (10) shows the steps of quantification of sample by Mass Spectrometry (Skoog et al., 1998).

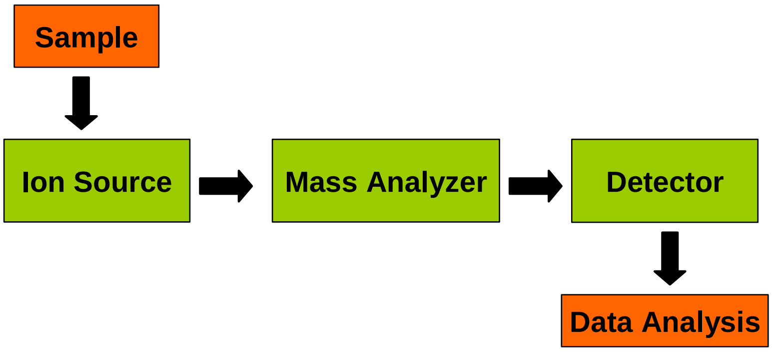


Figure 10- Step of quantification of sample by MS.

2.3 Chromatographic conditions and sample preparation

2.3.1 Condition of GC/MS

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

Table VI- Specific ions for detection and quantification of investigated molecules.

molecules	**Specific ions (m/z)**
DEA	68/172/174/187
atrazine	68/200/202/215
chlorotoluron	72/212/214
isoproturon	72/146/206
linuron	61/160/248
alachlor	146/160/162/188
metolachlor	146/162/238
trifluralin	264/290/306
aclonifen	182/194/264
fenpropimoroph	128/129
flusilazole	206/233/234
cyproconazole	125/139/222/224
tebuconazole	83/125/127
epoxiconazole	138/192/194

2.3.2 Chemical and reagents

Pesticide analyses are performed by solvents of analytical grade (« pestipure » by SDS, Solvent Documents Syntheses, Peypin, France). Anhydrous sodium sulphate from SDS was used for drying the organic phases. Dr Ehrenstorfer’s prepared- pesticide standard (mix 44) was purchased from C.I.L. Sainte - Foy - la- Grande, France.

As we said earlier, water sample was extracted with the LLE method and then the residue were recuperated by 2 ml Hexane in ultrasound bath and stored in GC vials before injection.

2.3.3 Calibration standards

Calibration standards of each pollutant was prepared in Acetonitrile and stored in GC vials before injection. A volume of 1 µL of each standard was injected into the GC/MS. Calibration curves were obtained by plotting peak area against the concentration of each standard.

2.3.4 Detection limit

The lower at which detection become problematic is defined as detection limit (Ellison et al., 2000). In our study the detection limits for 14 pesticides were obtained based on the signal as three-fold of the baseline noise (S/N=3), and the value could reach 0.001-0.003 $\mu g.L^{-1}$ (1-3 $ng.L^{-1}$) at most depending on the molecules involved.

2.4 Analytical methods to measure controlling factors (COD, COP, pH, EC)

2.4.1 Dissolved and Particulate organic carbon (DOC-POC)

DOC analysis was done with an analyzer of total organic carbon (Shimadzu TOC-Analyser 5500 - Shimadzu, Kyoto, Japan). The principal measurement is based on detection of carbon dioxide formed after catalytic oxidation at high temperature (680°C) of organic matter. The test was done on not purgeable organic carbon (NPOC). The organic carbon is measured in a sample acidified with HCL (6N; pH=2) in order to remove inorganic carbon.

The mean of 3 to 5 injections of 100 µl is reported for every sample and precision, described as the coefficient of variance (C.V), was < 2% for replicate injections and Etalon (Reagecon 1000 $mg.L^{-1}$ of DOC) with different concentration was used for calibration.

POC can be measured by determining mass lost upon combustion of a sample. In aqueous samples, this can be done by measuring the dry mass of a filter that had a known amount of water passed through it before and after it is subjected to combustion. This method requires that the filter is purged of extraneous POC before filtration (by combusting it at 550°C for 2 hours), and that the filter and sample are dry (by putting them in a warm oven at 60° C) at their pre-combustion weight measurement.

In our study POC on the glass fibre filters (Whatman GF/F, 0.7 µm pores (Germany) was analyzed by CHN analyzer (NA 2100). Water samples were shaken, and aliquots of each (a different volume was taken for each sample depending on the suspended matter) were vacuum filtered on the glass fibre filters. Ultrapure water (Millipore) was filtered through some filters, which were then analysed as negative control samples. Before using the CHN analyzer, the filtered papers containing suspended sediment were acidified with HCL 2N in order to remove carbonates and dried at 60 °C for 24 h (Cauwet et al., 1990).

2.4.2 General physico-chemical parameters

Physical and chemical characteristics of the water (Temprature, pH, EC) were recorded at the sampling sites by using WTW tool (pH/Cond 340i/SET).

3 Hydrograph separation

3.1 Hydrograph deffinition

A hydrograph describes the whole time history of the changing flow from a catchment due to a rainfall event (Shaw, 1983).Therefore a hydrograph is a plot of discharge versus time (figure 11).

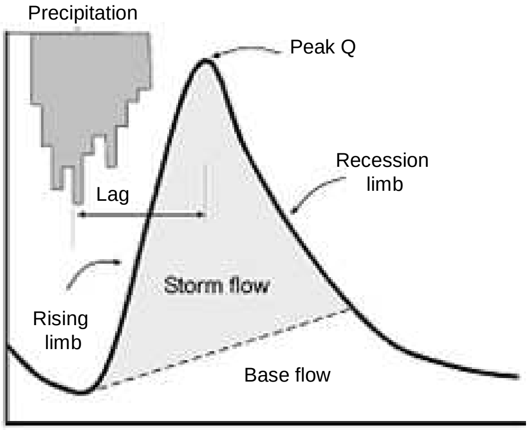


Figure 11- A typical hydrograph showing the 2 flow components and the corresponding rainfall hydrograph.

A hydrograph tells more about the hydrology of a catchment than any other measurement (Ward and Elliot, 1995). The discharge hydrograph has two main components: the area under the hump labelled as《stormwater runoff》in figure 11 is produced by the volume of water derived from a rainfall event (Shaw, 1983). The other major component is the broad band near the time axis which represents the《baseline》the area under the baseline is named baseflow. The volume of stormwater runoff equals the area of the hydrograph minus the area under the baseline. The rise in the flow at the beginning of a rainfall event is referred to as the rising limb.

The length of delay and steepness of the rising limb depend on the wetness of the catchment before the rainfall event, and the intensity of the rain (Shaw 1983). The recession curve is the depreciation of the flow as the catchment returns to the baseline.

Forest type catchment, or catchment with large areas of dense bushland, scrub or grassed areas, tend to have recession curves where the elevated flow above the baseline can continue for days after the rainfall event. This can be caused by infiltration of stormwater into soil, percolation into groundwater recharge, losses due to evaporation and transpiration into grass and plants (Ward and Elliot, 1995). Similar to one which can be observed in the Save watershed.

Stormwater runoff from small, urban type catchment, in which most of the area contains sealed or impervious surface, often have hydrographs that are termed «Flashy» (Ward and Elliot, 1995). These flashy hydrographs have discharge peaks shortly after the most intense rainfall occurs, with the flow decreasing rapidly after the rainfall stops. This kind of hydrograph pattern is observed in the Auradé catchment.

3.2 Different storm flow components

- **Surface runoff**

This is the amount of water available at the surface after all losses have been accounted for. Losses include evapotranspiration by plants, water that is stored in surface depressions caused by irregularity in the soil surface and water that infiltrates into the soil. The interaction between infiltration rate and precipitation rate mainly governed the amount of surface runoff. Intense rainstorms tend to produce much surface runoff because the rate of precipitation greatly exceeds the infiltration rate. On the other hand, the remaining water flows over the ground surface referred to as direct runoff (sometimes referred to as stormwater runoff or surface runoff).

In sum, the rapid transfer of pesticides to surface waters mainly occurs due to surface runoff. And we are interested in factors which trigger the outbreak of the runoff. Some of these factors are: ***saturation state of soil:*** that is to say, the wetter the soil becomes, the quicker it reaches the saturation state. ***soil characteristics:*** including its ability to infiltrate, low infiltration capacity lead to a large portion of the water runoff. ***slope:*** if the slope is high, the movement of surface runoff is also high and less water infiltrates into the soil. ***barriers to runoff:*** the hedges and banks represent barrier to surface runoff with a purifying effect assumed against pesticides (Carluer, 1998). ***vegetation cover:*** the soil with high vegetation cover has more capacity to retain the water, therefore less amount of surface runoff.

- **Subsurface (Interflow) runoff**

The residual water in the soil will move along the soil horizons, parallel to the ground surface. Interflow usually emerges near the bottom of slopes and in valley bottoms. In the other words subsurface water is a portion of the water infiltrating the soil zone that moves laterally through the upper soil horizons until its course is intercepted by a stream channel or until it returns to the surface at some point downslope from its point of infiltration.

- **Groundwater**

Groundwater is supplied by water which passes through the soil horizons into the parent material and /or bedrock underlying the soil. Groundwater tends to flow towards rivers channels where it emerges and supports flow during periods of little or no rain.

3.3 Separation of storm flow components

The streamflow component separation has been a debatable subject among the researchers for the last few decades. Hewlett and Hibbert (1967) reported the separation of surface runoff from baseflow is one of the most desperate analysis techniques in use in hydrology.

In our study hydrograph separation in different components (direct runoff on ground surface, subsurface or interflow and groundwater) is classically undertaken from a graphical decomposition method used by Barnes (1939). In this method, inspired from Maillet's work (1905-1906), river discharge during storm flow events in a mixture of three components: superficial runoff (surface plus subsurface) and baseflow contributing to river discharge in variable proportion.

The method which we used in our study is graphical method. The recession limb of a hydrograph is separated into three segments of different slopes, from which the quantity of water contributed to the stream by surface runoff, interflow and baseflow. In fact since Maillet (1905), the exponential function $Q_t=Q_0.e^{(-\alpha t)}$ has been widely used to describe the base flow recession after a storm event. Q_t stands for discharge at time t, Q_0 refers to the initial discharge in t=0, and α is the recession constant which can be considered to represent average response time in storage, and depends on physical characteristic of different reservoirs. In other words recession constant (α), is an index to the storage volume of a runoff component, reffered to as the storage delay time to drain the volume. The lower the value of α, the longer the storage volume will take to drain.

In fact the graphical separation methods are commonly used to plot the baseflow component of a flood hydrograph event, including the point where the baseflow intersect the falling limb, whereas there are some methods to select the inflection point or intersect point.

In our research we benefited from the technique proposed by Probst (1983, 1985 and 1986) for separation of different components in stream flow but with some modification.

In the hydrograph figure 12, different phases of the river can be observed at different levels in the watershed.

There is usually a time-lag between the moment the watershed received rainfall and its influence on the river. The amount of water runs at time (t) in the river is the result of an earlier phase (t_0) in the watershed. The initial discharge corresponding to surface runoff (Q_0S), is identified to the peak of the storm (P), at the time t_2. It is more difficult to determine the value of Q_0SS, the initial discharge of the subsurface water. According to Lambert (1968 and 1975), t_0SS is the beginning of the subsurface water discharge and it is determined by the hydrological characteristics of its phase by observation in the field. In our study Q_0SS is the peak of storm (A_0) and Q_0G is the first intersection point between the slop of surface and subsurface water on the recession phase of hydrograph (B_0) at time t_3.

In the paragraph above S and SS stand to surface and subsurface water, G is referred to groundwater and t represents time.

However, the study conducted by Muller (2003) shows the choice of the hydrograph separation method doesn't influence on hydrological classification of pesticide loads.

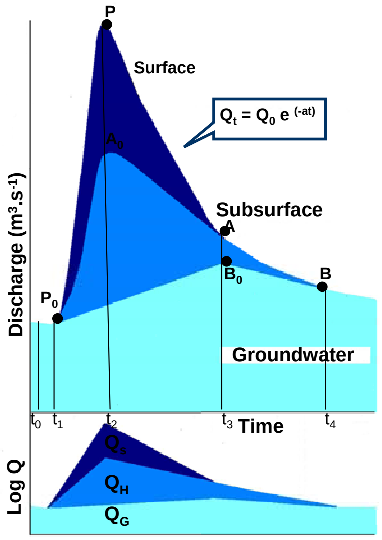


Figure 12- Separation of streamflow components (modified from Probst (1983, 1985, 1986), P_0 (beginning of stormwater), P (initial discharge of surface water), A_0 (beginning of subsurface drainage), B_0 (beginning of groundwater drainage), A (initial discharge of groundwater), B (end of the storm).

3.3.1 Limitation of hydrograph separation techniques

The idea of the recession limb of a stream flow hydrograph separation is based on an abstract assumption rather than a practical and visible separation to the human eye. Hence, hydrograph segmentation of different slopes from which the quantity of water contributing to the stream by (i) surface runoff, (ii) interflow and (iii) baseflow is a somewhat arbitrary process.

The absence of the constant intensity and evenly distributed precipitation, on the one hand, and clear cut change lacking in slopes together with heterogeneity of a typical catchment, on the other hand are all quite understandable natural and geological phenomenon.

The accuracy of a hydrograph separation technique has been a controversial issue among a number of researchers. Sklash and Farvoldon (1979), argue that ground water has a significant role in generating of storm and snow-melt runoff in streams than a hydrograph segmentation technique may help to predict.

Hubert (1989) set forth that a graphical separation technique can largely overestimate the contribution of direct runoff to the stream. He argues that if the reconstitution or prediction of the stream flow rate is what we want to know then the problem expressed earlier can not be considered as an important factor, though it becomes important if our aim is reconstitution or the prediction of the stream water quality.

Summary

This chapter began with introducing study area and also four families of pesticides all bonds together using 14 different molecules. In this investigation we have opted for the most commonly techniques in use in taking samples and analysis to achieve the objectives we have set in this research. Separation and quantification of the components of the samples were done by Gas Chromatography (GC) and Mass Spectrometery (MS), using a multi-residue approach. Measuring DOC, POC, TSM, pH and EC are used as a tool for controlling factors of distributing pesticides between dissolved and particulate phases. Finally we utilized the graphical method for separation stormwater's hydrograph to better understand the contribution of different storm flow components in transfer of each pesticide.

Chapter III

Spatial and temporal variations

Chapter III

Spatial and temporal variations

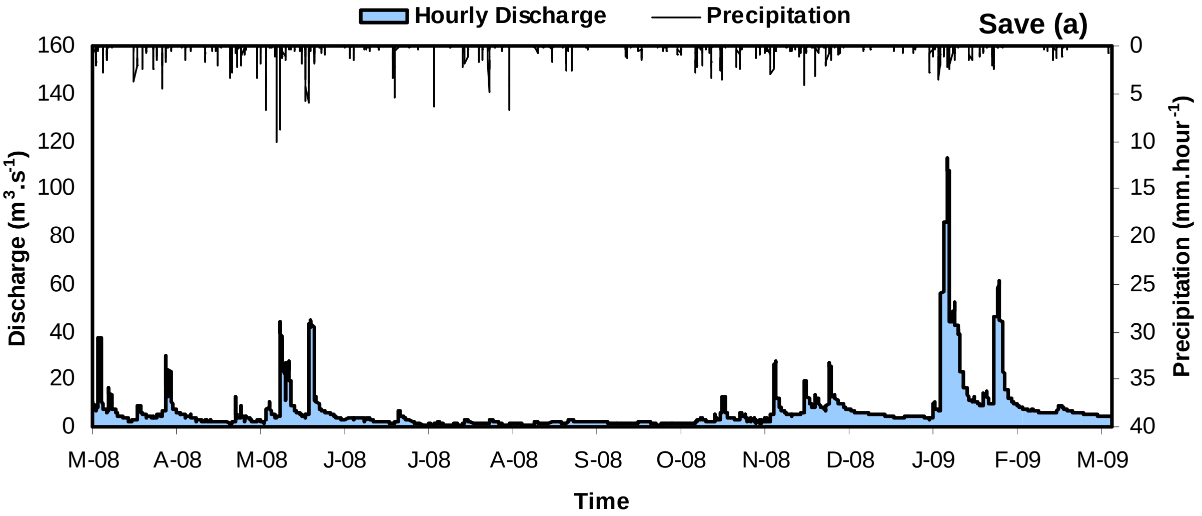
Introduction

Chapter 3 is dealt with spatial variation in Auradé catchment, on the one hand, and temporal variation in Save and Auradé catchments, on the other hand. We are also investigating, during the whole period of observation, the behavior of molecules of pesticide and its controlling factors. Numerous related analyses are shown graphically in this chapter.

1 Hydrological characterization of river discharge

Monitoring and analysis of the Save river ran for the year ending in March 2009. During this year long observation the catchment received some 910 mm of rainfall. July to October considered as a dry season since the discharge of the river does not exceed the mean of the annual discharge, i.e. ($6m^3.s^{-1}$). The rainfall data presented hereafter at the watershed scale is the arithmetic mean of the data measured by five rainfall measurement stations (figure 13a).

Auradé catchment monitoring ran from June 2007 to June 2009. During two years of investigation the catchment received 1311 mm of precipitation and for a year beginning from March 2008, 757 mm of precipitation was recorded. In this catchment the highest rate of water discharge normally occurs in February, March and April while the water flows more slowly from June to September (figure 13b).



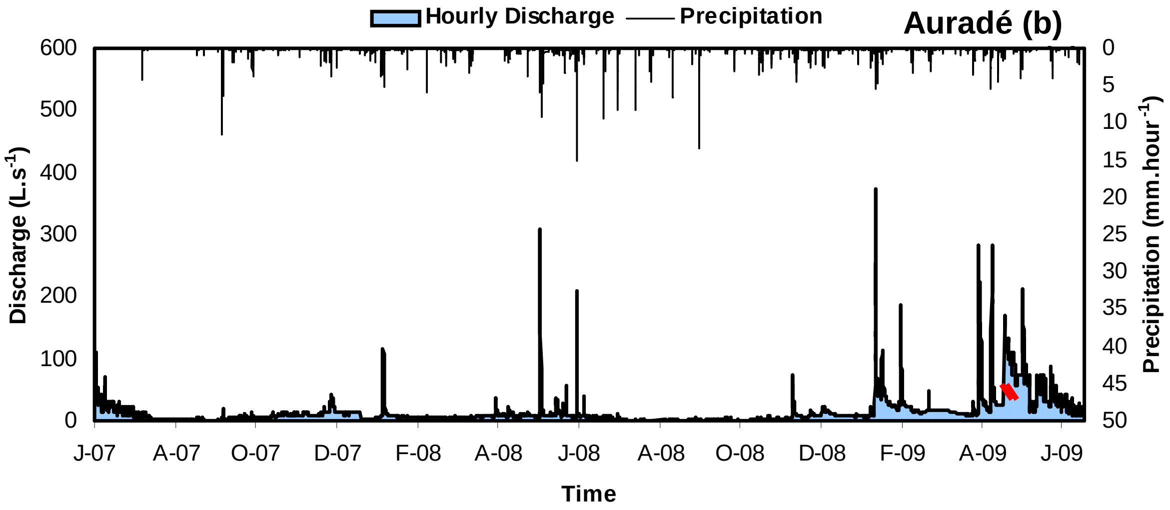


Figure 13- Pattern of rainfall and natural discharge variations of the Save (a) and Auradé (b) watersheds during the study period.

2 Spatial variation in Auradé catchment

2.1 Spatial variation of pesticide concentration

Two separate sampling campaigns launched to trace the course of pesticide distribution in the Auradé catchment in June 2007 and June 2009. Eight sampling stations (figure 7) have been selected from upstreamn to down stream on the different tributaries according to agricultural practices and cultivation. The level of pesticide concentration reveals to be higher in 2007 (figure 14). Different hypotheses may be put forward to explain why this pattern was produced. The explanation may come from the fact that the avrage amount of discharge in Montousse creek (Auradé) for the period of sampling from January to June 2007 is nearly 22 ($L.s^{-1}$) and the average amount of discharge for the same period in 2009 was registered at 19 ($L.s^{-1}$). Higher level of concentration in 2007 colud be the result of higher amount of discharge. Morover, in the day of sampling the mean daily discharge detected was 5.6 ($L.s^{-1}$) and 5.4 ($L.s^{-1}$) respectively in 2007 and 2009. Besides, abating in the use of pesticides for a variety of unclearly identified reasons, for example, lesser amount of pests in the environment obviously requires smaller amount of pesticides and, this could be regarded as an explanation.

In the first view, the spatial changes of pesticide’s concentration are remarkably higher in sampling campaigns of 2007 in all of the sampling spots. However, there is no relation between the molecules of pesticide and the type of culture in each plot neither for 2007 nor for 2009. In fact, from this observation we can conclude that pesticide concentration does not depend on spatial variation of culture.

The values of concentration are generally less than 0.1 (µg.L^{-1}) for all of the stations in a two-year investigation period. The maximum concentration is attributed to substituted urea family, especially in 2007.

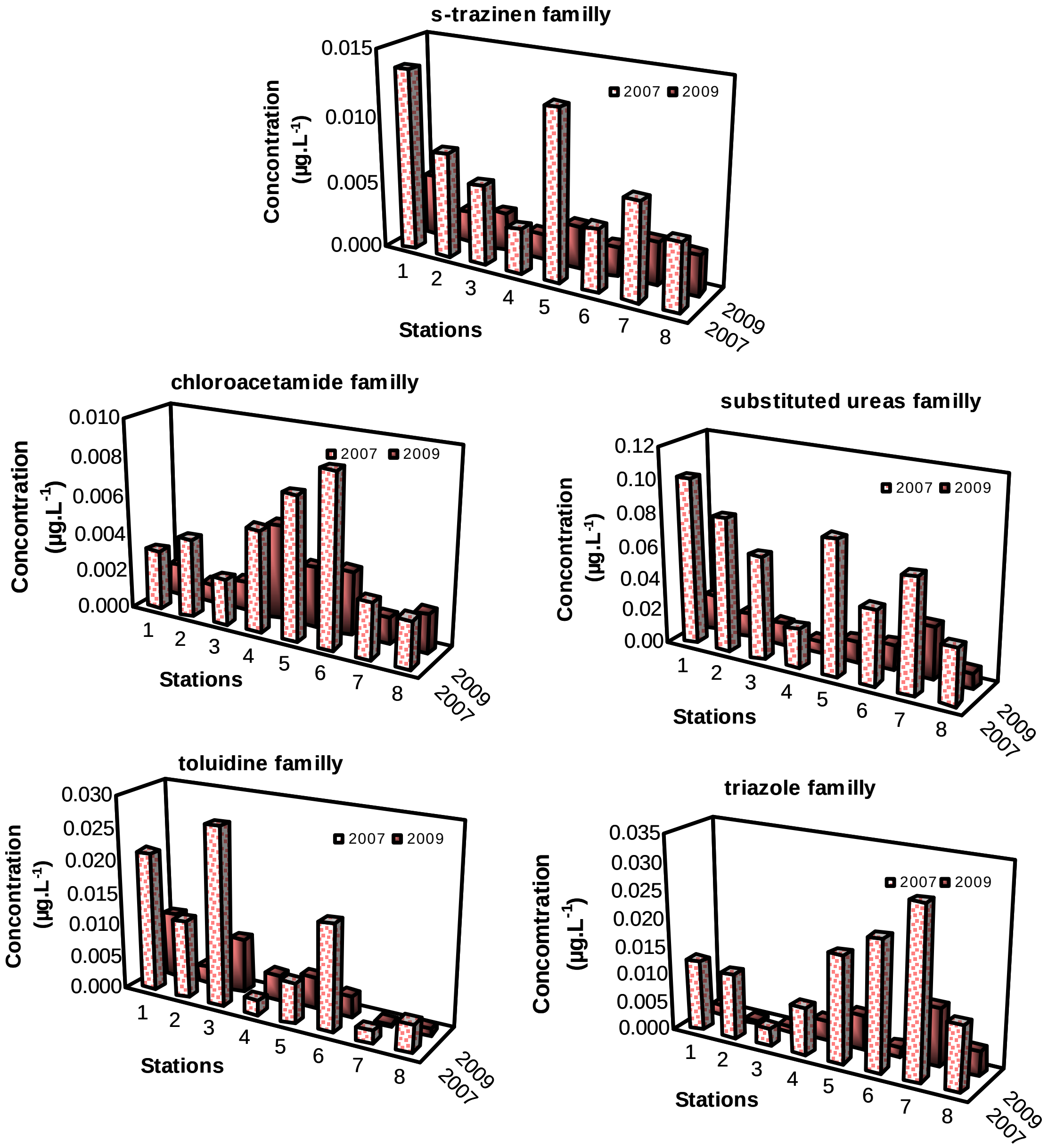


Figure 14- Average of pesticides concentration in all of the 8 stations in unfiltered water according to the pesticides' family.

Principal Component Analysis (PCA) was performed on a matrix of 36 cases by variables of fourteen molecules of pesticide for the year 2007 and 2009, and pH, EC, TSM and DOC.

The PCA was analyzed with the help of STATISTICA package to identify the underlying factors distributing molecules of pesticide and their controlling factors in each station. And, this procedure enables us to figure out the patterns of these variables in unfiltered water for every station during two separate sampling campaigns in 2007 and 2009 (figure 15). The results of the principal component analysis illustrate that the stations 6 and 7 are distributed separately in compared to other stations. This result is not surprising, since station 7 is a small pond with aquifer animals such as duck, which changes the characteristics of water in this station. And highlighted the importance role of small pond with aquifer organism in changing the characteristics of water.

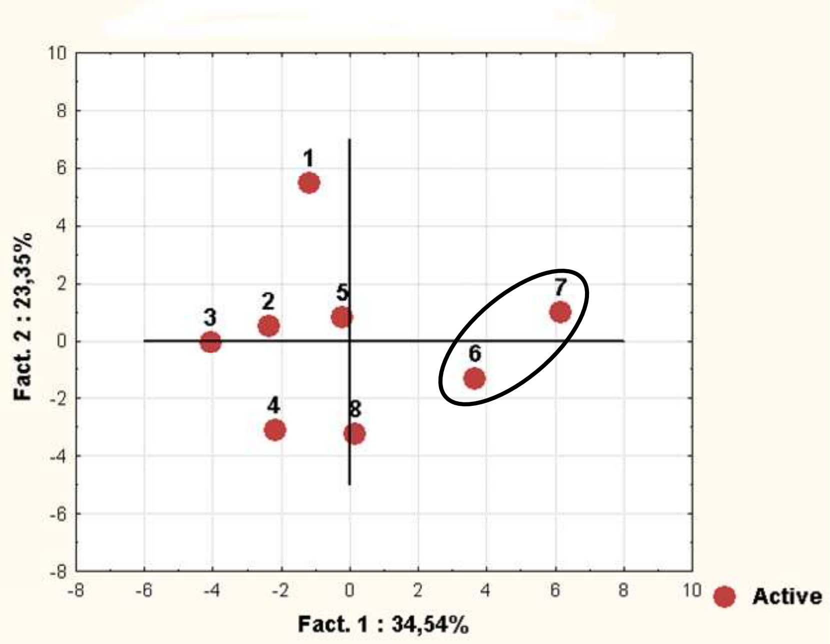


Figure 15- Principal component analysis and distribution of pesticide's molecules in unfiltered water in 2007 and 2009.

2.2 Spatial variation of controlling factors (DOC-POC-pH-EC and TSM)

The average of dissolved organic carbon (DOC) for all of the 8 stations is 2.9 and 3.4 mg.L^{-1} in 2007 and 2009 respectively. During two years investigation, the maximum of DOC was found in station 7. As this station has particular characteristics (a small pond with relatively stagnant water) therefore the high level of DOC is not surprising.

The ratio of DOC between other stations in compare to station one (outlet) shows greater values for the sampling campaign of 2007 (1.43 ± 0.31) than for 2009 (0.88 ± 0.28), mainly because DOC content measured at station one is higher in 2009 than in 2007.

The spatial distribution of TSM (figure 16) shows clearly an important role of station 7 for deposition of sediment, where we registered the minimum concentration of

TSM. The ratio of other stations compared to station one shows the value about 1.140 ± 0.81 and 1.67 ± 1.07 mg.L^{-1} respectively in 2007 and 2009.

pH and EC measured in Auradé catchment remain relatively high and with small variations. Besides, the spatial distribution of pH and EC in the area under our observation followed a constant trend except for station 7 where the highest value of pH and the lowest value of EC were registered. This phenomenon could be the result of the high rate of caco$_3$ precipitation in station 7 which logically reduces EC. The average values of pH and EC are respectively 7.73 ± 0.14 and 898 ± 78 in 2007 and 8.05 ± 0.52 and 801 ± 156 in 2009.

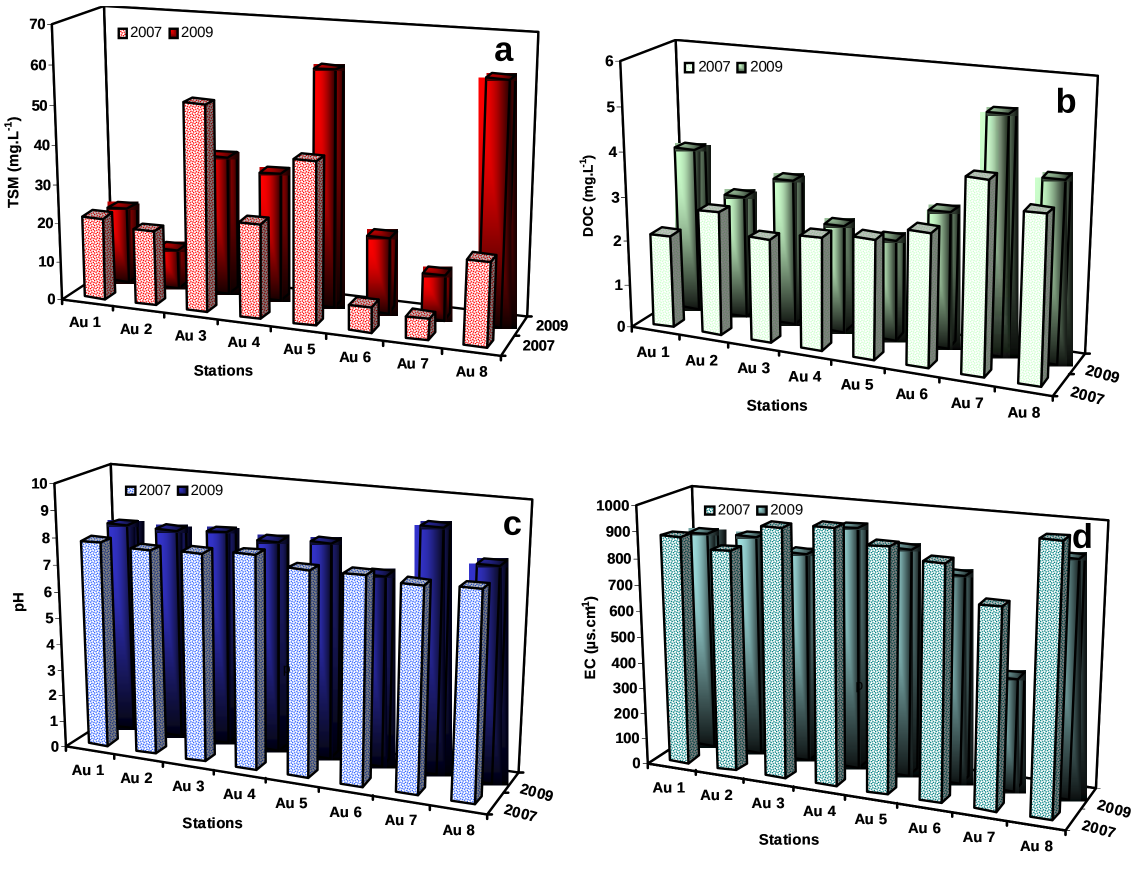


Figure 16- Spatial variation of controlling factors in Auradé catchment during 2 sampling periods, June 2007 and June 2009. a - TSM, b – DOC, c – pH and d – EC.

3 Pesticide occurrence in Save and Auradé catchments

The observation carried out on pesticide concentration reveals that the level of concentration tends to increase during flood events with increasing rate of discharge.

One hundred thirty (130) samples have been collected during the period of observation for the Save river, of which 82 samples during storm events. Half of the 82 samples was subject of a series of analyses in filtered water and the similar procedure was applied to the other half (41) in unfiltered water.

Two hundred fourty two (242) samples have been collected during two years research in Auradé catchment, of which 74 samples during storm events. One hundred twenty one (121) samples were subjected to our analytical thechniques in unfiltered water and the remaining samples were treated with the same procedure in filtered water.

Understanding of fourteen (14) pesticides molecules’ behaviour was the center of our attention in this research. Herbicides molecules such as phenylurea, chloroacetanilid, traizine and toluidine families, on the one hand and triazole’s families of fungicides on the other hand were received a particular attention in this study. Our findings show that the level of concentration tends to increase during flood events with increasing rate of discharge.

Pesticide concentration in unfiltered water proved to be higher than in filtered water, but this disparity becomes smaller as the degree of pesticide-molecules solubility increases, thus for a low degree of solubility of molecules the difference is quite significant.

The following tables help to focus attention on the detection frequency and concentration observed in sample collected at the out let of the catchment during the investigation periods.

Table VII- Number of pesticide detections, detection frequency and concentration of selected pesticides in unfiltered water (a) and filtered water (b) in Save watershed (In general, 65 sampling points are set as a total of 100%).

Molecules	Number of detection (n=65)		% of detection frequency		Number of detection during storm events (n=41)		% of detection frequency during storm events		Maximum (µg.L^{-1})		Average (µg.L^{-1})	
	a	b	a	b	a	b	a	b	a	b	a	b
DEA	63	61	97	94	39	38	95	93	0.08	0.06	0.023	0.016
atrazine	61	60	94	92	38	37	93	90	0.02	0.05	0.011	0.011
chlorotoluron	64	63	98	97	40	39	98	95	1.97	1.27	0.391	0.230
isoproturon	62	60	95	92	40	39	98	95	1.16	0.74	0.144	0.096
linuron	58	54	89	83	37	37	90	90	1.65	0.65	0.270	0.087
metolachlor	64	63	98	97	40	40	98	98	0.95	0.95	0.197	0.179
alachlor	46	40	71	62	28	27	68	66	0.05	0.04	0.007	0.005
aclonifen	60	48	92	74	39	36	95	88	1.34	0.17	0.144	0.024
trifluralin	54	44	83	68	34	28	83	68	0.51	0.09	0.076	0.016
fenpropimorph	53	50	82	77	36	31	88	76	0.02	0.02	0.004	0.002
fluzilazol	65	64	100	98	41	41	100	100	0.07	0.07	0.010	0.008
cyproconazol	50	39	77	60	29	29	71	71	0.12	0.10	0.020	0.013
tebuconazol	63	62	97	95	40	40	98	98	0.78	0.28	0.255	0.059
epoxiconazol	65	62	100	95	41	40	100	98	0.11	0.04	0.165	0.010

The maximum concentration of pesticide detected varied between 0.02-1.97 µg.L^{-1} and 0.02-1.27 µg.L^{-1} for unfiltered and filtered water, respectively.

The results show that the maximum concentrations of all of the molecules except atrazine, DEA, alachlor, fenpropimorph and fluzilazol exceed the EU drinking water quality criteria of 0.1 µg.L^{-1}; however, we observed the same patterns in filtered water, except for trifluralin and epoxiconazole, that is to say lower concentration from limit of authorization. It is worth noting the level of magnitude of concentration in filtered water is less than unfiltered water. Except for cyproconazol and alachlor, the pesticide detected showed the frequency more than 80% during all of the sampling period and storm events in unfiltered water.

Similarly the detection frequency was more than 80 % for most of the molecules studied in filtered water. However, it was less than 80% for cyproconazol, fenpropimorph, aclonifen, trifluralin and, alachlor during the whole period of observation and during storm events the detection frequency registered was less than

80% for the same molecules except aclonifen. Chlorotoluron is the molecule with the maximum average concentration both in unfiltered and filtered water.

Table VIII- Frequency and concentration of selected pesticides in unfiltered water (a) and filtered water (b) in Auradé catchment (In general, 121 sampling points are set as a total of 100%).

Molecules	Number of detection (n=121)		% of detection frequency		Number of detection during storm events (n=37)		% of detection frequency during storm events		Maximum (µg.L^{-1})		Average (µg.L^{-1})	
	a	b	a	b	a	b	a	b	a	b	a	b
DEA	121	115	100	95	37	36	100	97	0.070	0.068	0.001	0.012
atrazine	119	112	98	93	35	32	95	86	0.020	0.02	0.008	0.005
chlorotoluron	120	119	99	98	36	36	97	97	1.326	1.375	0.362	0.188
isoproturon	121	119	100	98	37	35	100	95	0.756	0.457	0.301	0.054
linuron	117	113	97	93	36	35	97	95	1.377	1.337	0.221	0.168
metolachlor	120	115	99	95	37	35	100	95	0.353	0.263	0.079	0.057
alachlor	117	89	97	74	37	30	100	81	0.202	0.151	0.022	0.012
aclonifen	118	108	98	89	37	32	100	86	1.519	0.051	0.142	0.004
trifluralin	113	105	93	87	36	35	97	95	0.829	0.232	0.078	0.044
fenpropimorph	93	80	77	66	28	24	76	65	0.071	0.042	0.003	0.002
fluzilazol	118	110	98	91	36	34	97	92	0.244	0.084	0.010	0.006
cyproconazol	97	76	80	63	29	26	78	70	0.305	0.251	0.006	0.004
tebuconazol	106	101	88	83	31	29	84	78	0.332	0.160	0.024	0.011
epoxiconazol	116	107	96	88	37	35	100	95	0.071	0.035	0.016	0.010

The highest level of concentration for pesticide detection varied between 0.02-1.52 and µg.L^{-1} in unfiltered water and 0.02-1.375 µg.L^{-1} in filtered water. In unfiltered water, epoxiconazol, fenpropimorph, atrazine and DEA have shown the concentration inferior to 0.1 µg.L^{-1}. In filtered water only the concentration of epoxiconazole, fenpropimorph, aclonifen, fluzilazol, atrazine and DEA was registered less than 0.1µg.L^{-1}. In unfiltered water fonpropimorph is the only molecule with the detection frequency less than 80% in all of the investigation periods. During storm events, fenpropimorph and cyproconazol have detection frequency of 76 and 78% respectively. In filtered water, cyproconazole, fenpropimorph and alachlor have a detection frequency of less than 80% during all of the sampling period. However, during storm events the detection frequency for all of the pesticides was more than 80% except for cyproconazol, tebuconazol and fenpropimorph. Isoproturon and chlorotoluron are the molecules with the maximum average concentration about 0.301 and 0.188 µg.L^{-1} during all of the study periods.

4 Temporal variations of pesticide concentration

4.1 Save river

As we said earlier, the occurrence of pesticides in water is controlled by myriad factors, including their physico-chemical properties, amount and rate of use, amount and intensity of rainfall or irrigation (Barbash et al., 1999; Garmouma, et al., 2001; Gilliom et al., 2006; Hancock et al., 2008).

The results of this section indicates distribution of selected pesticides in different families for 65 water samples from Save river and 121 samples from Auradé catchment that recuperated at the outlet throughout the investigation period. The seasonal variation in pesticide concentrations in surface water showed a marked increase during the main application periods. The temporal results also demonstrate the importance of storm events to transport of pesticides. The seasonal variation in pesticide concentrations in surface water showed an important increase during the main period of application and storm events for pesticides, which is in line with the result ascertain by Baker and Richards (1990), Thurman et al. (1991), Tisseau et al. (1996), Kreuger and Tornqvis (1998), Rawn et al. (1999), Konstantinou et al. (2006). The maximum concentration of all pesticides were registered in the first few events after application and concentrations decreased rapidly with time and subsequent events, as it is usually observed in field study (Wouchop, 1978).

Substituted Urea family, a highly soluble and synthetically produced pesticide, indicates pesticide concentration greater than 0.1 µg.L^{-1} in filtered and unfiltered water. Figure 17 shows the seasonal variations of chlorotoluron, isoproturon and linuron concentrations. It highlights the impact of agricultural practice upon water quality in the case of these molecules.

Chlorotoluron level of concentration during the storm of March 2008 was as high as 1.80 µg.L^{-1} for unfiltered water but for filtered water 1.2 µg.L^{-1} was registered.

During the storm event of January and February 2009, characterized as rather unusual with torrential rain, exceptional high level of chlorotoluron was observed. A high level of chlorotoluron could also be attributed to winter application of this pesticide on crops.

The highest concentration of isoproturon and linuron was registered during the main application period in April, May, and June 2008. The maximum concentration of isoproturon was around 1.2 and 0.8 (µg.L^{-1}) in unfiltered and filtered water respectively during June 2008.

Linuron has represented the highest level of concentration, around 1.6 µg.L^{-1} in April and June 2008. However, in filtered water the maximum concentration was registered about 0.7 µg.L^{-1}in the end of May and early June 2008.

In general, substitute ureas were detected in the river throughout the year and displayed the highest concentrations after the agricultural treatment. Our study underlines the large impact of agricultural treatment, especially substitute urea family on water quality in Save river (figure17).

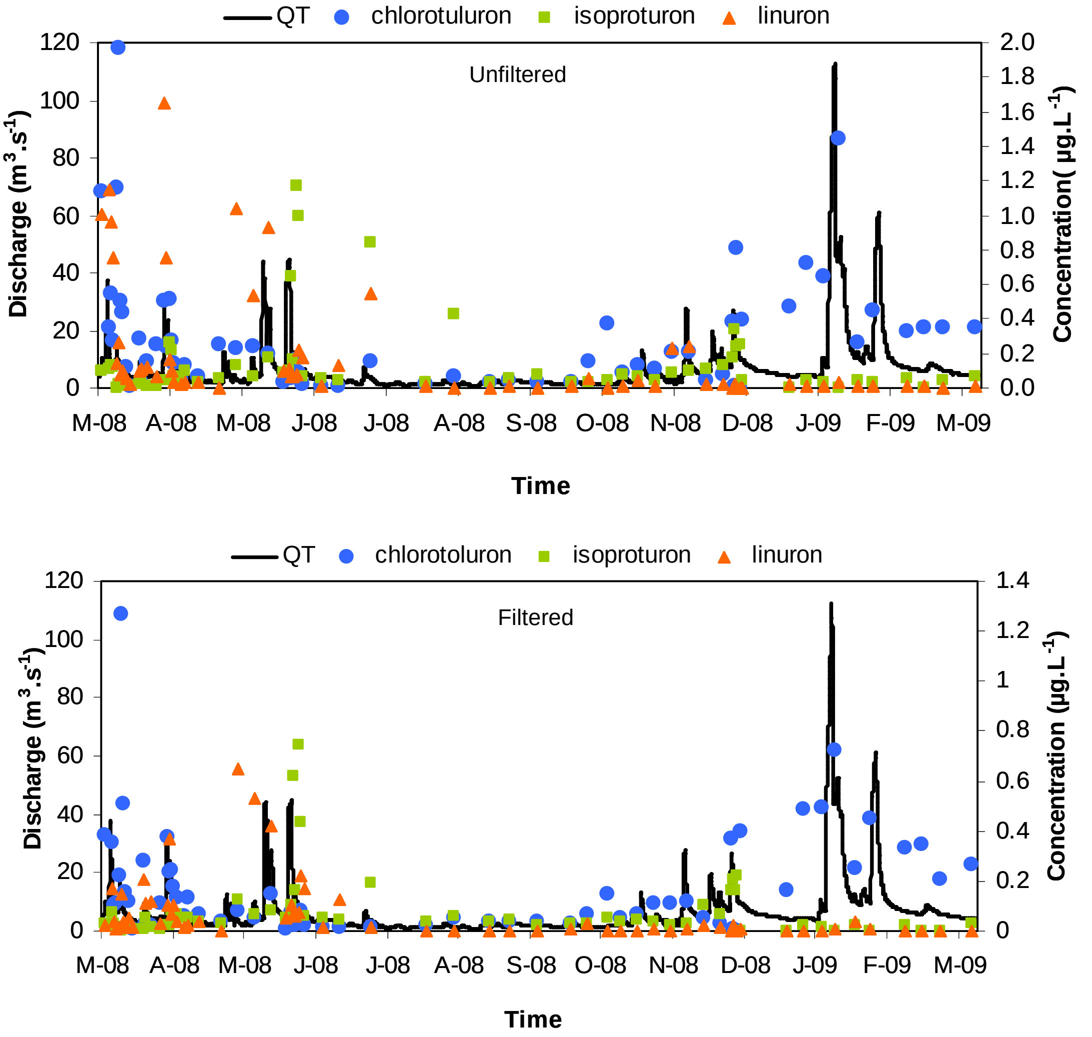
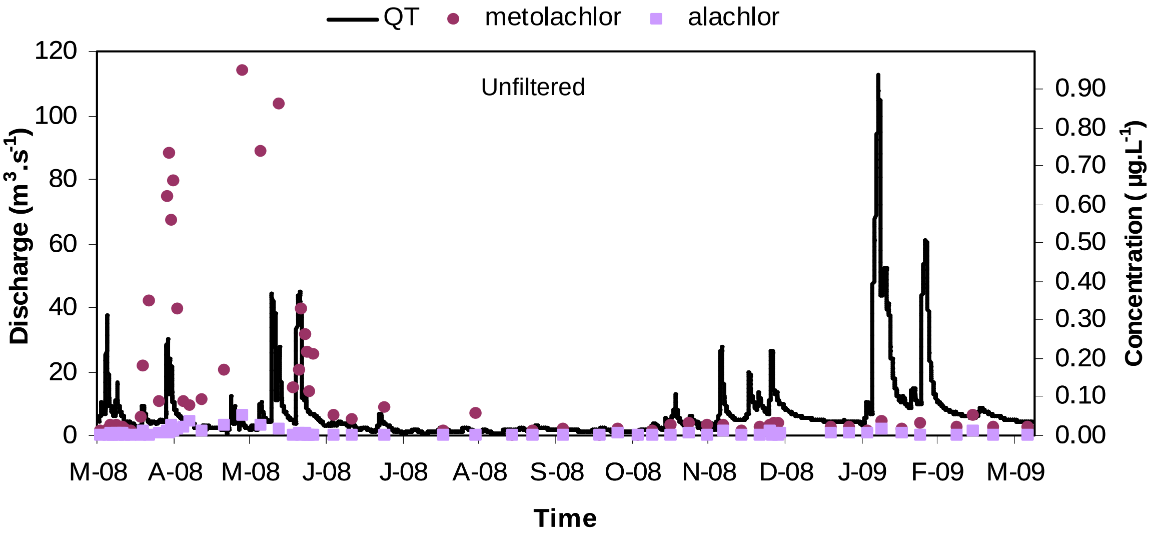


Figure 17- Temporal variations of substituted urea family in unfiltered (above) and filtered (below) water in Save river at the outlet during the period 2008-2009.

The study conducted by Gomme et al. (1991), show high pesticide occurrence in the river (chlorotoluron-isoproturon) correlated well with river flow, that brought about by flood and high river flow, especially in the winter and spring.

Concentration of chloroacetamide families (metolachlor, alachlor) was at its maximum in April to June 2008 (figure 18). Metolachlor concentration reaches nearly 1 µg.L^{-1} at most and the results show little variation for filtered and unfiltered water. Ng et al. (1995) reported that metolachlor concentration and losses were greatest in runoff events occurring shortly after herbicide application. Alachlor concentrations in April 2008 exhibit low fluctuations and remain within the authorised limit (0.1µg.L^{-1}).



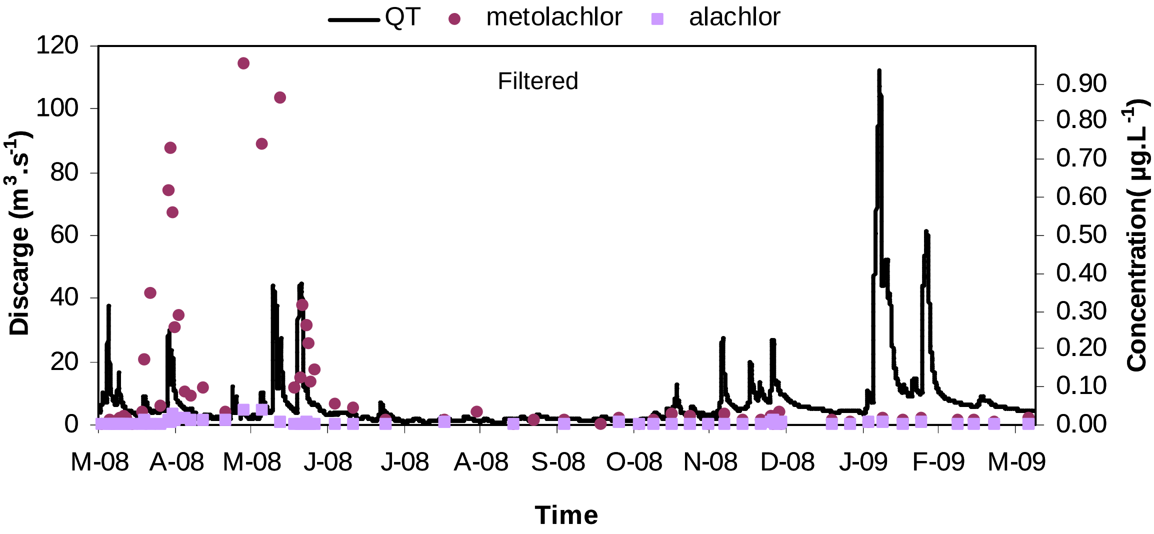


Figure 18- Temporal variations of chloroacetamide family in unfiltered (above) and filtered (below) water in save river at the outlet during the period of 2007-2009.

In this study the results shown that aclonifen and trifluralin were used as representative of toluidine family (figure 19). Aclonifen has proved to be the most effective against a broad spectrum of weeds, especially broad-leaf weeds (Covarelli, 1999). For these molecules the difference between unfiltered and filtered water is very significant. This phenomenon shows an important role of total suspended matter (TSM) in transport of these molecules.

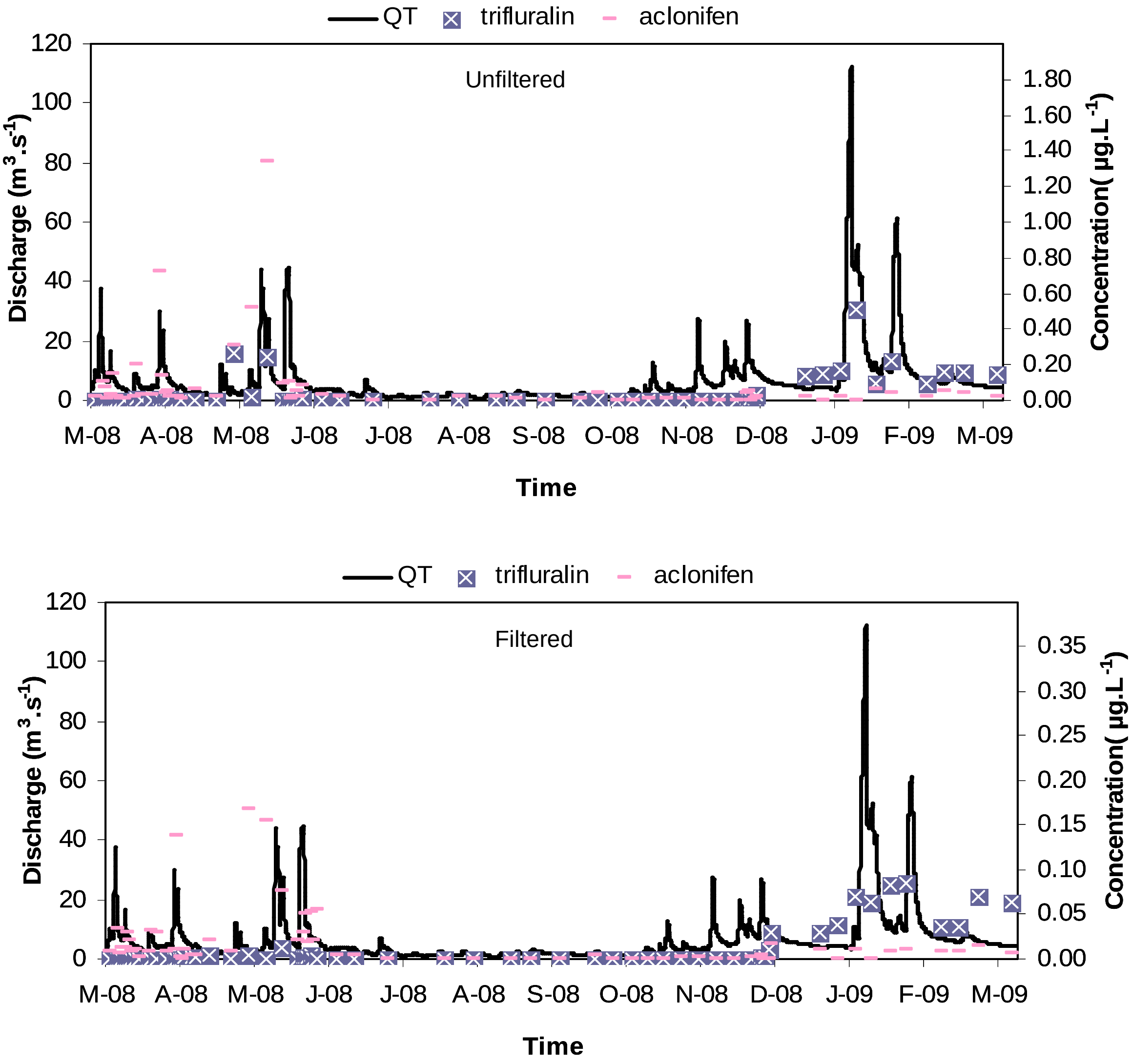


Figure 19- Temporal variations of toluidine family (trifluralin and aclonifen) in unfiltered (above) and filtered (below) water in Save river.

We observed the maximum concentration of aclonifen during storm of April to June, considered as an application period of pesticide. The maximum concentration is about 1.3 and 0.17 µg.L^{-1}, respectively for unfiltered and filtered water.

On the contrary trifluralin shows the maximum of concentration during floods of January and February in 2009, because there was probably a trifluralin application for winter crops. The maximum concentration of trifluralin is 0.5 and 0.09 µg.L^{-1} in unfiltered and filtered water respectively.

In the case of fungicides (figure 20), the presence of a large amount of tebuconazol, a fungicide commonly used in this catchment, was registered during storm of April and June. However, in our experimental conditions, the concentration of this molecule was more than two fold higher in unfiltered water (0.8 µg.L^{-1}) than filtered water (0.3 µg.L^{-1}). The concentration of cyproconazole and epoxiconazole is slightly higher than 0.1 µg.L^{-1} in unfiltered water. However, in filtered water the concentration of fungicides molecules remains less than 0.1 µg.L^{-1} except for teboconazole.

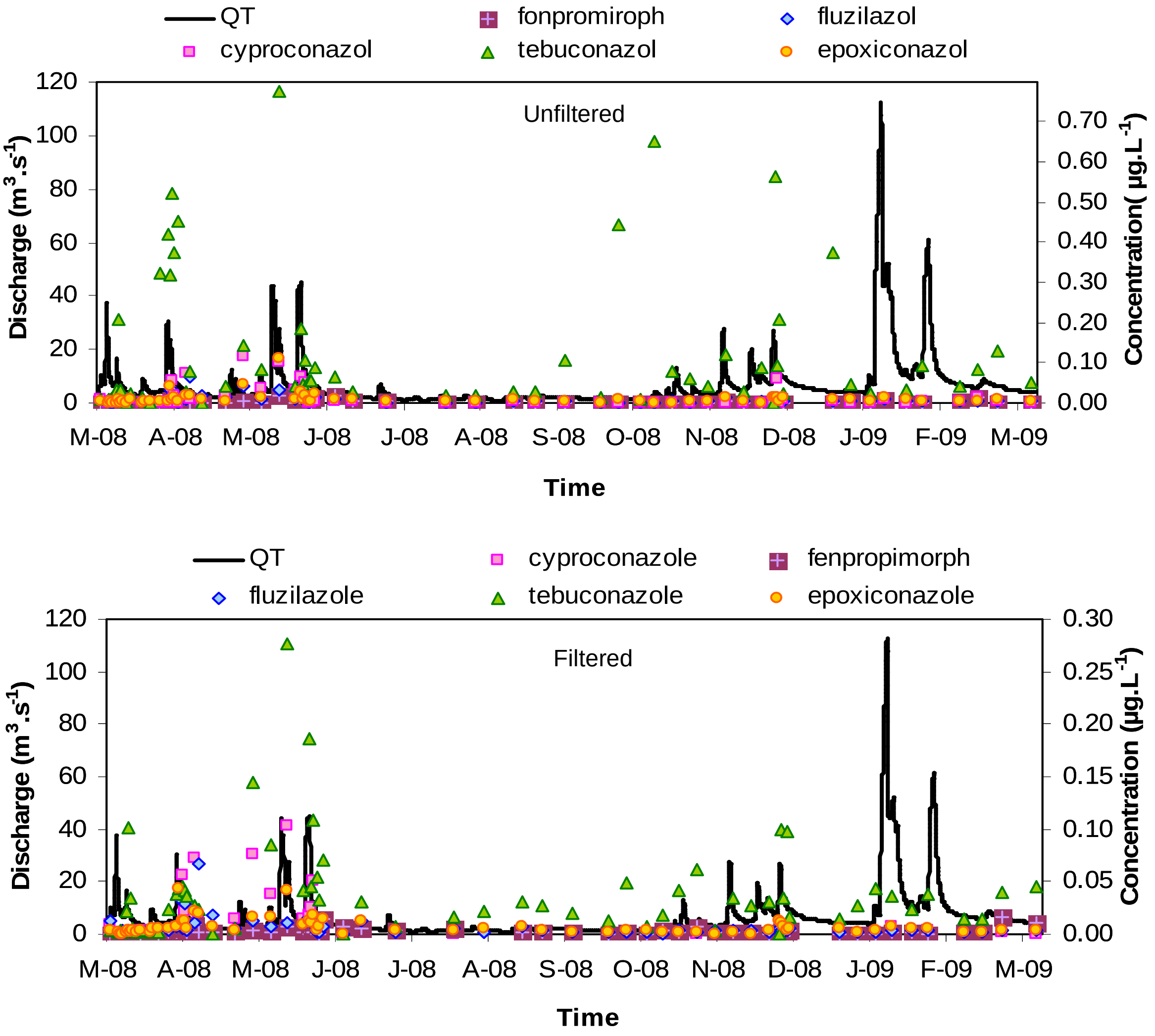


Figure 20- Temporal variations of fungicides family in unfiltered (above) and filtered (below) water in Save river.

Atrazine and its metabolite (DEA) are the molecules of s-triazine family, which are commonly used in agricultural settings. The use of Atrazine is forbidden since 2003.

Yet the results of our research represent the trace of these molecules in water. However, their concentrations remain less than 0.1 µg.L^{-1} (figure 21).

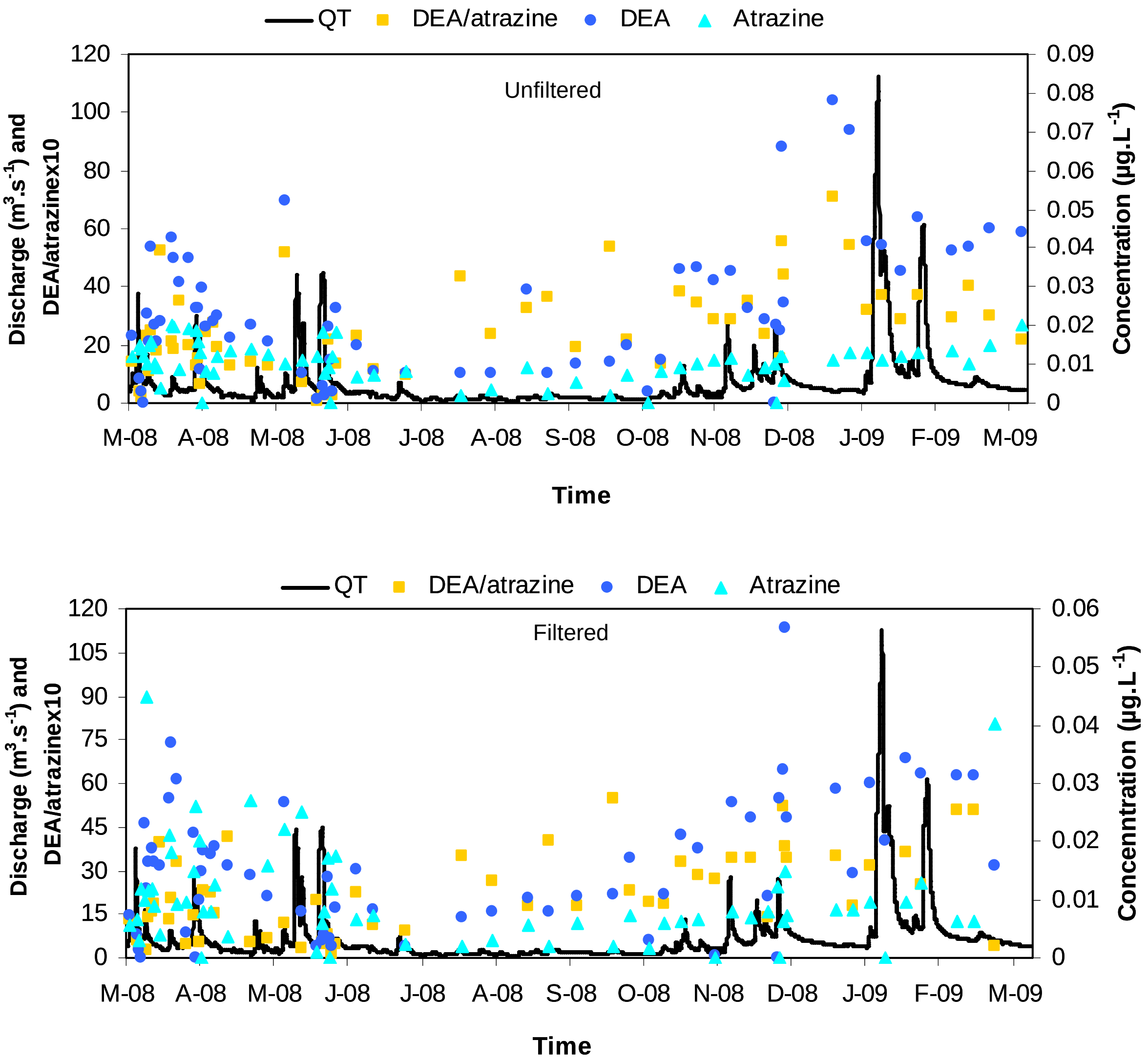


Figure 21- Temporal variations of atrazine and deethyatrazine concentration and of their ratio DEA/atrazine in unfiltered (above) and filtered (below) water in Save river.

As we said earlier DEA is a degradated form of atrazine and it has shown the level of concentration higher than atrazine, though the difference remains insignificant. In fact during baseflow condition, background atrazine and DEA concentration generally ranged less than 0.03 µg.L^{-1}, which means that all the aquifers of the catchment, both superficial and deep, were contaminated, however this level remains less the limit of authorization.

The concentrations level of atrazine and DEA have reached record high during storm events but showed a weaker response to storm flow comparing to the level of concontration of other herbicides. Puckett and Hughes (2005) reported maximum concentrations of both atrazine and DEA occurred during storm events in the spring following pesticide applications.

To investigate hydrological processes that influence the evolution of atrazine concentration in rivers, we utilized the desethylatrazine/atrazine concentration ratio (DAR), referred to by other authors, to determine the relative importance of the different input pathways for transferring of these molecules Adams and Thurman, (1991). The DAR might served as an indicator of the transport mechanism of atrazine (soil residence times) and its degradation in the environment.

Low DAR (<1) indicates that surface runoff has been subject to relatively little degradation during transport, whereas a high DAR (>1) indicates an aging atrazine load with groundwater displacement and interaction.

However, in our study the results of DAR showed a fluctuation throughout investigation period with most values greater than 1. This results confirm the contamination of ground water by atrazine and its degradate product.

4.2 Auradé catchment

During a two-year survey in Auradé catchment, substituted urea pesticide's family concentration remained greater than 0.1 $\mu g.L^{-1}$ in filtered and unfiltered water.

The value of concentration in unfiltered water were 1.3, 1.4 and 0.8 $\mu g.L^{-1}$ for chlorotoluron, linuron, isoproturon respectively. In filtered water, the maximum concentration of these substituted urea family remains relatively the same comparing to unfiltered water for chlorotoluron, linuron. However, the maximum concentration observed for isoproturon stands at 0.4 $\mu g.L^{-1}$ in filtered water and twice as much in unfiltered water (0.8 $\mu g.L^{-1}$).

The substitute urea family concentration remained relatively high and fairly stable during dry season (figure 22). However, fluctuations in concentration observed during storm events are related to the agricultural practice. Moreover, Shipitalo and Owens (2006) reported herbicide loss varied considerably in the watershedes and this variation is linked with the amount of rainfall and timing of precipitation. Reviewing Save and Auradé watersheds didn't reveal any simultaneous occurrence of herbicide during the common period of observation.

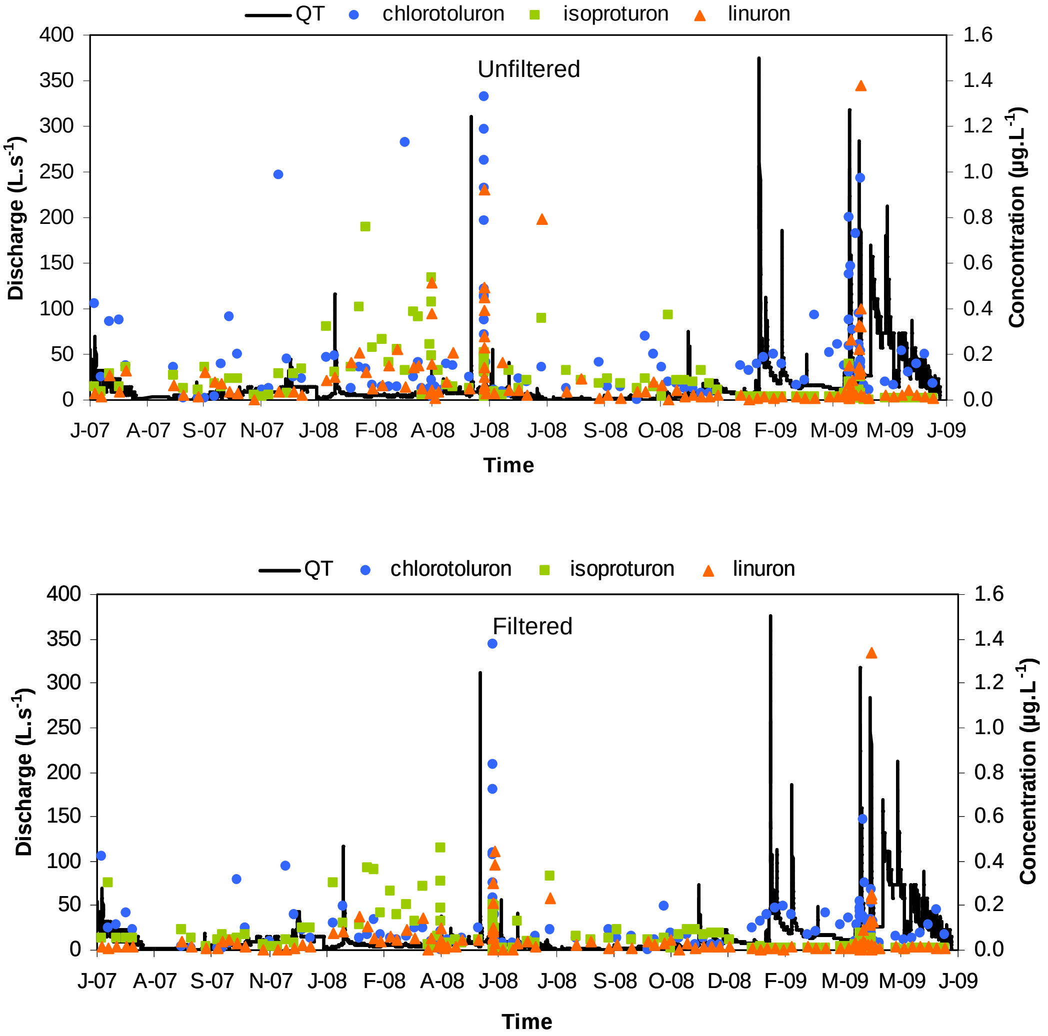
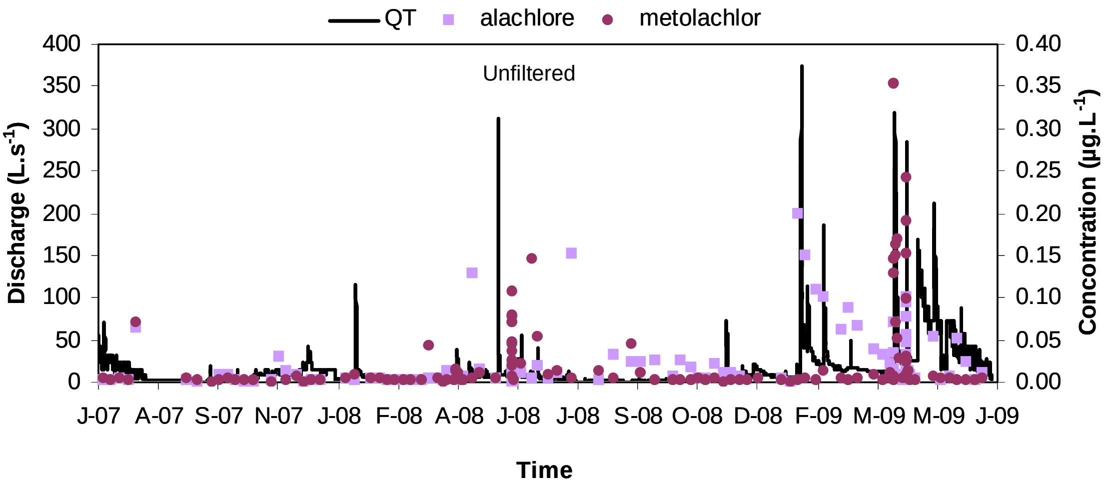


Figure 22- Temporal variations of substituted urea family (clorotuloron, isoproturon and linuron) in unfiltered (above) and filtered (below) water in the Montoussé river at Auradé during the period 2007-2009.

Chloroacetanilide family concentration (metolachlor and alachlor) is at its maximum in April and June. The concentrations of metolachlor and alachlor present little variation for filtered and unfiltered water (figure 23). The maximum value of concentration for metolachlor is about 0.35 µg.L^{-1} in unfiltered water and its concentration is approximately 0.30 µg.L^{-1}, for filtered water. The highest level of concentration for alachlor is around 0.20 µg.L^{-1} and 0.15 µg.L^{-1} respectively for unfiltered and filtered water in January 2009.



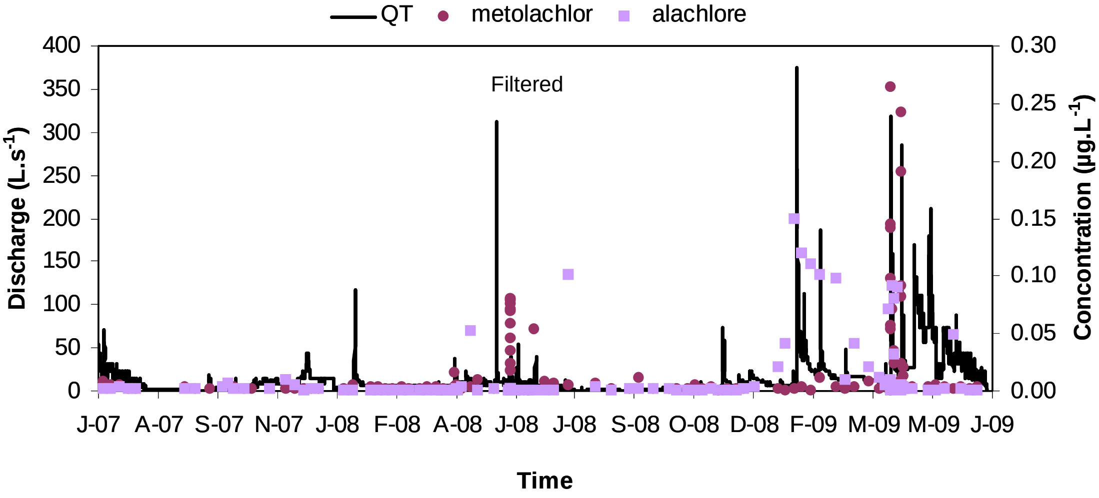


Figure 23- Temporal variations of chloroacetanilide family (metolachlor, alachlor) in unfiltered (above) and filtered (below) water in the Montoussé river at Auradé during the period 2007-2009.

In this study, aclonifen and trifluralin molecules with less degree of solubility were used as representative of toluidine family (figure 24). The concentration of aclonifen reached up to 1.5 µg.L^{-1} in unfiltered water during May 2008, whereas in filtered water its concentration remained less than 0.1 µg.L^{-1}.

The highest concentration of trifluralin was observed during storm of January and April in 2009 with less than 1 µg.L^{-1} in unfiltered water and around 0.2 µg.L^{-1} in filtered water, during May 2008 and April 2009.

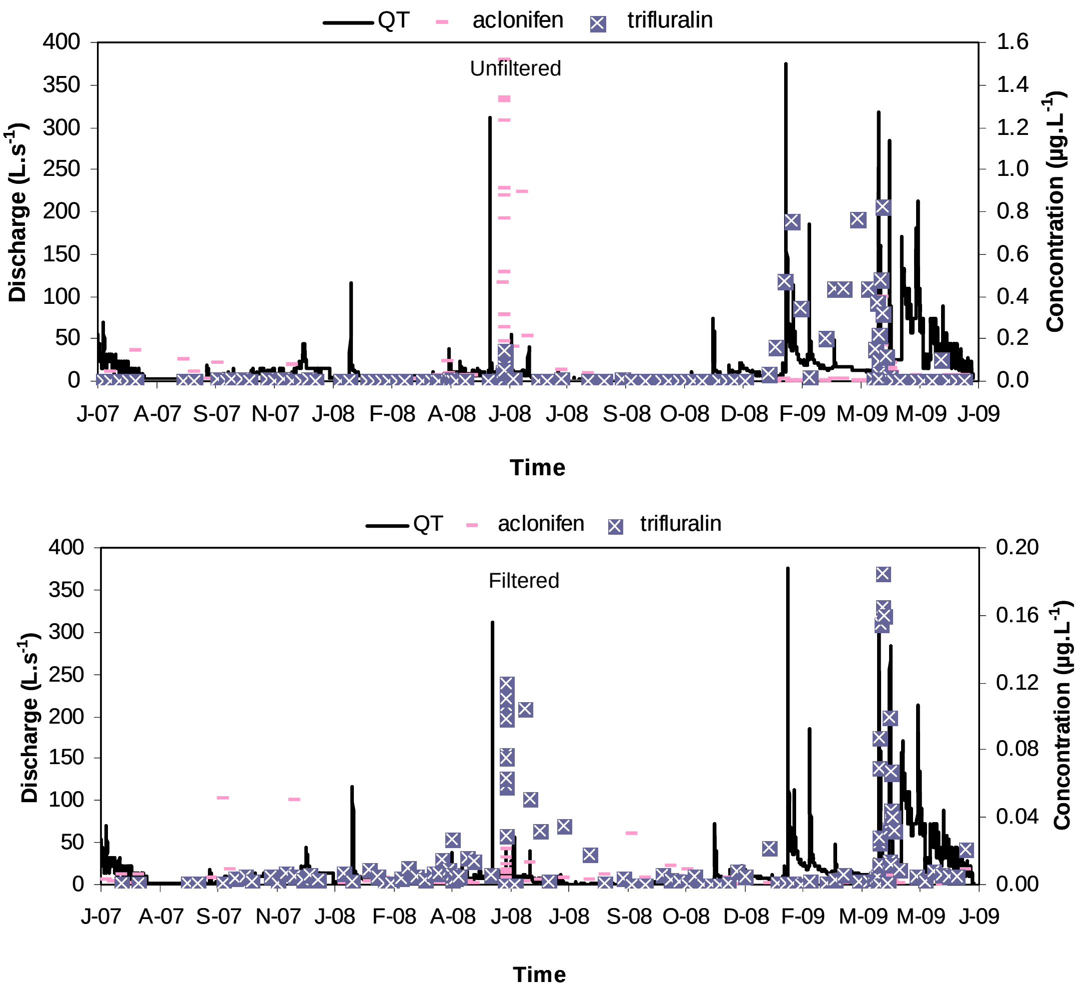


Figure 24- Temporal variations of toluidine family (aclonifen,trifluralin) in unfiltered (above) and filtered (below) water in Aurade catchment during the period 2007-2009.

In the case of fungicides molecules, fenpropimorph and epoxiconazole, the concentrations were relatively stable and inferior to 0.1 µg.L^{-1} in both unfiltered and filtered water (figure 25).

Cyproconazol and fluzilazol have shown relatively stable concentration during the entire period of investigation except in November 2007 where the concentration was higher than 0.1 µg.L^{-1} in both filtered and unfiltered water. This phenomenon might be due to pesticides application; however, no information is available to prove this hypothesis. The concentration of tebuconazole, the most concentrated molecules in fungicide family, was registered higher than 0.1 µg.L^{-1} in both unfiltered and filtered family.

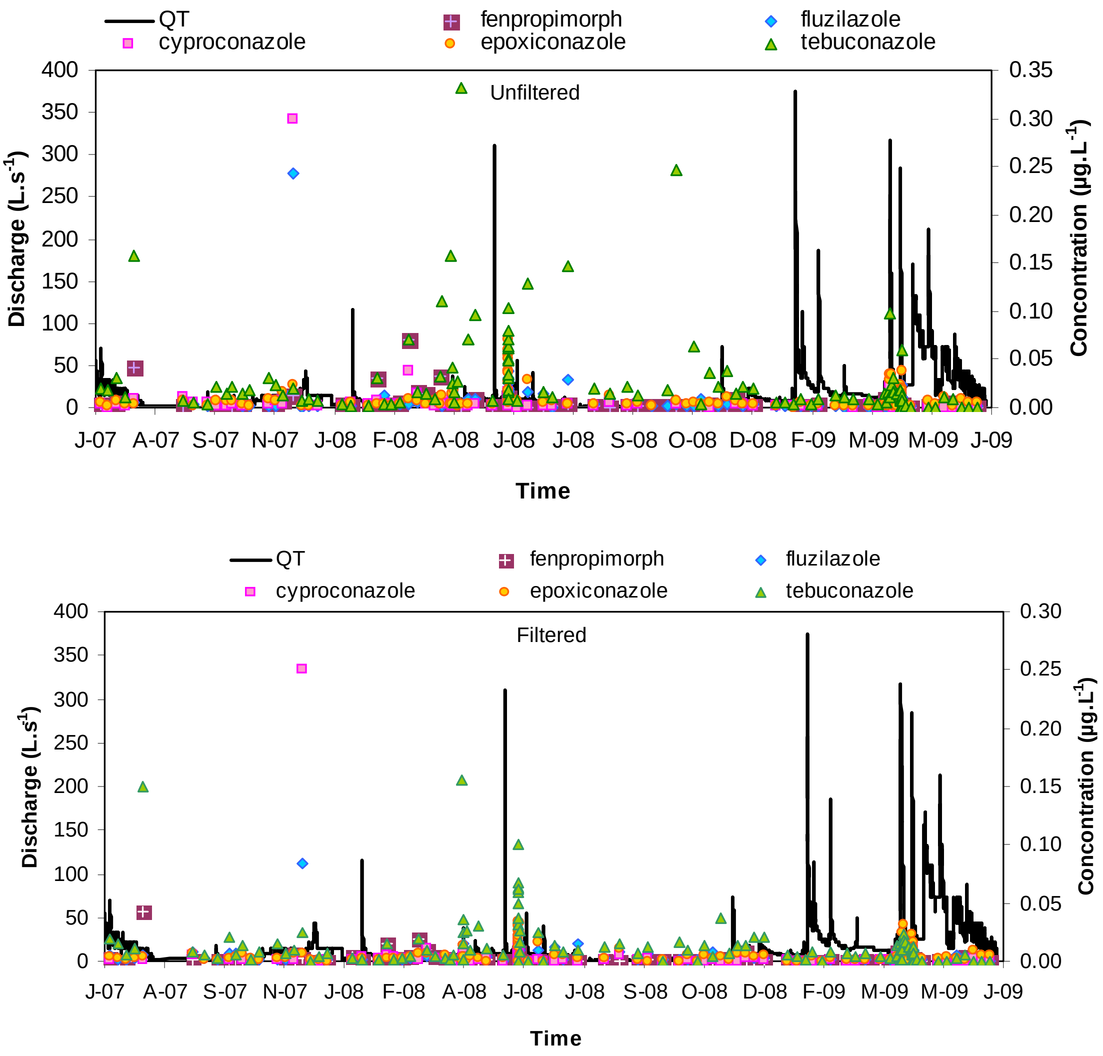


Figure 25- Temporal variation of fungicides in unfiltered (above) and filtered (below) water in the Montoussé river at Auradé during the period 2007-2009.

In the Montoussé river the concentration of atrazine and its metabolite (DEA) is less than 0.1 µg.L^{-1} as we observed for Save river. Atrazine also shows a level of concentration less than 0.1 µg.L^{-1} and smaller fluctuation than DEA (figure 26).

The reason for increasing atrazine and its metabolite concentrations in river water during storm events can be speculated on the ground that a large amount of herbicides may have been accumulated in the watershed including: in the soils, tributaries and river banks, in other words we have storage of these molecules in basin which is referred to as «basin storage». This argument is in line with other autheurs, Squillace and Thurman, (1992).

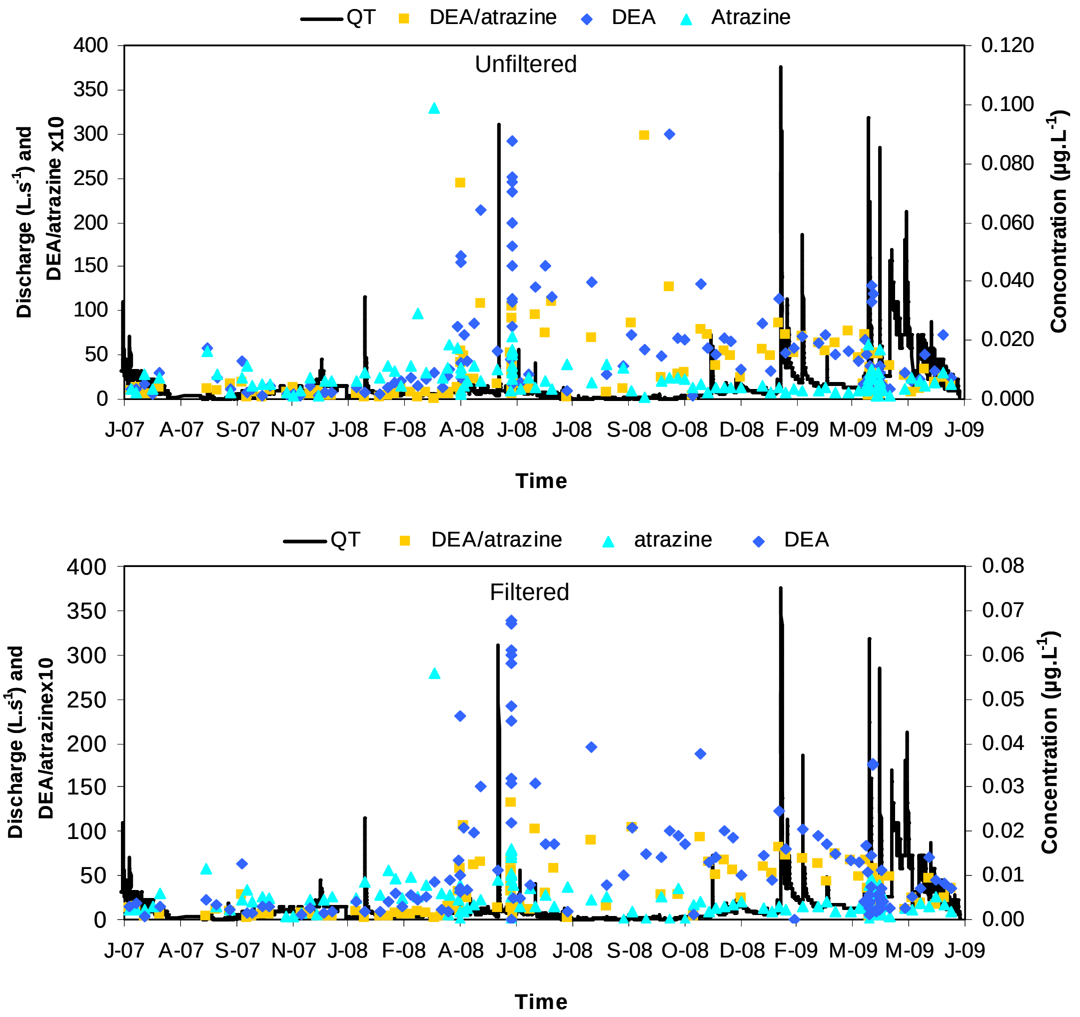


Figure 26- Temporal variations of atrazine and deethyatrazine in unfiltered (above) and filtered (below) water in Aurade catchment during the period 2007-2009.

The desethyatrazine/atrazine concentration ratio (DAR), at Montoussé river also shows a value more than 1 which indicates the contamination of ground water by atrazine and its metabolite (DEA), as we observed earlier in Save catchment.

5 Temporal variations of controlling factors (DOC, TSM, pH and EC) at the outlet of Save and Auradé catchments

The variations of total suspended matter (TSM) and dissolved organic carbon (DOC) of samples collected at the outlet of the catchment respectively at Larra (Save) and Montoussé (Auradé) stations are shown in figure (27,28). Dissolved organic carbon (DOC) went up during storm events and stood high throughout the wet season and decreased to the lowest and fairly constant level in the dry season (2-3 mg.L^{-1}). The results presented here concerning DOC virtually demonstrated a positive correlation between the release of DOC and stream discharge, with maximum DOC concentrations occurring during storm events. This result is in accordance with those of others (Lewis and Grant, 1979; Reid et al., 1981; Edwards et al., 1987; Grieve, 1984; 1990; Muscutt et al., 1990; Chapman et al., 1993; McGlynn and McDonnell, 2003; Cooper et al., 2007). Hernes et al. (2008) pointed out DOC concentration varied significantly according to the hydrologic regime, with more than doubling values during storm water in comparing to baseflow periods. However, it is important to note here the temporal dynamic of DOC is very complex (Jones et al., 1996) and can be controlled not only by inputs of DOC but also by microbial activity in sediments (Bicudo et al. 1998) and by variations in POC (Vervier et al., 1993; Jones et al., 1995). TSM concentration generally increased with increasing water discharge and the TSM concentration was at the highest during the storm events, this result is in accordance with the researched was done by many authors for example (Hwang and Foster, 2006). pH and EC remain fairly constant during whole period of observation.

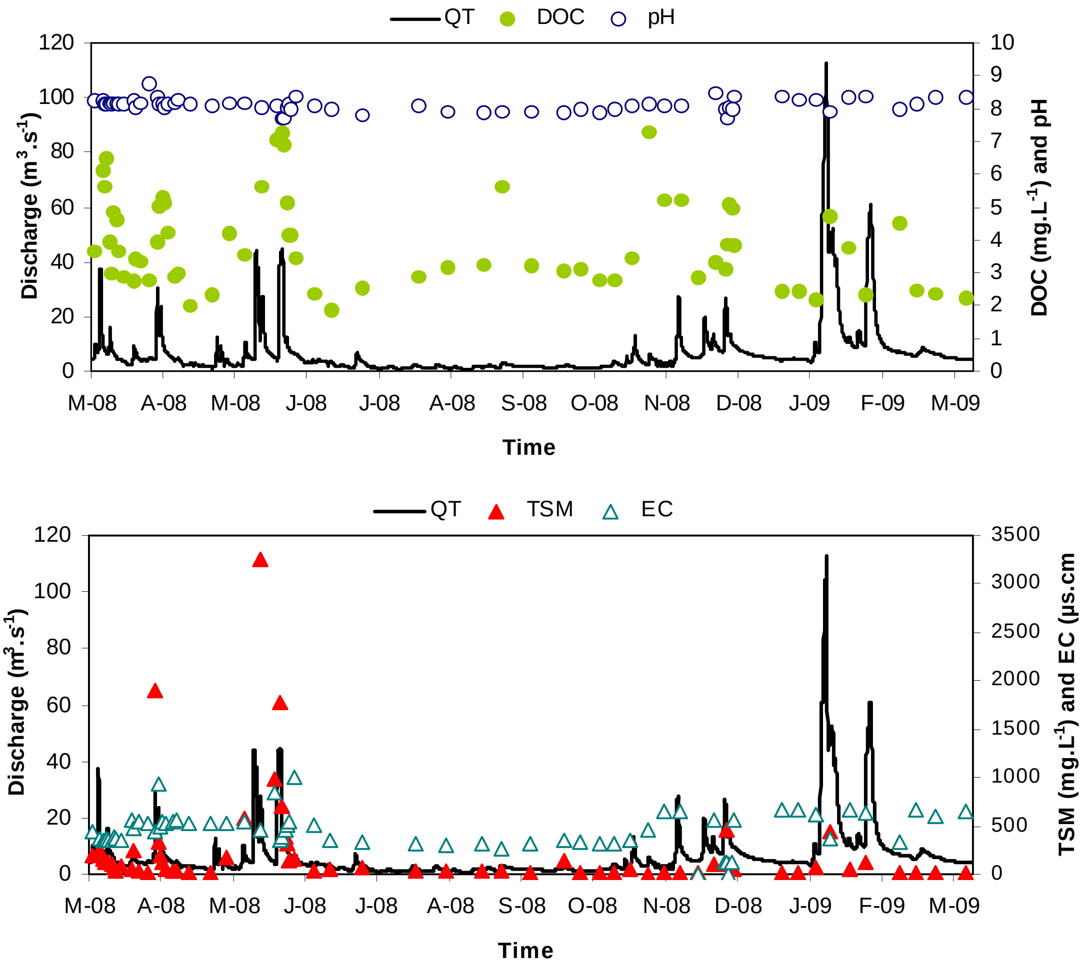


Figure 27- Hourly discharge with temporal variation of DOC, pH and TSM, EC in the Save river at Larra station during the period 2008-2009.

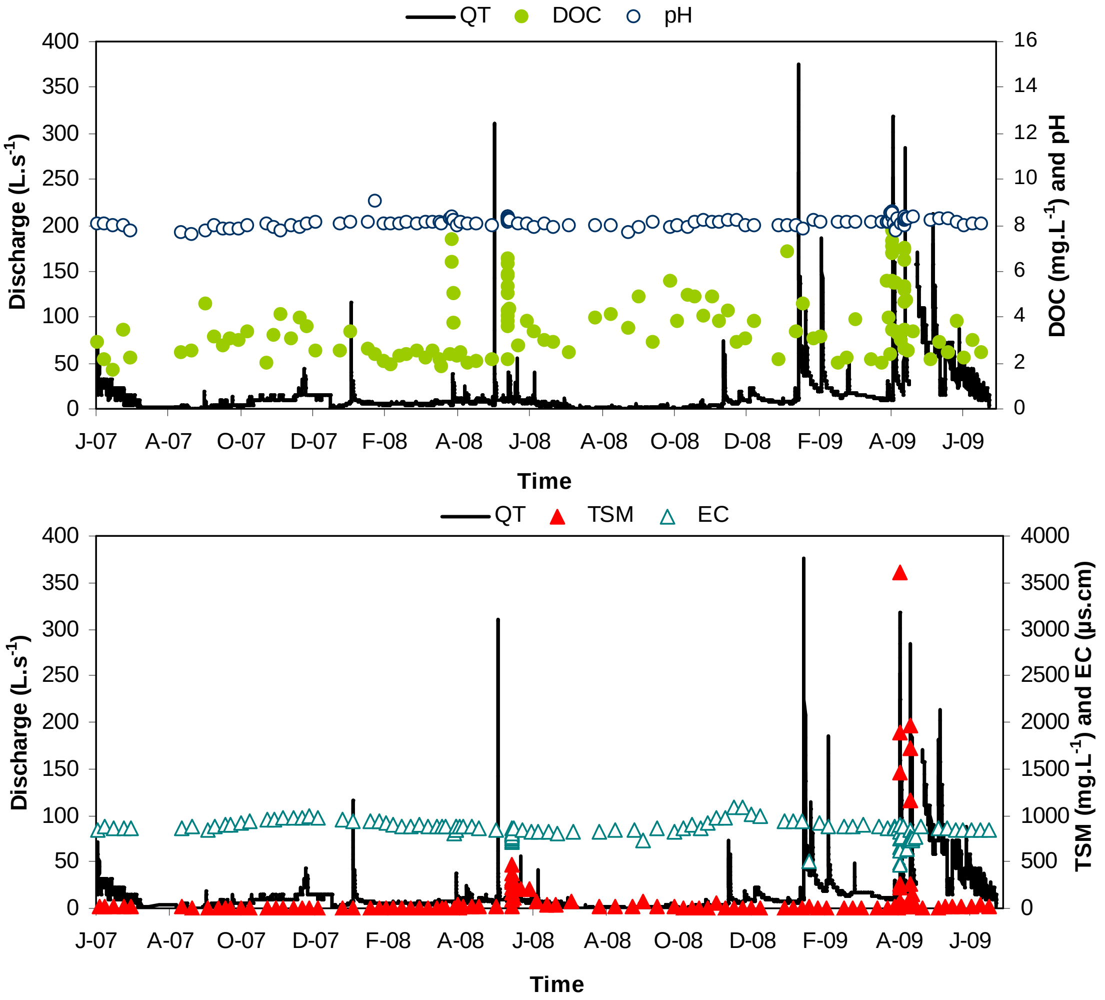


Figure 28- Temporal variation of DOC, pH, TSM, EC and discharge during two-years observation (2007-2009) in the Montoussé creek at Auradé.

Given this fact the pH and EC were high and relatively constant in our study area, therefore we don’t have any real fluctuation for these parameters, as a matter of this fact we focus our investigation on DOC and TSM. DOC and TSM showed a positive relationship with water discharge as shown by the fitted curves in figure (29), but the coefficient of determination was quite low. However, the variation of DOC was relatively smaller compared with that of water discharge and total suspended matter. The highest DOC concentration (7.285 mg.L^{-1}) observed for Save catchment in November was about four times of the lowest DOC concentration (1.881 mg.L^{-1}) observed in July; and the highest and lowest concentration of DOC for Auradé catchment as registered in April and July with the value of 7.74 and 1.68 (mg.L^{-1}) respectively. The average value of DOC is 4.2 for Save and 5 (mg.L^{-1}) for Auradé catchments. Hope et al., 1994 have established a positive relationship between DOC concentration and stream discharge which is perhaps one of the most consistent observations about DOC dynamic (Billett et al., 2006). The high DOC concentration in that period was related to the increased transport of organic matter from the allochtonous sources. The observed tendency for DOC concentration-increased with stream flow-has been driven by heavy pricipitation that has caused DOC leaching and /or increased flow through surface organic-rich horizons (Tranvik and Jansson, 2002; Hongve et al., 2004).

The highest TSM concentration (3255 mg.L^{-1}) observed in June was more than 350 times of the lowest quantity (9 mg.L^{-1}) registered in January and in Auradé catchment the maximum TSM (mg.L^{-1}) was observed in April (2009) and in concomitants with the storm events and the lowest one was registered in October (2008) with a value of 0.23 (mg.L^{-1}).

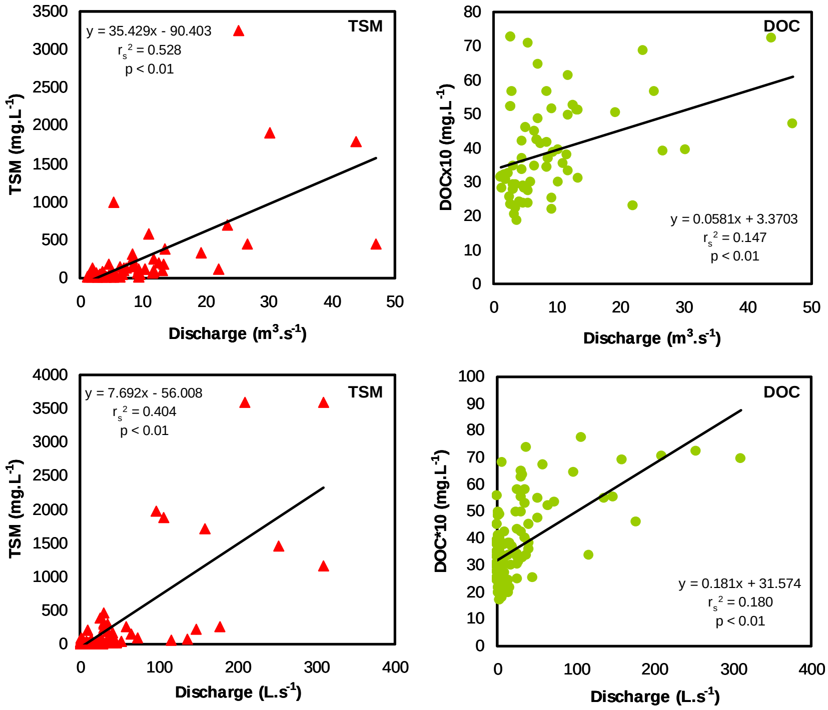


Figure 29- Relationship between TSM (left) and DOC (right) versus discharge in Save (above) and Auradé (below) catchments.

Milliman and Meade, (1983) and Syvitski, (2003) assert that precipitation has a predominant influence on river water flow and suspended sediment discharge and this finding is broadly shared by many researchers.

Wu et al. (2004) have made known in their report that the release of suspended material depends on soil erodibility, water flow, water chemistry, soil management practices and vegetation cover. Hwang and Foster (2006) have reported total suspended solids (TSS) in storm flow were much higher than those in base flow.

Also a positive coefficient of determination was observed between DOC and total suspended matter which indicated that DOC had a dominant allochthonous source from terrestrial environment (plant and soil), and its transport coincided with surface erosion process and soil leaching (figure 30).

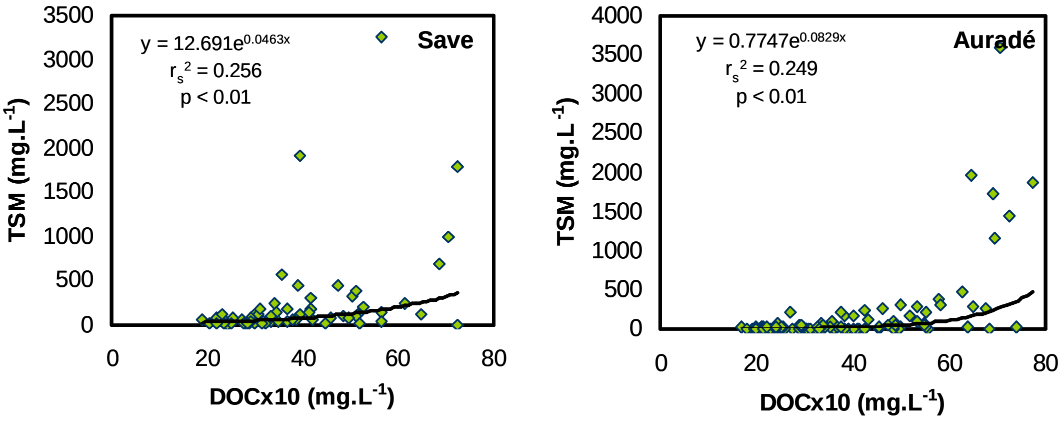


Figure 30- Relationship between DOC and TSM in Save (left) and Auradé (right) catchments.

Particulate Organic Carbon (POC) (expressed in percentage) decreased with increasing TSM concentration, (figure 31). Similar relationships have been observed in most of the river systems in the world (Meybeck, 1982, Ittekkot, 1988; Martins and Probst, 1991; Ludwig et al., 1996; Gao, 2002; Balakrishna and Probst, 2005; Gao et al., 2002). There are several possibilities to explain the inverse relationship between particulate organic carbon content and total suspended sediment (Gao et al., 2002). Firstly, the high TSM concentration leads to the reduced light availability which can hamper the growth of phytoplankton and reduce the contribution of autochthonous carbon, secondly with the intensifying soil erosion, the riverine POC can be diluted with the mineral matter coming from the soil erosion or remobilization of mineral matter in the river bed. A third explanation is that mechanical erosion with different intensity can reach different horizon of soil profile. Hence, intensified erosion in the deeper soil horizons will result in lower content of organic carbon in the river sediment. Probst, (1992) shows in Garonne river, that the high percentage of POC occurs in dry season. Moreover, this period is concomitant with phytoplankton's production, and the low percentage of POC related to a period with high level of discharge that leads to transport of the allochtonous POC.

As shown in figure 31 the concentration of particulate organic carbon (POC) is strongly related to the sediment loading in water. Particulate organic carbon became predominant in water with heavy sediment loading. In fact this positive relationship explains that the quantity of POC versus TSM grow together, in other words, there is a positive relationship between POC and TSM and, this correlation shows very clearly that proportion of POC in total suspended matter increases when the quantity of total suspended matter is diminishing (Tipping et al., 1997; Munson and Carey, 2004). According to our investigation, the average proportion of particulate organic carbon (POC in % of TSM) in total suspended matter (TSM), for Save and Auradé catchments are 3.2 and 2.1 percent respectively which correspond more or less to the average carbon content in the upper horizone of soils in this region.

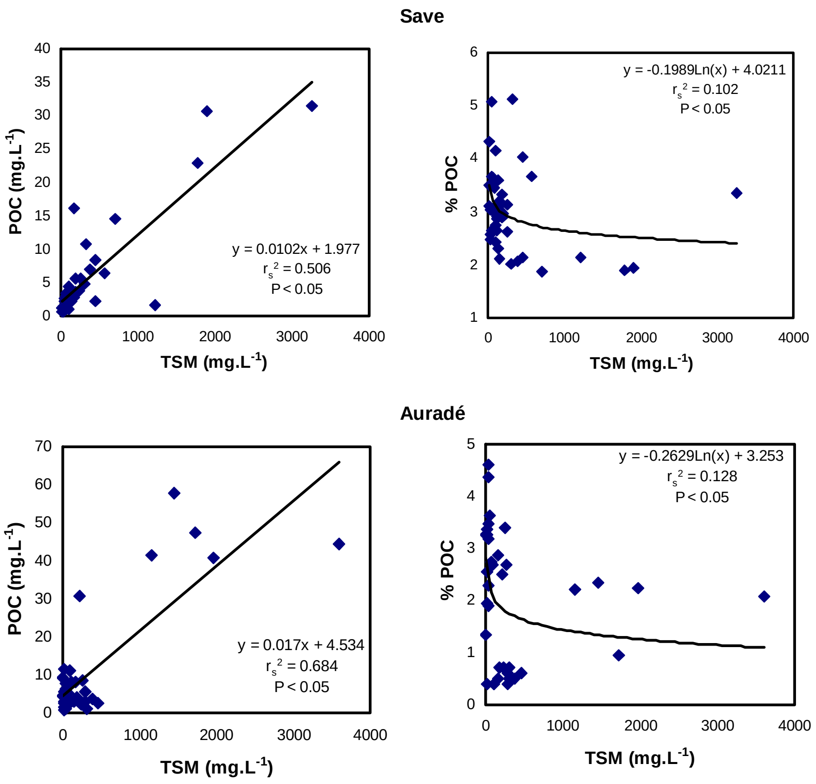


Figure 31- Relationship between particulate organic carbon (POC) and total suspended matter (TSM) in Save (above) and Auradé catchments (below).

Summary

The observation reveals that the maximum concentration of some herbicide molecules occurred during period of high flow. Similar pattern was observed for fungicide molecules, suggesting rapid losses during storm events whereas, the fungicide’s concentration is not high in the whole period of our research, except for tebuconazole. Readman et al. (1997) and Konstantinou et al. (2006) have mentioned, fungicides were not generally present at high concentration in European surface water and usually their precence is below the detected levels.

Increase in concentration of pesticides during storm events show the important role of this period in occurrence of pesticides in stream whereas, the Save and Auradé data indicate that the relation between storm discharge and pesticide concentration during flow varies between compounds and differs from one storm to another, and not all storm flows produce a high level of pesticide concentration.

In fact the surface water contamination at the outlet of the Save and Auradé catchments basin clearly shows the pollution of water by pesticides and high level of concentration during the period of storm event. This phenomenon of increasing in concentration of pesticide during storm event has also been noted by different authors (Schiff et al., 2002; Phillips and Bode 2004). Furthermore, Phillips et al. (1999) have shown that pesticides and pesticide degradates are rapidly transported from the soil to the water table after rain events.

It is important to remember groundwater has its greatest influence on surface water chemistry during baseflow of the year whereas; shallow subsurface drainage and surface runoff dominate stream chemistry during high flow period. These hydrogeological dynamics lead to larger concentrations of pesticide and their degradate during period of storm events, and lower concentration during periods of baseflow.

The overall findings of this investigation demonstrated that pesticide concentration was higher during the application season, or shortly thereafter, with maximum concentration occurring during runoff periods.

Some pesticides were detected at low concentration for an extended period of time; and this could indicate that these pesticides are likely to persist in shallow groundwater. Variation of controlling factors, such as TSM and DOC, indicates the role of storm events in transporting of these parameters. However, there are significant relationships between TSM and DOC with water discharge during the whole study period. The pH and EC are not related to river discharge and their values remain fairly constant during the entire sampling period.

The relationship between TSM and DOC highlighted that both their displacement coincide with surface erosion processes and soil leaching. There is a significant relationship between particulate organic carbon content (POC) and total suspended matter concentration (TSM) but when the TSM increases the percentage of POC in the suspended matter decreases as already observed for most rivers in the world.

Chapter IV

Contribution of different stormflow components

Chapter IV

Contribution of different stormflow components

Introduction

In this chapter hydrograph separation technique to estimate and show the contribution of each storm component is proposed. And relationships between water discharge, pesticides and the controlling factors as well as hysteresis patterns and processes of pesticide transport are reviewed. The relationships between discharge of storm components with controlling factors are also determined in this chapter.

1 Study of storm flow components

1.1 Hydrograph separation

A runoff event is driven by meteorological episode that is precipitation. Precipitation entering a watershed travels to a stream by three main pathways: surface runoff, interflow, and baseflow. The discharge measured in a stream and plotted as a hydrograph combines all three components. The amount of water contributed to the stream by each of the three processes is reflected in the shape of the streamflow hydrograph. For a better understanding of the dynamic of transfer of the pesticides we separated each storm water in three components:

- ***Surface***
- ***Subsurface***
- ***Groundwater***

The principle of hydrograph separation is based on the recession limb of a hydrograph which is separated into three segments of different slopes from which the quantity of water contributed to the stream by surface runoff, interflow and baseflow can be determined. And the different slope of recession curve (α coefficient) is a characteristic of each recession.

In fact the recession coefficient, α is the ratio of the volume of water to the flow of runoff within a given period of time. α characterizes the time that each reservoir component needs to drain. The lower the value of the depletion ratio or α, the longer the time storage volume will take to drain.

In our study the small difference of the depletion ratio between runoff components implies that the soil of the watershed has a good moisture holding capacity (table IX). Probst (1983) obtained similar values for α in this region.

Castany (1971), USAE (1999), Dewandel et al. (2003), have all reported that the recession coefficient (α) can be associated with morphological characteristic of the catchment and its hydrodynamical properties.

Table IX- Coefficients (α) of the nonlinear reservoir, determined for flow recessions measured in hour-scale for Save and in minute-scale for Auradé Catchments. α_G for groundwater, α_{SS} for subsurface runoff and α_S for surface runoff.

River	Periods	Storm events	α_G	α_{SS}	α_S
Save	**March 2008**	1	-0.003	-0.012	-0.023
		2	-0.004	-0.014	-0.059
		3	-0.005	-0.015	-0.058
	April 2008	1	-0.003	-0.009	-0.022
		2	-0.002	-0.007	-0.048
	June 2008	1	-0.001	-0.005	-0.015
		2	-0.001	-0.006	-0.012
		3	-0.002	-0.011	-0.016
		4	-0.001	-0.007	-0.039
		5	-0.002	-0.009	-0.048
	December 2008	1	-0.001	-0.008	-0.025
		2	-0.001	-0.005	-0.020
		3	-0.001	-0.006	-0.031
	January 2009	1	-0.001	-0.007	-0.023
		2	-0.001	-0.007	-0.002
Auradé	**April 2008**	1	-0.0001	-0.004	-0.012
	May 2008	1	-0.0001	-0.003	-0.010
	April (1) 2009	1	-0.0004	-0.003	-0.022
	April (2) 2009	1	-0.0004	-0.004	-0.013

As we showed earlier graphical method was used to separate different discharge components. Discharge of each stream flow with their percentage is reported in the annexes I, II for Save and Auradé catchments respectively.

In the first place, we clearly determined the hydrograph separation of different storm events. Once the above observation was done our following step was to evaluate the amount of water discharge of every single stream flow versus the total water discharged. Based on the available evidence, we can assess the role of each stream flow in pesticides displacement.

By conducting these experiments in ground and subsurface water two phenomenons emerged: (i) where the quantity of discharged water is less than 15 ($m^3.s^{-1}$), groundwater discharge increases and spots of discharge value began to cluster and, (ii) beyond that point, i.e. 15 ($m^3.s^{-1}$), groundwater discharge appeared to be dispersing (figure 32). The clustered spots of water denote that the groundwater reservoir is replenishing and beyond this area (15 $m^3.s^{-1}$) the dispersed spots depict that the reservoir is saturated and starts for drainage. The occurrence of this disparity could be explained by spatiotemporal variability in rainfall, landuse and soil texture.

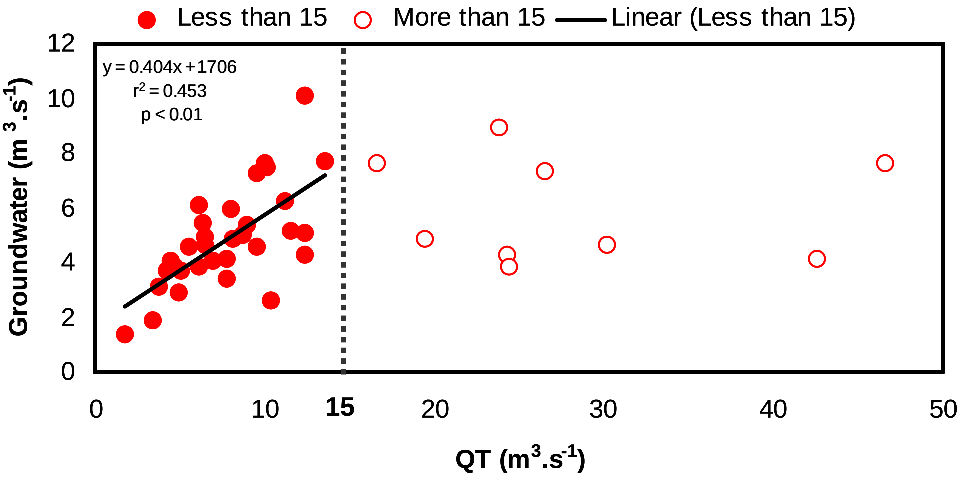


Figure 32-Relationship between discharge of groundwater and total discharge of the Save river.

The relationship between total discharge and discharge of groundwater in Auradé catchment has depicted in figure 33. As it can be seen in figure 33 there is a tiny fluctuation in discharge of groundwater when the total discharge is less than 73($L.s^{-1}$).

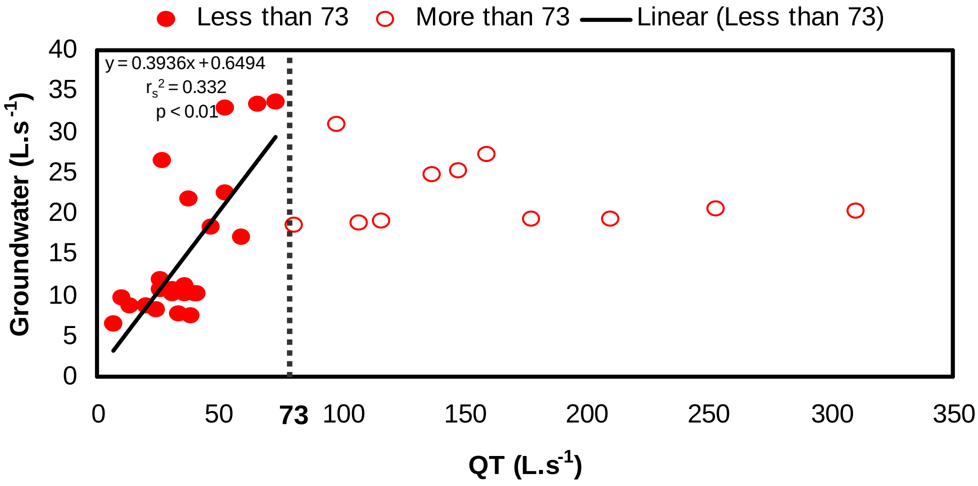


Figure 33- Relationship between discharge of groundwater and total discharge in Auradé catchment.

When the discharge of stream flow exceeds 73 (L.s^{-1}), it leads to a situation where the storage of ground water becoming saturated and smoothly getting to a nearly stable position.

Moreover, the relationship between the contributions (%) of the groundwater discharge versus total river discharge clearly shows that as the discharge increases the contribution of groundwater decreases both for Save and Auradé catchments (figure 34).

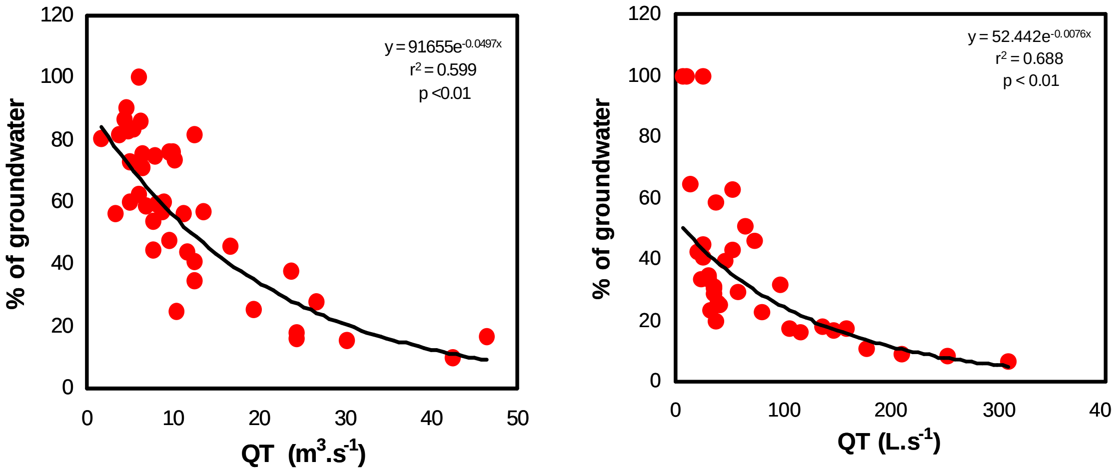


Figure 34- Relationships between total discharge and the contribution (%) of groundwater discharge for Save (left) and Auradé (right) catchments.

A series of similar experiments conducted on subsurface water prove to follow the same pattern. However, in the case of ground and subsurface water there is no significant and meaningful correlation between dispersed spots of water. Although these spots of water occupy an area which only subject to tiny fluctuations (figure 35).

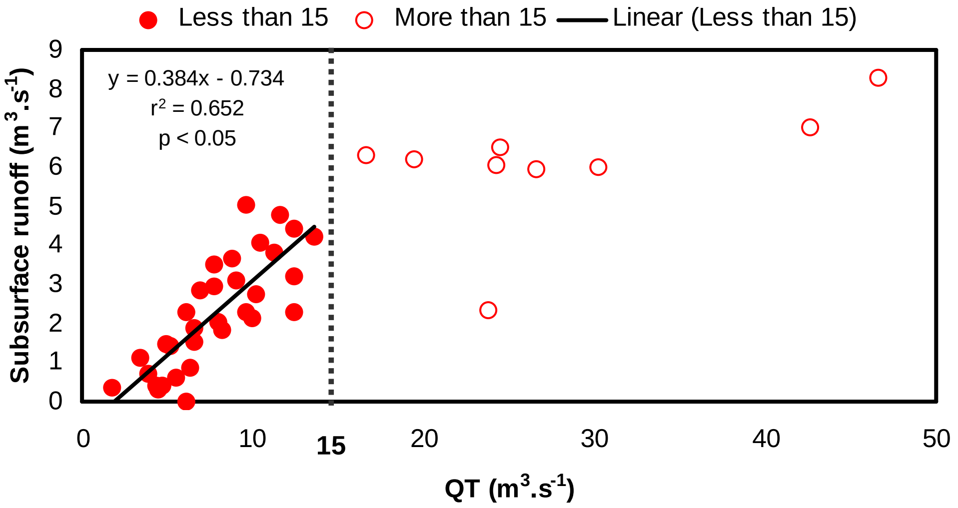


Figure 35- Relationship between subsurface water and total discharge in Save catchment.

The relationship between subsurface water and total discharge in Auradé catchment shows the same pattern as the one it was observed for Save chatchment , that is to say, an increase of subsurface discharge takes place with increase of total discharge, which means that when the level of total discharge augments the contribution of subsurface water increases too (figure 36).

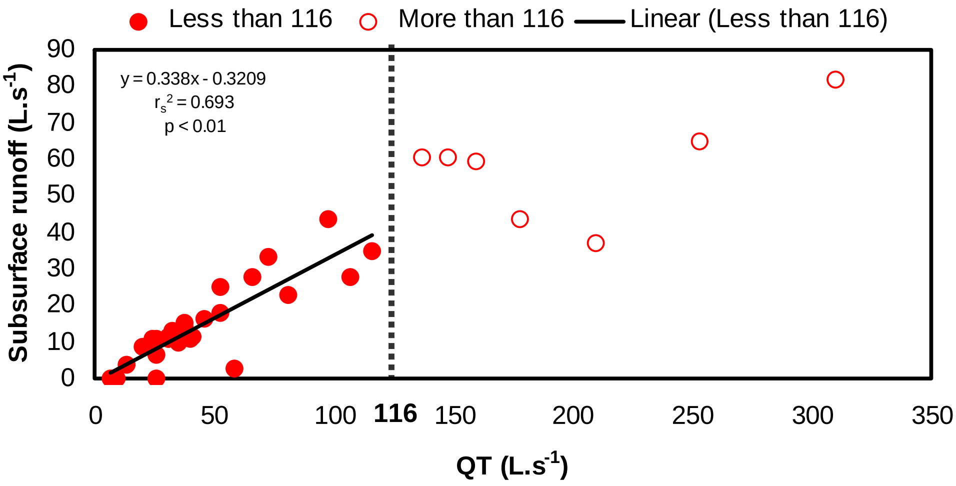


Figure 36- Relationship between subsurface water and total discharge in Auradé catchment.

In the simplest view the relationship between percentage of subsurface discharge and total discharge shows a bell-shape graph with the slow drainage of water in the soil for Save catchment, however, in Auradé catchment this phenomenon is less clear.

This pattern shows that the contribution (%) of subsurface runoff increases rapidly at the beginning of the storm, reaches a maximum when the river discharge is about 10 ($m^3.s^{-1}$) for the Save and 73 for Auradé and decreases progressively when the river discharge continues to increase (figure 37).

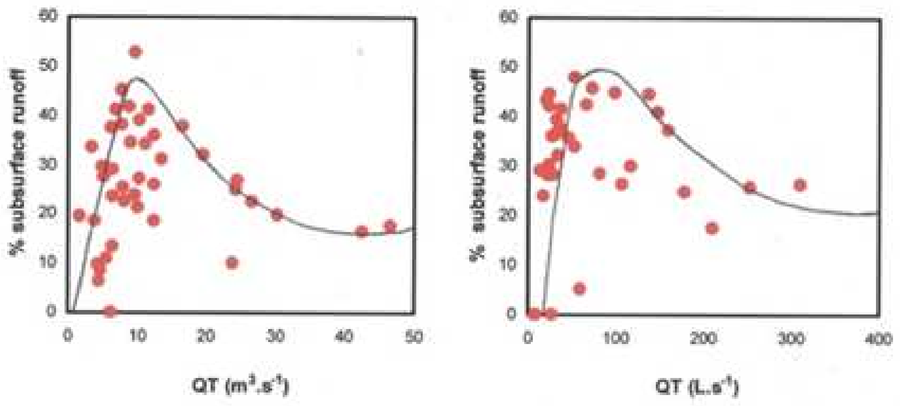


Figure 37- Relationships between percentage of subsurface discharge and total discharge in Save (left) and Auradé (right) catchments.

Given that reality the contribution of sampling spots at the beginning and at the end of storm water’s hydrograph is insignificant, furthermore, for the accuracy of our study and in order to understand the relationship between the surface water and total discharge, the spots of sampling with no significant contribution in surface water have been omitted.

As it is illustrated in figure 38 and 39 our observation finds a similar pattern for surface runoff, that is to say, as the total discharge increases so does the surface and the proportion of surface runoff. Moreover, a linear relationship between the surface runoff discharge and the total discharge can be observed.

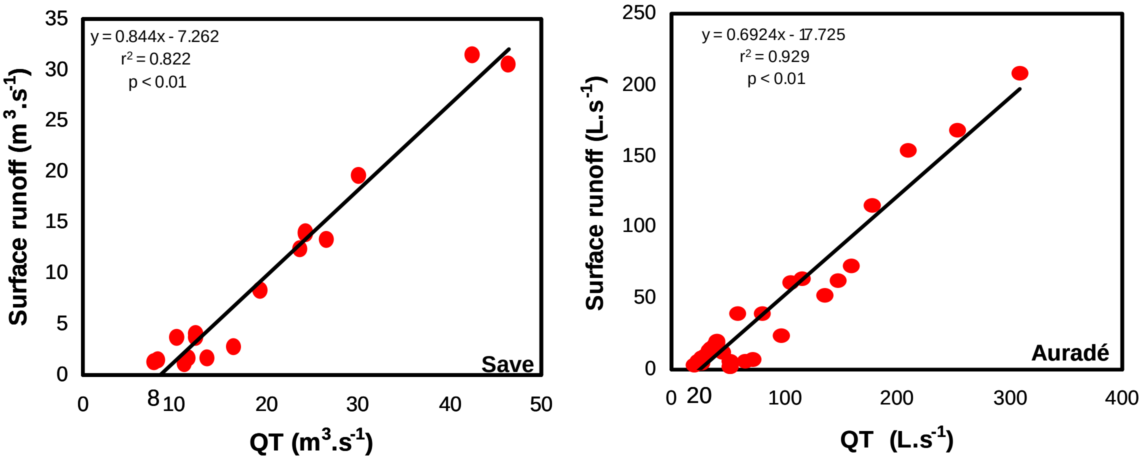


Figure 38- Relationships of surface runoff versus total discharge in Save (left) and Auradé (right) catchments.

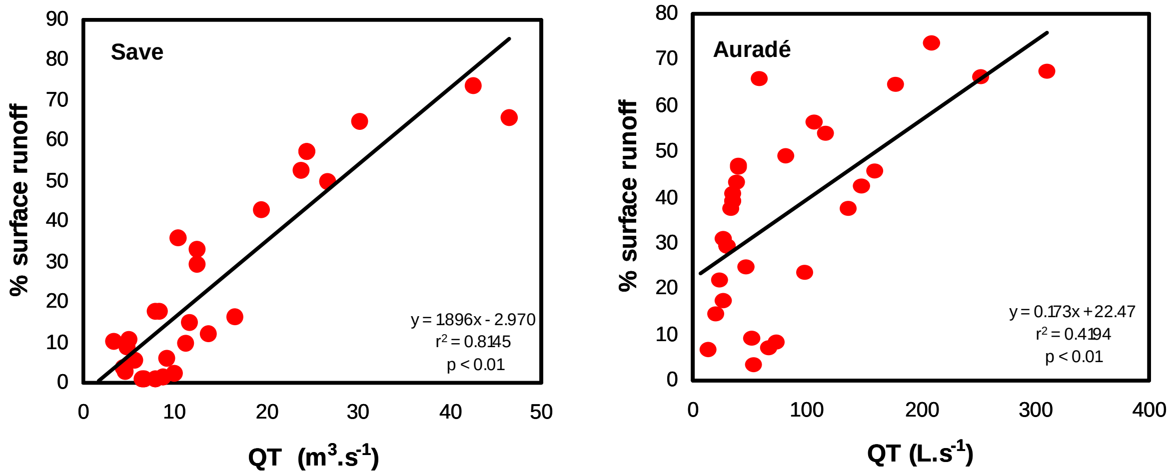


Figure 39- Relationships between the proportion of surface runoff with total discharge in Save (left) and Auradé (right) watersheds.

Storm separation in three components for all of the storm events was illusterated in annexe III, respectively for Save and Auradé catchments. As an example, storm of

April (2008) in Save river and storm of April (1,2) in 2009 in Auradé catchment was illusteredted separately as follows, figures 40,41 .

Figure 40- Hydrograph separation for storm of April 2008 in Save catchment. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.

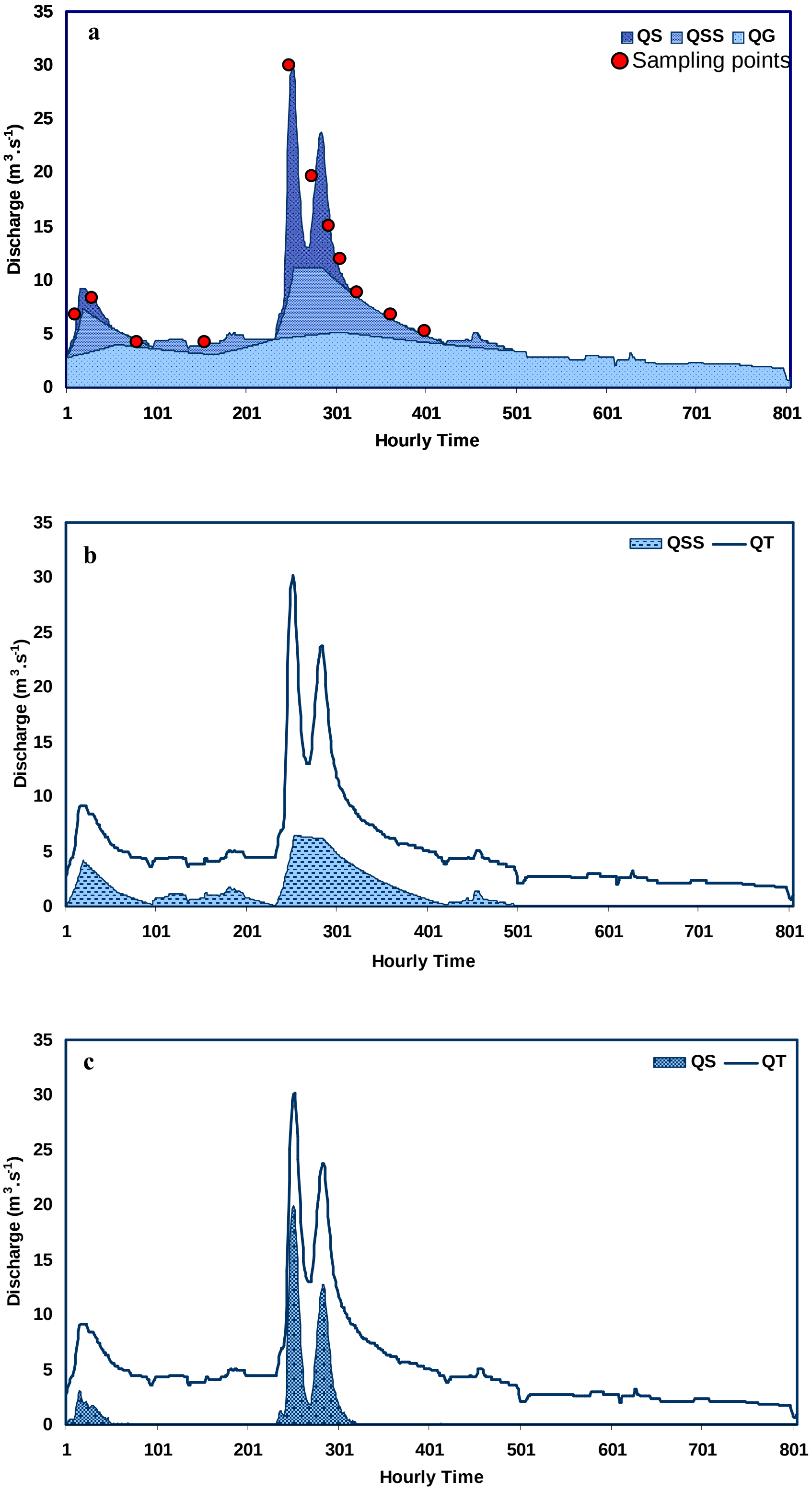
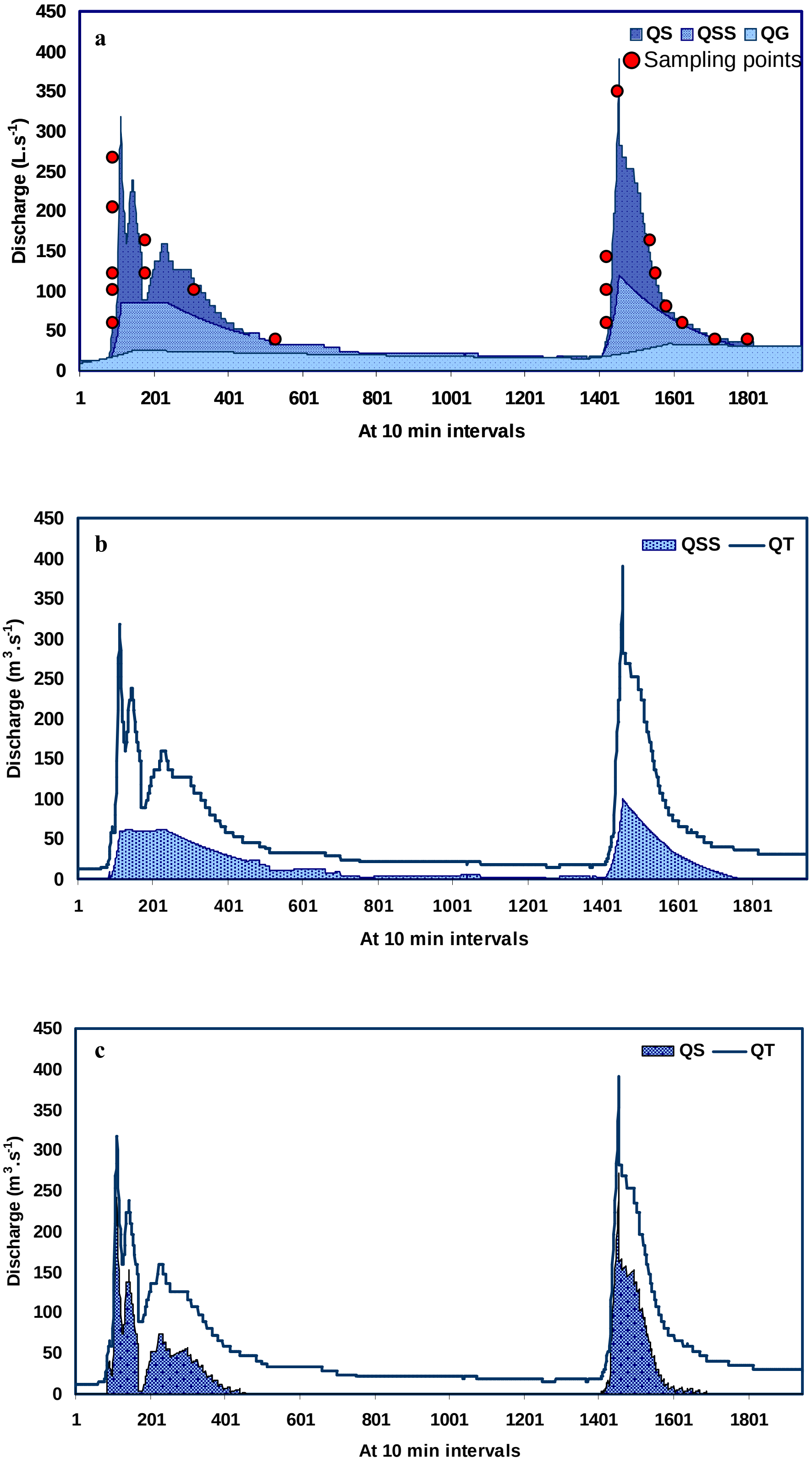


Figure 41- Hydrograph separation for storm of April (1,2) 2009 in Auradé catchment. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.



2 Relationships concentration – discharge: Hysteresis phenomenon

In natural environment, the results of concentration are more variable, especially due to different intensity of rainfall and initial condition of environment (Wauchope, 1978; Leonard, 1990, Zhang et al., 1997).

Mainly three types of evolution in concentration can be observed in each runoff or storm events: (i) the concentration of pesticide follows the pattern of discharge of the water that is to say as the discharge increases so does the level of concentration (Wu et al., 1983), (ii) the concentrations reach the highest level when:

a. the storm water begins and ,
b. it starts decreasing as time goes by (Baker, 1978; Rohde et al., 1980; Pantone et al., 1992 and1996; Zhang et al., 1997), (iii) the level of concentration grew in inverse relation to the level of discharge (Cessna et al., 1994).

Koskines (1979) stated hysteresis, a term for a time lag between isotherms of adsorption and desorption. In other words, a hysteresis is a dynamic relationship between discharge and dissolved or particulate concentration during storm events and this relationship may be represented in a circular pattern.

Different storms produce different level of concentrations of solutes and as the consequence the pattern of the relationship between discharge and concentration is circular. Evans and Davies (1998) have reported that stream water concentration can be dynamic in periods of increased discharge. They have demonstrated that the patterns of the C-Q hysteresis could be explained by using a mass balance mixing model with two or three input components (surface, subsurface runoff and groundwater) and proposed a classification of C-Q hysteresis according to their relationship patterns (clockwise/anticlockwise), curvature (convex/concave) and trend (Positive/negative/null).

Previous studies shows rising limb is dominated by surface runoff in the early storm event, and then on the hydrograph's falling limb the contribution of subsurface and ground water increase. This phenomenon has been shown that a system can follow the pattern of surface runoff, soil water, and then groundwater dominance. Walling and Webb (1986) have shown that C-Q hysteresis analysis is rarely linear, and that it tends to produce a circular pattern from the differing concentration on the rising and falling limbs. This circular pattern is called a C-Q hysteresis loop (Carroll et al., 2007).

2.1 TSM, DOC and POC relationships with discharge

Understanding how discharge and controlling factors affect each other's behaviour help us to follow up the process of transporting these parameters.

Interpretation of hysteresis phenomenon helps us to understand the origin of each parameter in inducing a hysteresis. And, this is the reason we are paying attention to this issue, i.e. hysteresis phenomenon, around which our study is focussed.

In our study the interaction between discharge and controlling factors presents different type of hysteresis, that is to say, clockwise, anticlockwise and mixed-shaped hysteresis loops (mixed-shaped hyseresis loops means the combination of clockwise and anticlockwise that occurs especially when we have different peaks of discharge).

Hysteresis phenomenon occurs due to a time lag between a peak discharge and the peak of parameters concentration. Williams (1989), presents three classes of typology for hysteresis phenomenon, for the relationship between discharge and total suspended sediment concentration (TSS). In the first class simultaneous peaks of SSC and discharge occur. Since rising and falling course of the hydrograph show similar patterns. In the second class, the peak of TSS arrives before the peak of discharge which clockwise hysteresis explains this pattern. In the third class, the peak of TSS arrives after the peak of discharge that shows anti clockwise hysteresis.

The study of hysteresis phenomenon in a single storm event can help us to identify the source of different elements within a drainage system (Peart and Willing, 1982; Lefrancois et al., 2007). In the case of suspended sediment, Jansson (2002) stated hysteresis phenomenon offers a useful insight into the suspended sediment sources and mechanisems of sediment delivery.

In our research, TSM observations in Save and Auradé catchments illustrate clockwise and anti clockwise patterns. A good example for clockwise in Save catchment is during the flood event of April 2008. Clockwise hysteresis pattern for sediment was also observed by Dugan et al. (2009). Winston and Criss (2002) have reported usually rising flood waters show increases in sediment load, in other words, clockwise hysteresis appear with the higher TSM concentration on the rising limb of the flood than at the same discharge on the falling limb (Schumm, 1977; Meybeck, 1985).

Lopez-Tarazon et al., (2009) reported clockwise hysteresis observed when rainfall occurred near the catchment outlet. And, the rainfall was responsible for transporting of sediment that was already deposited in the drainage channel of basin. And, as the discharge increases so does the total suspended matter. We have an augmentation of total suspended matter with increase of discharge.

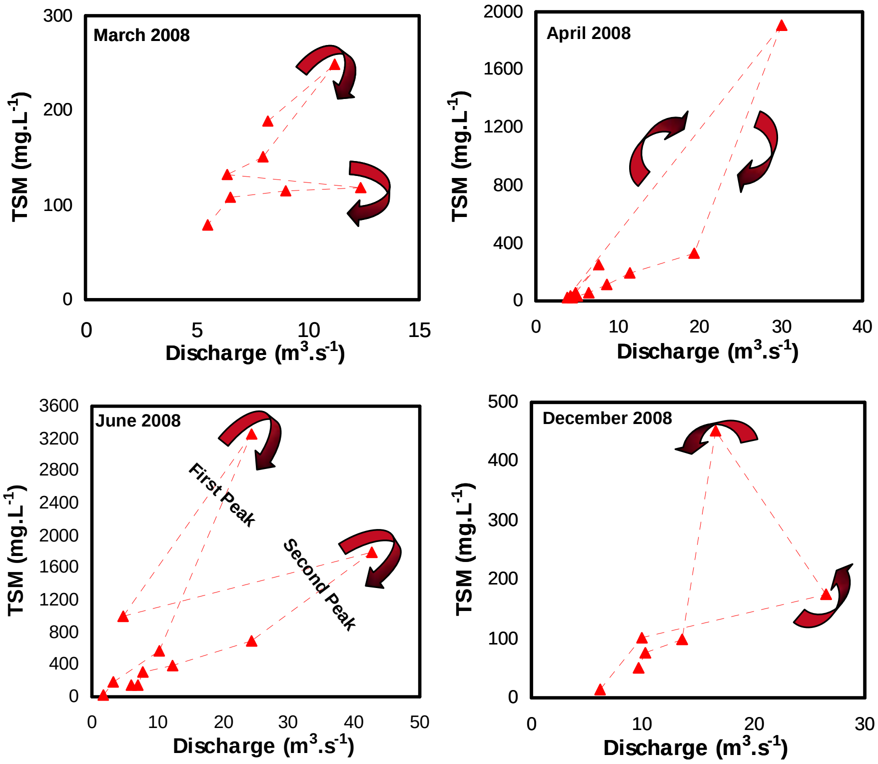


Figure 42- Relationships between discharge ($m^3.s^{-1}$) and Total suspended matter (TSM) in ($mg.L^{-1}$) for the Save river during the storm events.

In our investigation, the clockwise hysteresis observed in April 2008 could be attributed to the transport of eroded sediment deposited close to the outlet and is displaced by following storms. Anticlockwise hysteresis observed in storm of December. We can conclude that sediment sources for this event come far from the catchment outlet (figure 42).

In Save catchment we also observed a complex hysteresis. And this pattern of hysteresis appeared when the flood is complex (e.g. June 2008), and each peak corresponds to the peak of discharge. No hysteresis was registered for storm of January (2009).

A total of four storm events were observed in Auradé catchment. Two of them show an anticlockwise hysteresis in May 2008 and April (2) in 2009. In fact anticlockwise hysteresis loops take place when the source of sediment was far from the out let (figure 43).

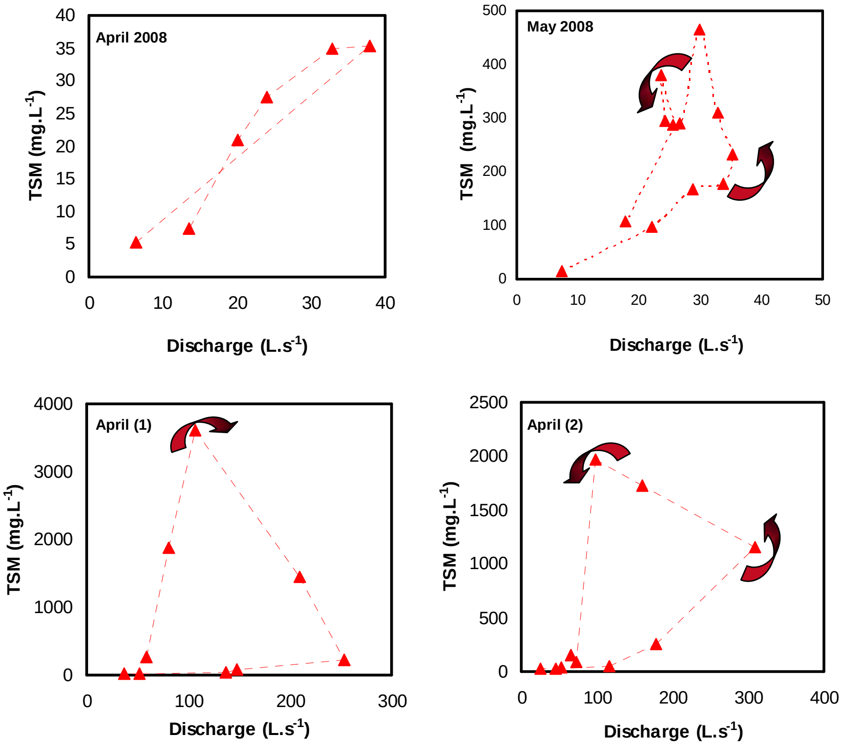


Figure 43- Relationships between discharge ($m^3.s^{-1}$) and Total suspended matter (TSM) in ($mg.L^{-1}$) for the Auradé catchment during 4 storm events.

Lopez-Tarazon (2009) explains two reasons for this type of hysteresis. Firstly, the rainfall events located in the headwaters, produce high volume of water, but the quantity of sediment flow is relatively low. Secondly, when rainfall distributed along the whole basin, the runoff volume of these types of storm events is relatively low but the sediment flow was very high.

In Auradé catchment we have also registered one clockwise hysteresis for storm of April (1), knowing that this storm event occurs after a fairly long period (one month) without any flood, and then after the deposited sediment in the catchment was transported by the first runoff (figure 43). Moreover, for the storm of April 2008 no hysteresis pattern was registered.

In the case of DOC, anticlockwise hysteresis observed in storm of April, December and January could be attributed chemical erosion or leaching of soil and it is responsible for transferring of dissolved organic carbon (figure 44). There is not registered any hysteresis pattern for storm of March and June.

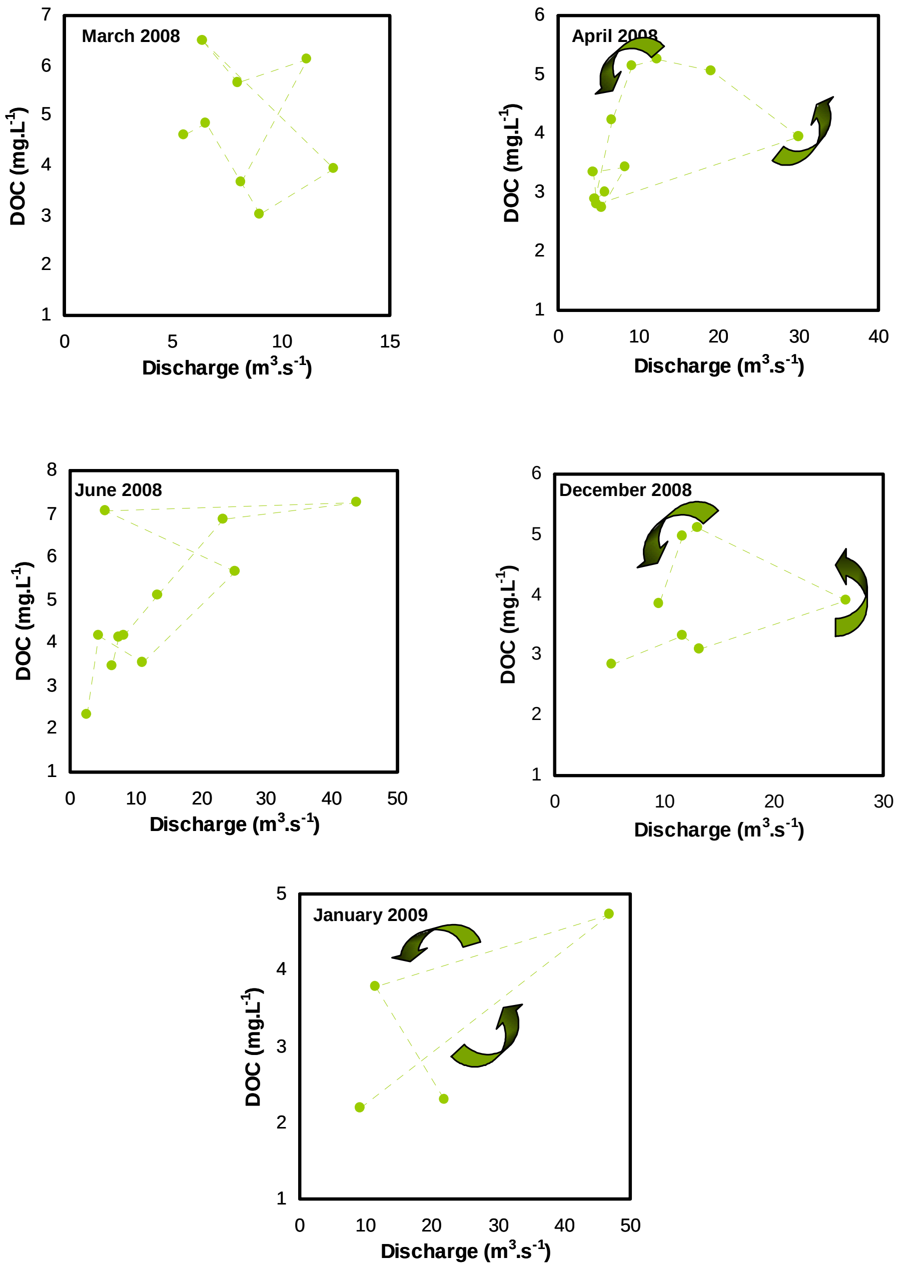


Figure 44- Relationships between DOC and total river discharge during 5 storm events in Save catchment.

One clockwise hysteresis was registered in Auradé catchment in April (1) 2009 for dissolved organic carbon (DOC). Before this event, we had a relatively long period without any floods; thus, floods of April 2008-2009 could be responsible for transporting of DOC by surface water.

May 2008 and April (2) 2009 have represented anticlockwise hysteresis, that is in agreement with finding from many previous studies of DOC dynamic (figure 45). Leaching of soil by subsurface water could be the source of DOC during these events since before these floods we had other flood events.

Grieve (1984) and Edwards and Cresser, (1987), indicated hysteresis effects often occur during runoff events, at a given discharge, on the falling limb of hydrograph.

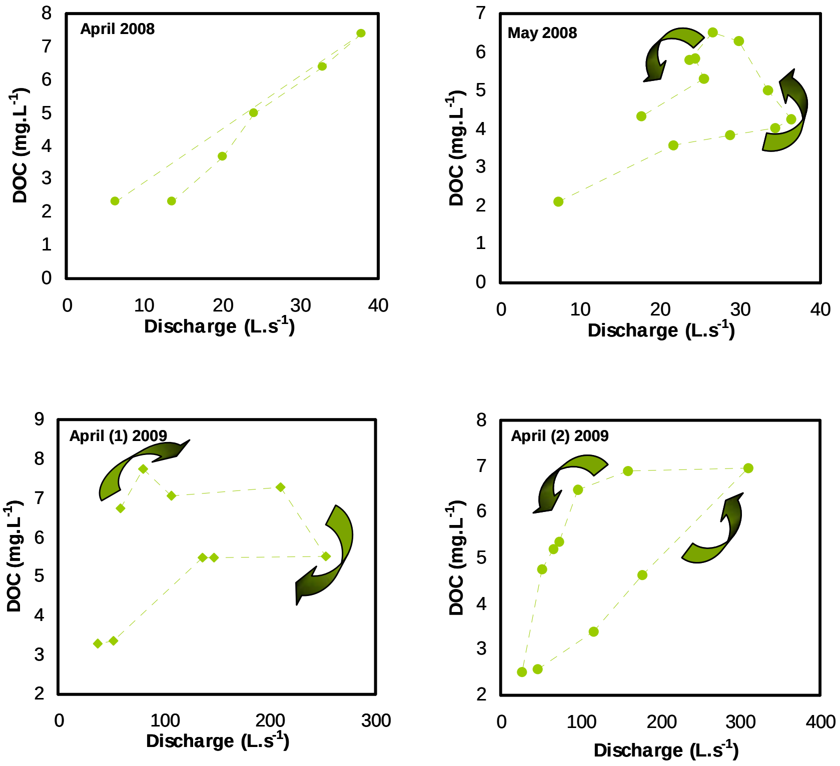


Figure 45- Relationships between DOC and total river discharge during 4 storm events in Auradé catchment.

Hangen et al. (2001) indicated that DOC typically peaks after the peak of discharge in a forested catchment in southwest of Germany, this pattern generated an anticlockwise hysteresis for this element. Butturini et al. (2006) have presented anticlockwise hysteresis during the autumn-winter period in three Mediterranean streams. According to their research the DOC peaks are probably generated by leaching of a large amount of organic matter stored on the dry stream bed, this result is in agreement with the study conducted by Acuna (2004).

Concerning POC, the results have shown a clockwise hysteresis for storm of April and an anticlockwise hysteresis for storm of December but the amplitude of the hysteresis is very low showing that the POC content peak corresponds more or less to the maximum discharge (figure 46).

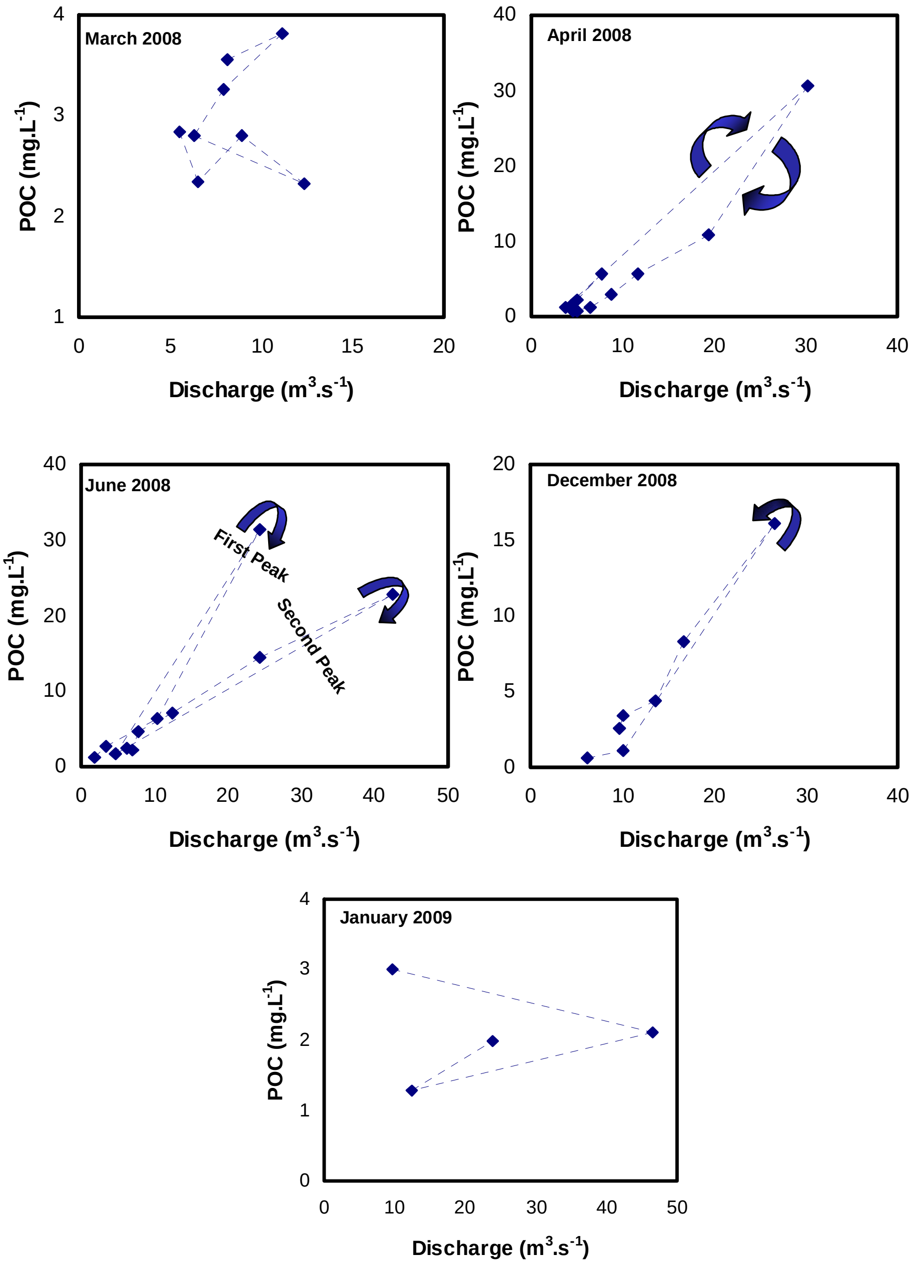


Figure 46- Relationships between POC and total river discharge during 5 storm events in Save catchment.

The same pattern of hysteresis was observed for total suspended matter (TSM) during these events, which could be due to a direct relation between TSM and POC.

In storm of June 2008, we have observed a complex of hysteresis with two peaks of POC concentration. Interestingly, the high level of POC concentration correlated simultaneously with the high level of TSM and discharge. The results concerning the storm of May 2008 and January 2009 did not indicate any hysteresis for relationship between POC and discharge.

Relationship between POC and discharge in Auradé catchment have shown two type of hysteresis; clockwise hysteresis for April 2008 and April (1) in 2009, and anticlockwise hysteresis for May 2008 and April (2) in 2009 (figure 47). The same pattern of hysteresis was observed for TSM during all of the storm events, except during storm of April 2008.

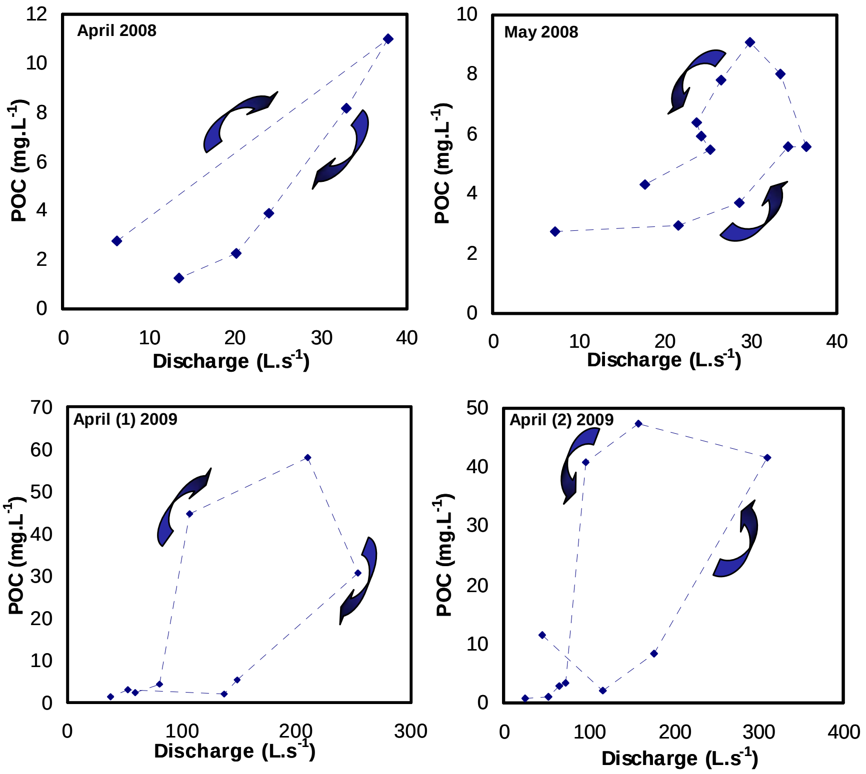


Figure 47- Relationships between POC and total river discharge during 4 storm events in Aurade catchment.

2.2 Hysteresis phenomenon and pesticides molecules

A biogeochemical interaction in river systems at the time when the rate of discharge is towering has attracted the attention of a good number of researchers. Cyclical trajectories relationship have been reported between discharge and solute concentration during storm events (Walling and Foster, 1975; Bond 1979;Trudgill et al., 1981; Jardine et al., 1990; McDiffett et al., 1989; Swistock et al., 1989; Hill 1993). However, none of these studies have analysed the hysteresis phenomenon on pesticide’s concentration, and pesticide transport was rarely observed from this particular angle.

In fact when pesticide is introduced into the environment, a part of it stays in the area where it is applied, but a large proportion of the pesticide gets transported to various environmental compartments. Pesticides' properties vary according to the degree of its absorption onto particles and its displacement by particulate phases. Pesticides also interact with solid state organic or inorganic matter in the soil (Spark and Swift, 2002).

There are other classes of pesticides which are complexed by dissolved phases and transported, particularly, by dissolved organic carbon. In fact, transport of pesticide may be the result of processes such as the formation of soluble complexes with soil solution components like dissolved organic matter, and organic matter may be a vector for transport of pesticide and heavy metal that adsorbed onto the organic fractions (Karickhoff et al., 1979; Voice and Webber, 1983; Thouvenin et al., 2007).

Since understanding of pesticide dynamic in the environment is important to prevent pollution and having a better management strategy for water resources, (Muller et al., 2003) we focused our research upon hysteresis phenomenon that gives us some ideas of how each pesticide is transported. Evans and Davies, (1998), demonstrated how the characteristic of the hysteresis loops can be used to evaluate the temporal variation of the contribution of different stream flows such as groundwater, subsurface and surface water. In our research hysteresis behaviour of each pesticide has been investigated in detail during each storm event. Given the fact that the total concentration level of pesticide varies during rising and falling of a storm flow, thus, the pattern of the relationship between discharge and concentration becomes circular.

And this circular pattern of hysteresis loops during most storm events, highlighting the complex relation of pesticide's concentration and discharge during storm hydrograph. The findings of our study on the Save river show that storm events produce hysteresis loops in circular patterns for some pesticides, except for storms of March 2008 and January 2009. In Auradé catchment this phenomenon observed during storm of May 2008 for aclonifen, linuron and metolachlor.

2.2.1 Save river at Larra

In storm of April (2008), clockwise hysteresis observed for aclonifen and linuron that shows the role of surface water in displacement of these molecules, with increasing concentration of herbicide on the rising limb of hydrograph, and decreasing of its intensity thereafter (figure 48). As it has been pointed out earlier total suspended matter and particulate organic carbon show the same pattern of hysteresis, which concludes the role of particulate matter in the transfer of these pesticides.

Flury et al.(1995) and Johnson et al. (1996) reported direct flow of water through soil is considered as an important mechanism by which agrochemicals can be rapidly transported from their target site to surface water. This result is in accordance with the results of the research carried out by Harris et al. (1994). In the case of filtered water no hysteresis pattern for pesticide molecules was observed.

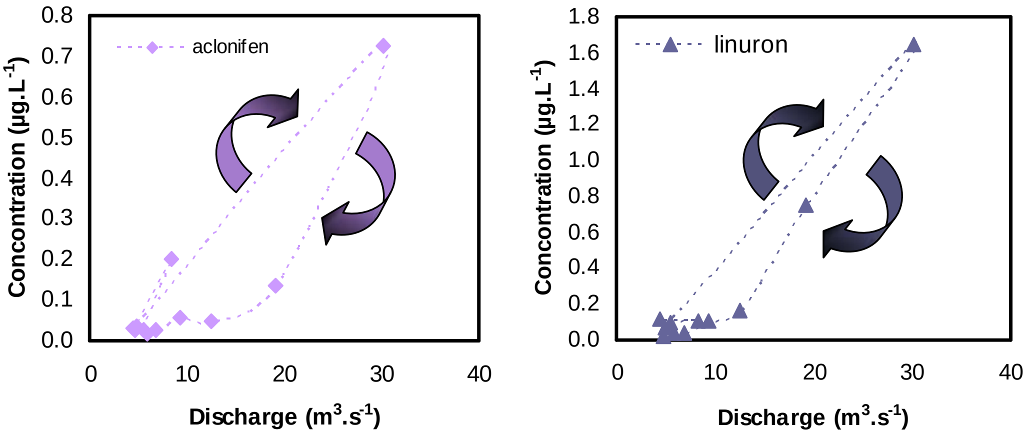


Figure 48- Discharge – pesticide concentration relationships: Hysteresis patterns in unfiltered water for aclonifen and linuron during storm of April 2008 for the Save river.

The findings of previous studies show the relative importance of dissolved organic matter in displacement of hydrophobic pesticide. Carter and Suffet, (1982) reported that riverine carbon plays an important role in the transport of organic pollutant such as pesticides. This finding is in line with the results of the studies establishing the association of hydrophobic pesticides with dissolved organic matter (Kan and Tomson, 1990; Kulovaara, 1993; Fitch and Du, 1996). The form of hysteresis we observed in April (2008) for metolachlor, in unfiltered and filtered water (figure 49), is similar to that of dissolved organic carbon which shows the important role of DOC in transport of metolachlor. And also it indicates the similar way for transporting of these elements. The findings of the study conducted by Hyer et al. (2001) identified the similar pattern of hysteresis loops for atrazine (another hydrophobic pesticide) and DOC.

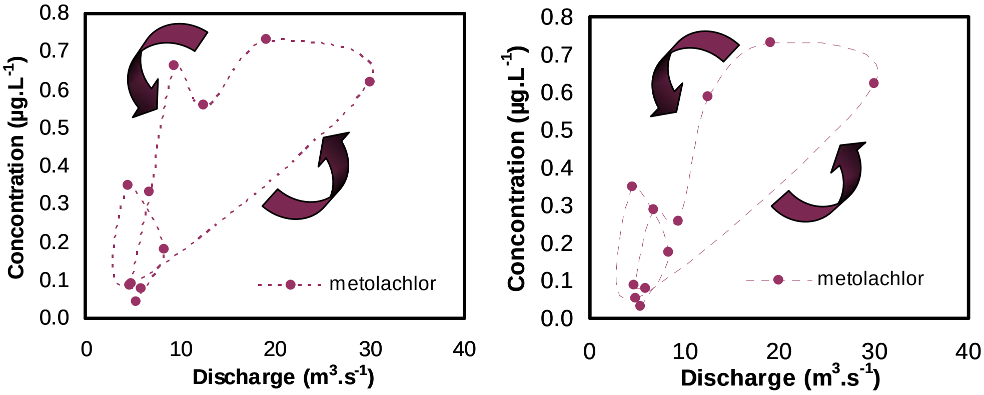


Figure 49- Discharge – pesticide concentration relationships: Hysteresis pattern in unfiltered (left) and filtered (right) water for metolachlor during storm of April 2008 for the Save river.

Storm of June 2008 is a complexed storm where we have different peaks of discharge. And as the consequence different complex patterns of hysteresis can be observed for each pesticide.

A complex hysteresis that we observed for aclonifen during storm of June (2008) is similar to total suspended matter (TSM) in figure (42). This phenomenon shows the important role of TSM in transporting of aclonifen in unfiltered water. In fact, two peaks of aclonifen and TSM concentration coincide with the two peaks of discharge. We observed also the same pattern of hysteresis for linuron as a modaratly soluble molecule during this storm episode (figure 50).

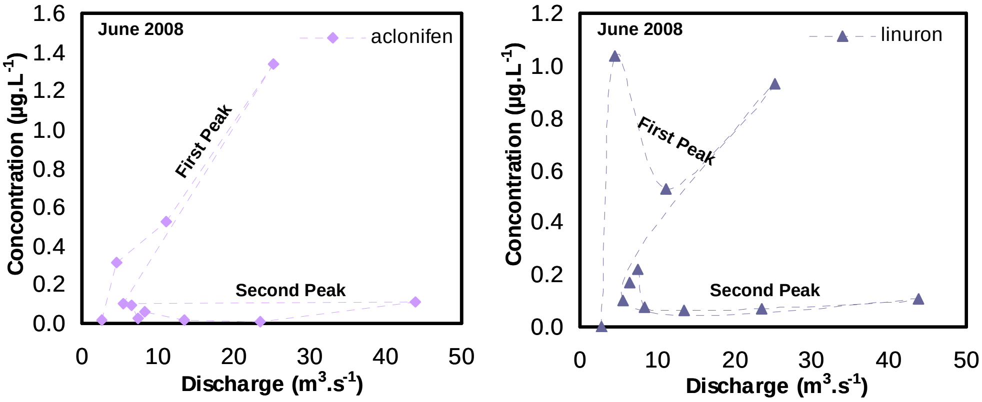


Figure 50- Discharge – pesticide concentration relationships: Hysteresis pattern in unfiltered water for aclonifen (left) and linuron (right) during storm of June 2008 for the Save river.

For molecules with a high level of solubility such as metolachlor, the pattern of hysteresis is relatively similar in unfiltered and filtered water, with two separate patterns, which correspond to two peaks of discharge (figure 51). However, it is important to note that DOC didn't show any hysteresis pattern during this event.

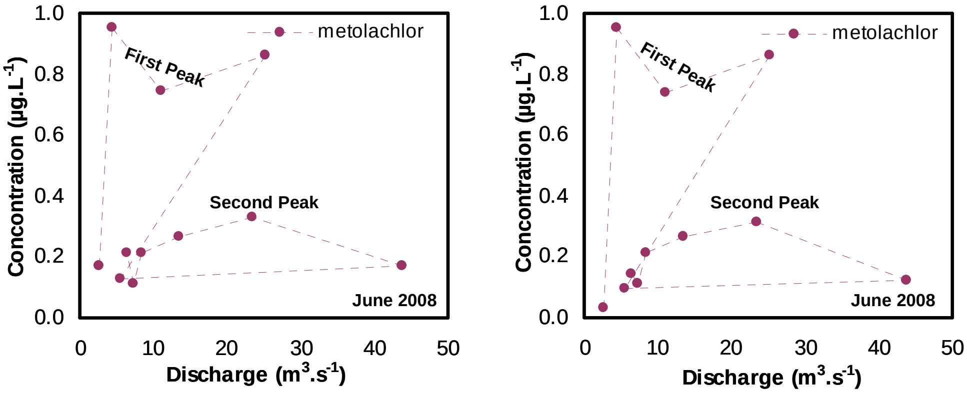


Figure 51- Discharge – pesticide concentration relationships: Hysteresis pattern in unfiltered (left) and filtered (right) water for metolachlor during storm of June 2008 in the Save river.

In the case of fungicides (excepting fenpropimorph) the pattern of hysteresis is the same, showing the way of transport of these molecules is similar (figure 52). Moreover, this similarity of pattern is true for unfiltered and filtered water

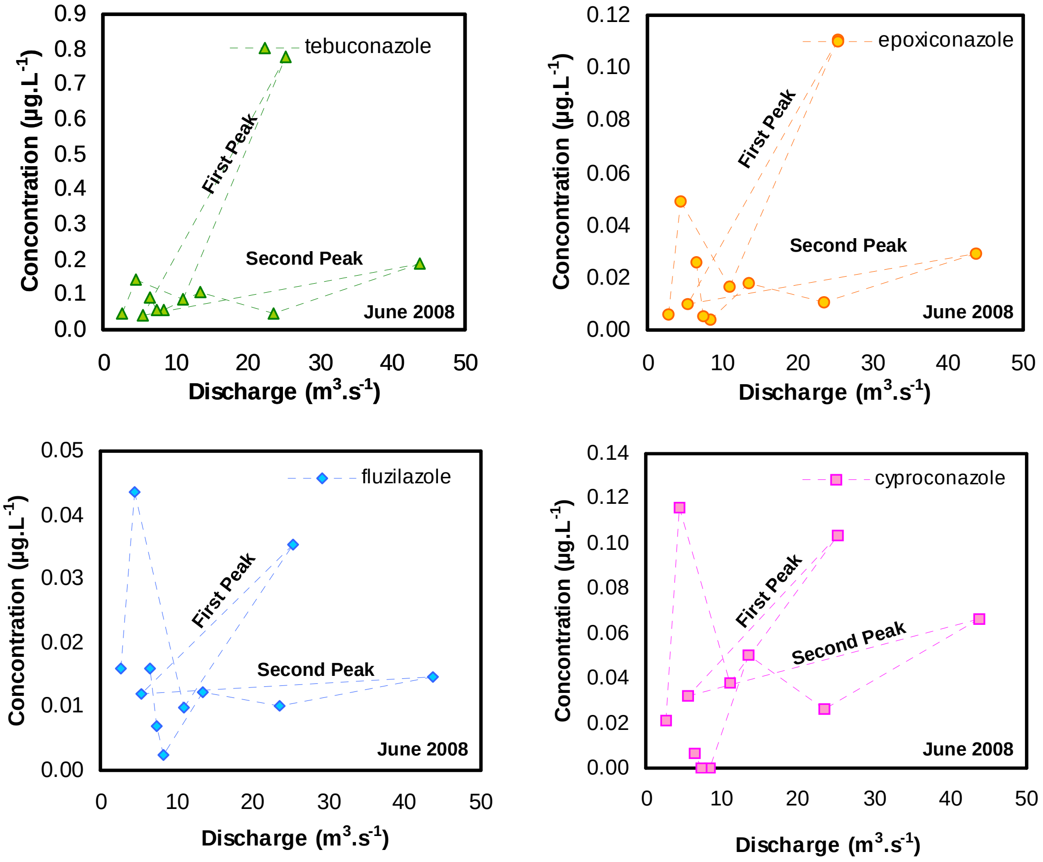


Figure 52- Discharge-pesticide concentration relationships: Hysteresis pattern for fungicides in unfiltered water during storm of June 2008 in the Save river.

2.2.2 Montousse creek at Auradé

In Auradé catchment, the hysteresis phenomenon for aclonifen, linuron and metolachlor, was only observed during storm of May (2008). The pattern of hysteresis for all of the three molecules is anticlockwise, with higher pesticide concentration on the falling limb of the hydrograph as comparing with rising limb. This pattern indicates that water entering the stream during the first stage of flood event had lower pesticide concentration than water entering the stream after the peak discharge.

In the case of metolachlor, the anticlockwise hysteresis was observed for unfiltered and filtered water, but for aclonifen and linuron the hysteresis pattern observed was just as in unfiltered water. Anticlockwise hysteresis was also observed in the case of TSM, POC and DOC during storm of May (figure 42,44 and 46) .

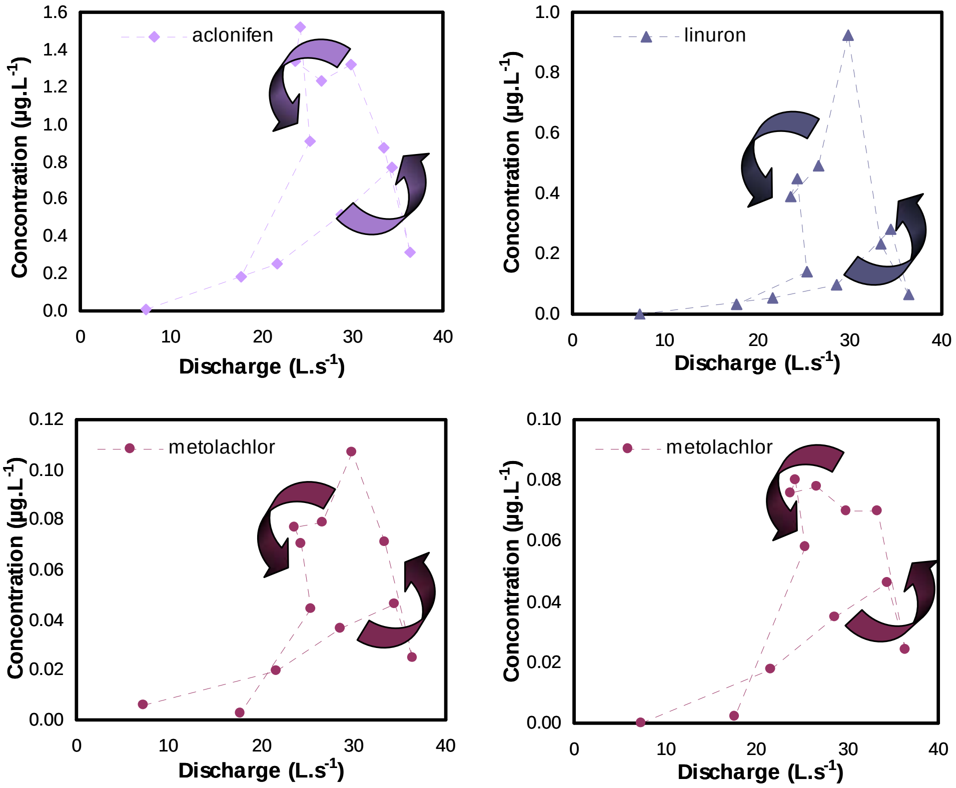


Figure 53- Anticlockwise hysteresis in unfiltered water for aclonifen, linuron (above) and metolachlor in unfiltered water (left) and filtered water (right) during storm of May (2008) in Auradé catchment.

3 Relationships between concentration and discharge of storm flow components

First, hydrograph separation technique was used to evaluate the role of different stream flow components in pesticide movement. We then used the discharge of different stream flows to plot the relationship between the value of discharge with pesticide and controlling factors concentration in order to trace the principal pathway of pesticide and controlling factors exportation. This kind of relationship between some particulate and soluble elements with stream components was previously demonstrated, particularly for nitrate and TSM concentrations.

Probst (1985) came to the conclusion that for elements of lower degree of solubility, such as phosphorus, the pathway of exportation is surface runoff, whereas elements with higher degree of solubility, for example, nitrate, the main exportation route is paved by subsurface flow. The studies conducted by Kattan et al. (1986) and Wagner et al. (2008) highlight the contribution of subsurface runoff to the total storm flow as being the main pathway to exporting nitrate as a soluble element during storm events. Puckett and Hughes (2005) pointed out that groundwater had its greatest influence in decreasing the concentration of Cl^-, NO^-_3 and pesticide during low flow period. In contrast, subsurface water increases the concentration of these elements during storm flow, showing the role of subsurface water in increasing their reverin concentration and exporting of these elements.

In the case of total suspended matter (TSM), the previous studies have shown a significant relationship between the volume of surface runoff and suspended sediment concentrations (Walling and Webb, 1985; Probst, 1983; Etchanchu and Probst, 1986; Probst and Bazerbach, 1986; Probst and Sigha, 1989), and highlighted the important contribution of ratio of surface runoff in transporting of total suspended matter. But to our knowledge, little is currently known about the contribution of each stream component in transporting of pesticides and their controlling factors such as POC and DOC, and that is why, we have paid special attention to understand the main pathway of transport of pesticides and their controlling factors.

3.1 Save catchment

3.1.1 Relationship with surface plus subsurface flows

Our findings during the entire storm events show the important role of these events in the transport of total suspended matter due to a large contribution of surface and subsurface runoff. The result of interaction between the proportion of surface and subsurface runoff with TSM and POC exhibits an exponentially positive relationship with relatively strong value of Spearman rank correlation ($r_s^2 = 0.832$ and $r_s^2 = 0.407$)

that show TSM and POC have been displaced remarkably when the contribution of surface plus subsurface flows were more than 80% of total discharge (figure 54).

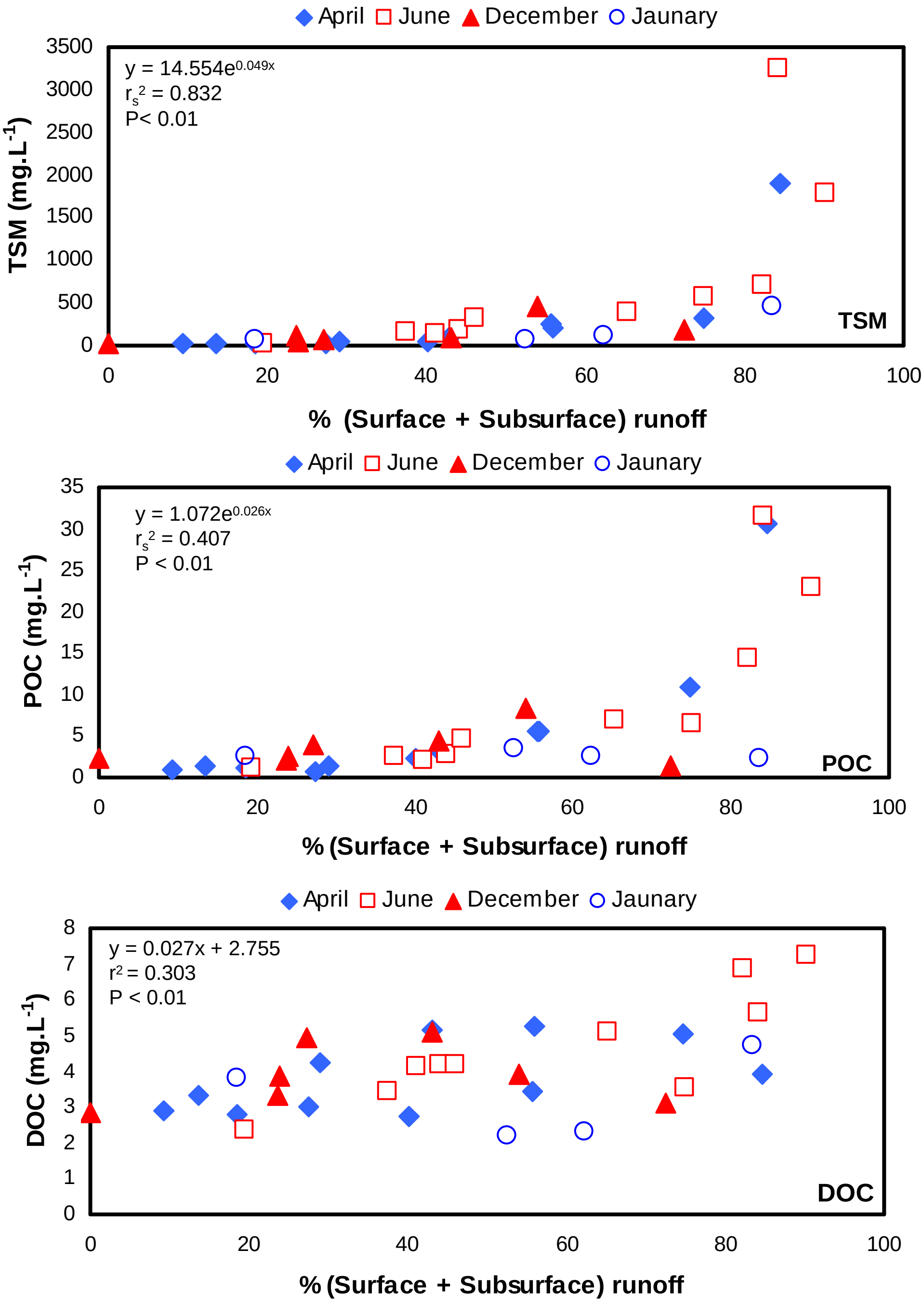


Figure 54- Relationships between TSM (above), POC (meddle) and DOC (below) concentrations and the contribution (%) of surface plus subsurface runoffs for the Save river during 4 storm events.

Dissolved organic carbon (DOC) shows less variability in concentration with discharge during storm events, since the Pearson coefficient ($r^2 = 0.303$) presents lower value (figure 54). This finding highlights that discharge is probably not the sole factor which controls DOC concentration. Nevertheless Wagner et al. (2008)

suggested that DOC is probably exported via a combination of overland flow and preferential flow through soil macropores.

3.1.1.1 Relationship with each storm flow component discharge

Hydrograph separation enables us to estimate the contribution of each stream flow component during every flood event. It is also a means to determine the main route of transport of each one of the element by plotting the relationship between the reverine concentration and the discharge of each stream flow components (figure 55).

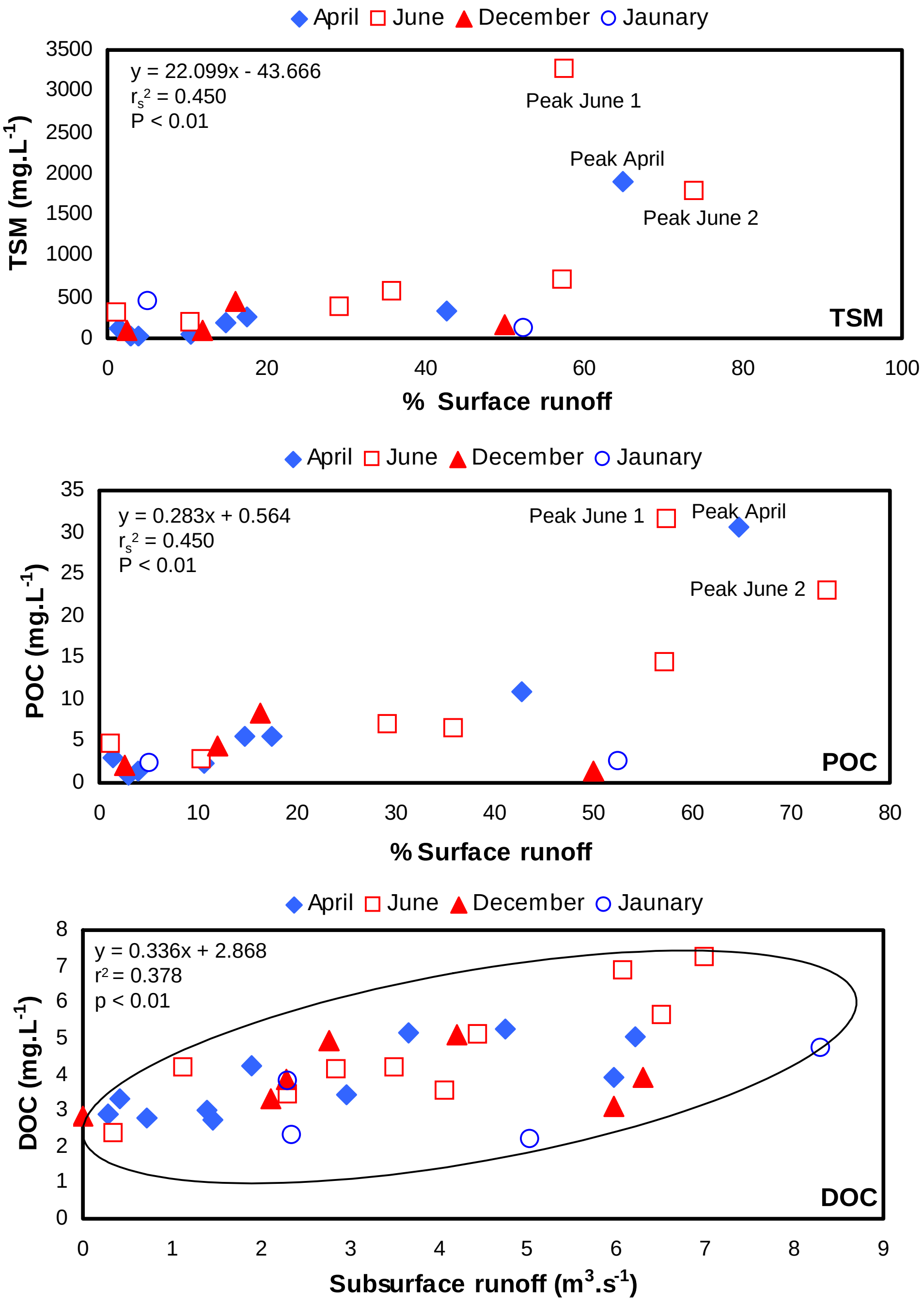


Figure 55- Relationships between TSM, POC and DOC riverin content and the contribution of surface or subsurface runoff to Save river discharge.

The findings of this interaction show the particulate fractions such as TSM and POC are correlated with the proportion of surface runoff in the total discharge and more exportation occurs when the contribution of surface runoff is higher than 60%. However, the soluble fraction is correlated with discharge of subsurface water.

As illustrated above in the case of TSM and POC, generally the maximum concentration of pesticide is appearing during peak of discharge.

The discharge peak of April storm and the first discharge peak of June 2008 storm are responsible for transporting of aclonifen with concentrations higher than 0.6 (µg.L^{-1}). Other sampling points show concentrations inferior to 0.3 (µg.L^{-1}), whereas, the contribution of superficial flow is higher than 80% of the total flow for some sampling points. Linuron shows concentrations higher than 0.6 (µg.L^{-1}) for 4 sampling points. Two of them are the sampling points during the peak of storms and the others correspond to the sampling points after (in April) and before (in June) of the peak discharge. Out of these points the concentration of linuron remains relatively stable and less than 0.3 (µg.L^{-1}) (figure 56).

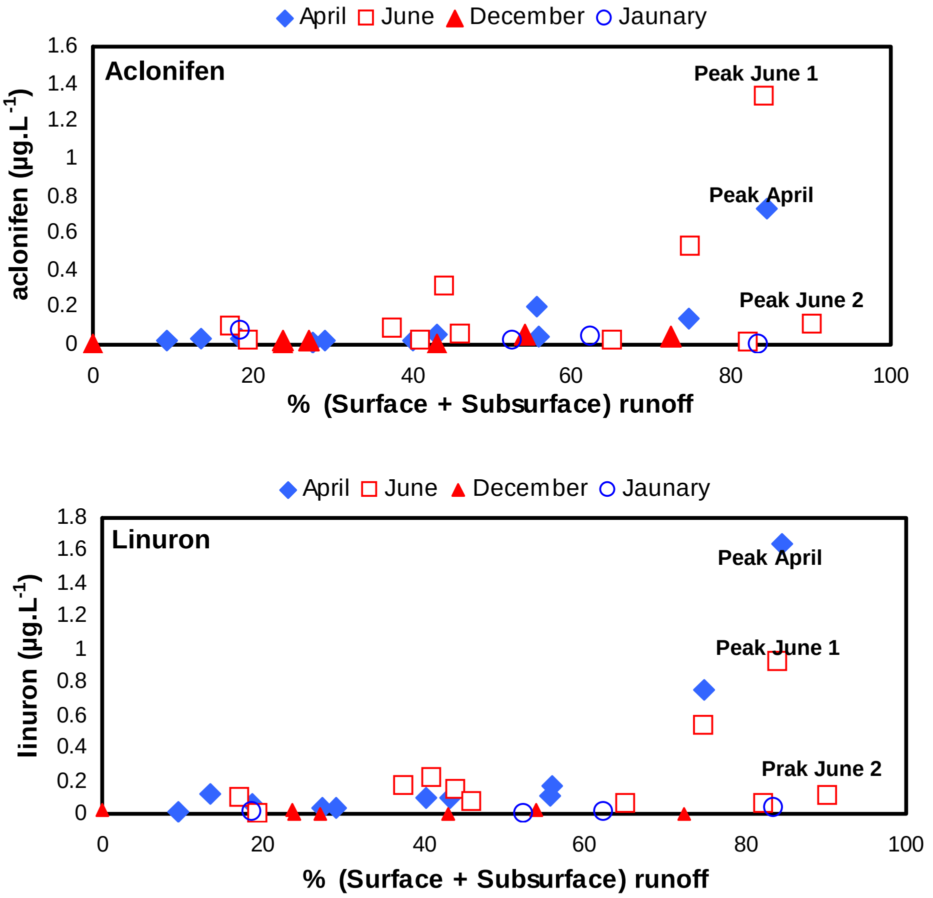


Figure 56- Relationships beteen aclonifen and linuron riverine concentration and the contribution (%) of surface plus subsurface flows in the Save river for 4 storm events.

Among all the molecules studied in the course of our research only aclonifen, a molecule with a low degree of solubility, and linuron, a moderately soluble molecule, produced a pattern of relationship with each stream flow with a high degree of concentration for both molecules when the storm reaches its highest level. Despite the existence of a pattern of relationship between a proportion of surface runoff with aclonifen and linuron concentration, this pattern of relation is not statistically significant ($r_s^2 = 0.139$, $p = 0.087$ and $r_s^2 = 0.071$, $p = 0.20$) respectively for aclonifen and linuron. But, the interaction of these molecules shows the important role of surface runoff in exportation of these pesticides especially during peak of April 2008 storm and the first peak of June 2008 storm as a representative of complex flood. Figure 57 shows that the peak of April storm and the first peak of storm during the complex storm of June in (2008) show the maximum exportation of aclonifen and linuron.

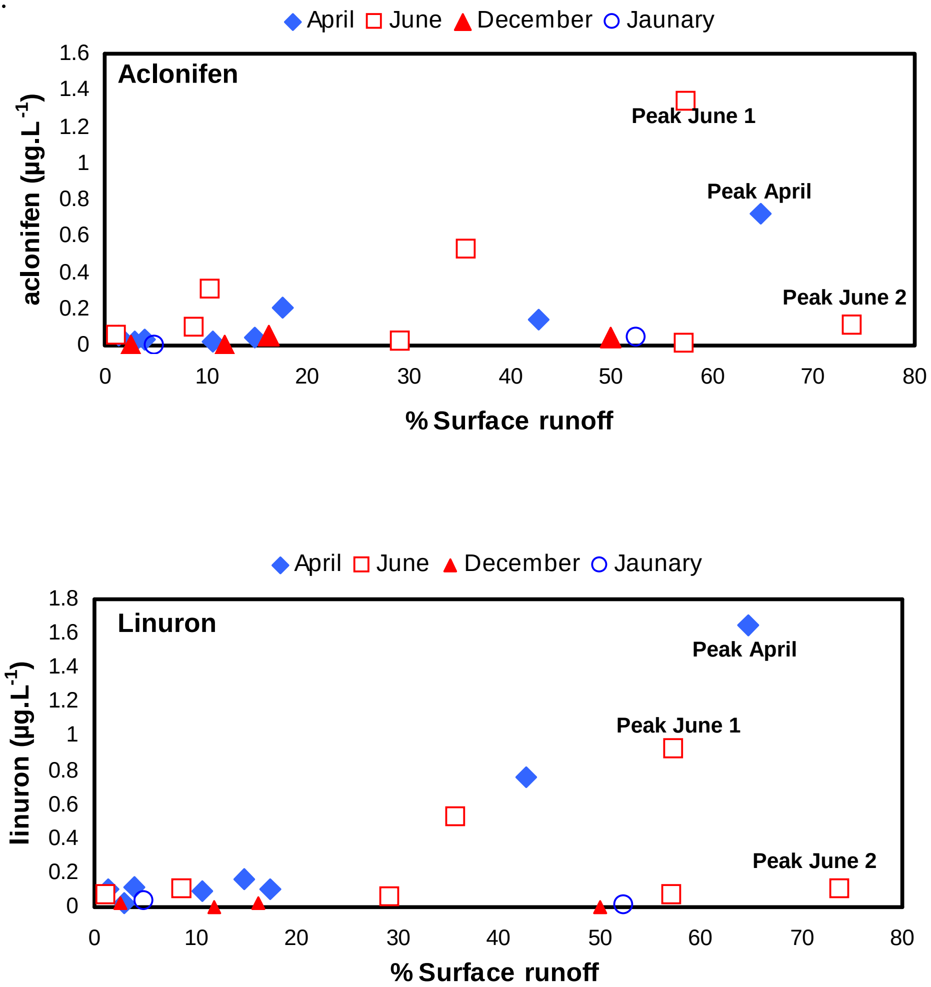


Figure 57- Relationships between aclonifen and linuron riverine concentration and the contribution (%) of surface runoff to the Save river discharge during 4 storm events.

A single storm case study: April 2008

Our effort has focussed on identifying the mechanism of pesticide transport and its controlling factors. To do so, storm of April was singled out since:

- during this period the contribution of surface and subsurface water is relatively similar. This similarity would facilitate the comparison and to discover the differences between them (table X).
- this period is coinciding with the application period and, moreover, our sampling points are nearly covered all of the storm phases (rising and falling limbs).

Table X- Contribution (%) of each stream flow components to the total volume of Save river discharge during the different storm events.

Storm period	Ground water		Subsurface runoff		Surface runoff		Total water
	m^3	%	m^3	%	$m^3.s^{-1}$	%	m^3
March 2008	$5.8x10^6$	59	$1.9x10^6$	19	$2.2x10^6$	22	$9.9x10^6$
April 2008	$7.5x10^6$	58	$3.2x10^6$	25	$2.1x10^6$	17	$12.8x10^6$
June 2008	$10.1x10^6$	32	$7.2x10^6$	23	$14x10^6$	45	$31.3x10^6$
November 2008	$4.9x10^6$	55	$2.7x10^6$	30	$1.3x10^6$	15	$8.9x10^6$
December 2008	$10.5x10^6$	65	$3.7x10^6$	23	$1.9x10^6$	12	$16.1x10^6$
January 2008	$23.6x10^6$	33	$17.7x10^6$	24	$31x10^6$	43	$72.3x10^6$

The relationships between TSM, POC, pesticides concentration and the contribution (%) of surface plus subsurface flows during the storm event of April 2008 in the Save river is depicted in figure 58.

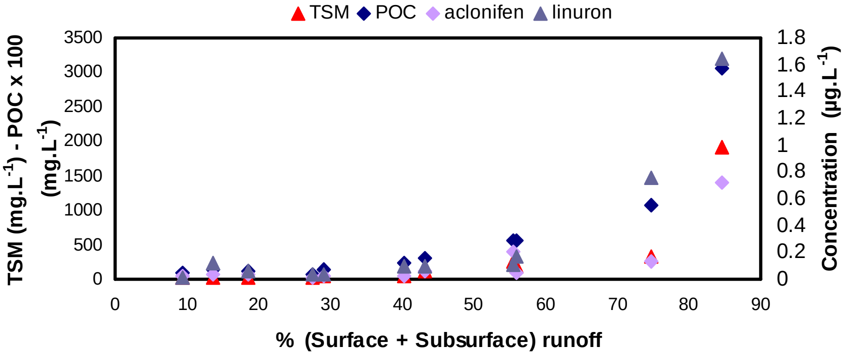


Figure 58- Relationships between TSM, POC, and pesticides concentration and the contribution (%) of surface plus subsurface flows during the storm event of April 2008 in the Save river.

The interaction between the contribution of superficial flow (surface plus subsurface) with the concentration of controlling factors and concentration of pesticide shows the maximum concentration of all of the elements observed when the contribution of surface plus subsurface discharge is more than 80 % of the total river flow (figure 58). The different equations adjusted to the relationships between TSM, POC and pesticides concentration and the contribution (%) of the surface plus subsurface flows to the total Save river discharge are depicted in table XI.

Table XI- Equations adjusted to the relationships between TSM, POC and pesticides concentration and the contribution (%) of the surface plus subsurface flows to the total Save river discharge.

y- factors	Equation	r_s^2	p-value
TSM ($mg.L^{-1}$)	$y = 10.915e^{0.053x}$	0.893	<0.01
POC ($mg.L^{-1}$)	$y = 43.699e^{0.0453x}$	0.826	<0.01
Aclonifen ($\mu g.L^{-1}$)	$y = 0.0112e^{0.039x}$	0.599	<0.01
Linuron ($\mu g.L^{-1}$)	$y = 0.0163e^{0.0471x}$	0.597	<0.01

By plotting the relationships between the concentration of aclonifen and linuron with each stream flow component, the main exporting pathway could be traced. The result shows a good relationship between the concentration of aclonifen, linuron and the ratio of surface water to the total flow. This finding highlights the important contribution of surface water to the displacement of these pesticides. The most noticeable relation was also recorded with the ratio of surface water on the total discharge for TSM and POC as it is depicted in figure 59.

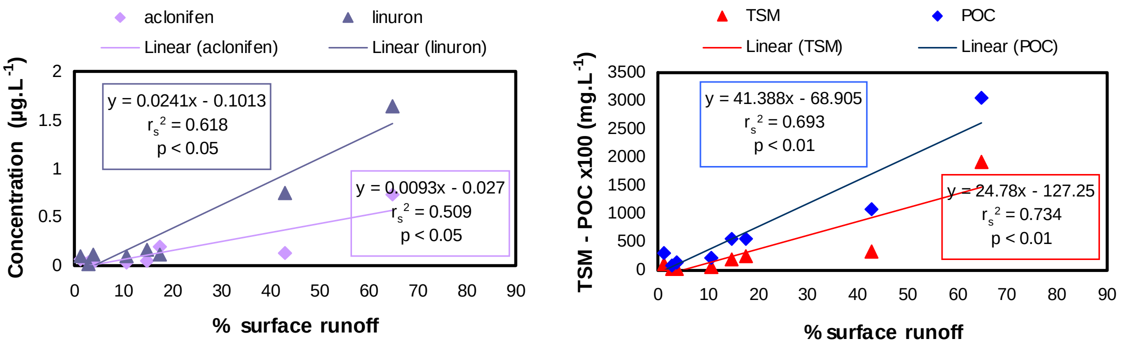


Figure 59- Relationships between TSM, POC ($mg.L^{-1}$) and pesticide (left) concentration and the contribution (%) of the surface runoff to the total Save river discharge during the storm event of April 2008.

The relationships between controlling factors (TSM-POC) and the concentrations of pesticides (figure 60) are clearly indicating the important role of POC and TSM in aclonifen and linuron transport. Linuron also shows a positive relation with the total discharge of stream flows (r^2=0.440, p-value=0.026), which explains the fact that TSM and POC are not the only influencing factors in transporting of linuron.

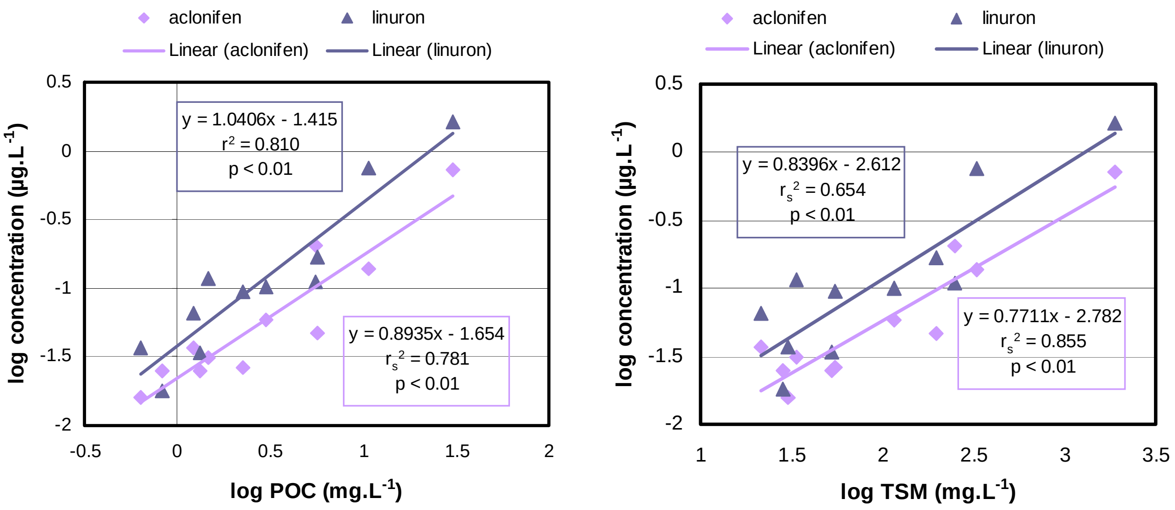


Figure 60- Relationships between the concentrations of pesticides (aclonifen, linuron) and the controlling factors (TSM, POC).

In storm of April 2008, the relationship of metolachlor as a soluble molecule and DOC in filtered water, with each stream flow was verified. The result shows a significant relationship between the discharges of surface and subsurface runoff separately with metolachlor, moreover the contribution (%) of surface and subsurface runoffs to the total river discharge also shows a positive relationship with concentration of metolachlor. Though, this relation is more significant with subsurface runoff (table XII).

Table XII- Coefficient of the relationships between metolachlor concentrations and the streamflow components.

Pesticides	**Pearson coefficient**	**Surface runoff**		**Subsurface runoff**		**Surface plus Subsurface runoff**	
Metolachlor ($\mu g.L^{-1}$)		$m^3.s^{-1}$	%	$m^3.s^{-1}$	%	$m^3.s^{-1}$	%
	r^2	0.455	0.546	0.726		0.582	0.544
	p-value	0.023	0.009	0.001	-	0.006	0.010
DOC ($mg.L^{-1}$)	r^2	-	-	0.582	0.403	-	-
	p-value	-	-	0.006	0.036	-	-

Our observation reveals that subsurface water is the most important pathway for transporting of metolachlor and DOC. Nervertheless, our findings also demonstrated the role of other stream flow components in transporting of these elements especially in the case of metolachlor. Since, total river discharge of stream flow also indicates a positive relationship with metolachlor (r^2=0.636, p-value=0.003).

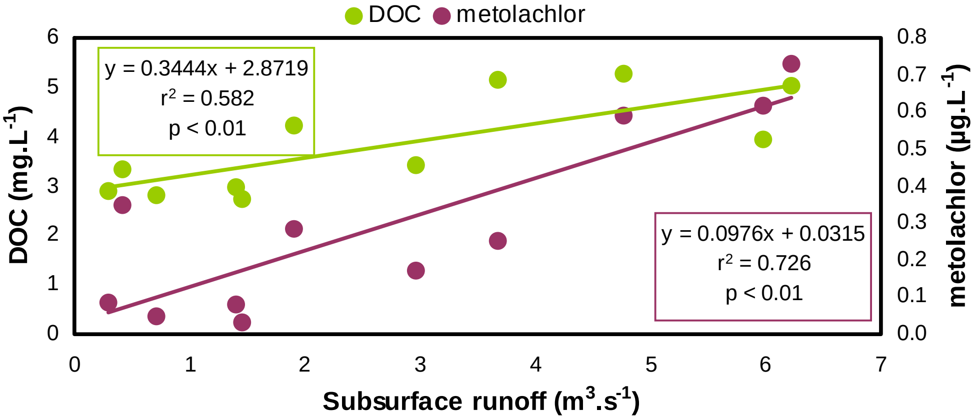


Figure 61- Relation between the concentration of metolachlor and DOC and the discharge of subsurface runoff during storm of April 2008 for the Save river.

Plotting the interaction of metolachlor and DOC illustrated a positive correlation between them as shown in figure 62.

- DOC plays an important role in metolachlor's displacement ,
- Metolachlor and DOC are transported together by complexation processes.

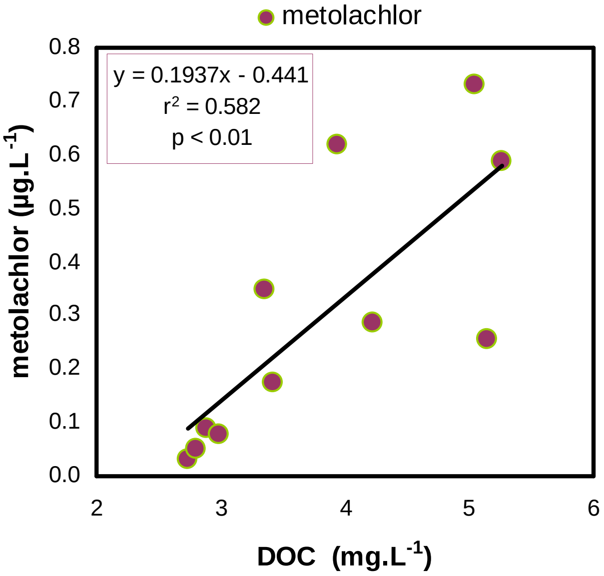


Figure 62- Relationship between metolachlor and DOC contents in filtered water during storm of April 2008 for the Save river.

3.2 Auradé Catchment

3.2.1 Relationship between pesticide and the controlling factors with stream discharge

Our study found no evidence, in the course of four monitored storms in Auradé linking the concentration of controlling factors and pesticide's molecules with the superficial discharge and discharge of surface and subsurface runoff separately. One major assumption to explain this result is the absence of data for all of the storm events in this catchment. Therefore, storm of May 2008 was chosen as the focal point of this part and the reason is two fold:

- the relatively same contribution of each flow components (table XIII),
- the hysteresis pattern and the relationship of two molecules of pesticide (linuron – aclonifen) with the controlling factors of these elements were demonstrated in this catchment (Taghavi et al., 2010, annexe V).

Table XIII- Contribution (m^3 and %) of each stream flow components to the total Montoussé discharge for 4 storm events for the investigated storm events

Storm period	Ground water		Subsurface runoff		Surface runoff		Total water
	m^3	%	m^3	%	m^3	%	m^3
April 2008	$9.3x10^3$	51	$7.9x10^3$	43	$1.1x10^3$	6	$18.3x10^3$
May 2008	$13.7x10^3$	50	$7.8x10^3$	29	$5.6x10^3$	21	$27.1x10^3$
April (1) 2009	$54.5x10^3$	29	$72.0x10^3$	38	$63.6x10^3$	33	$190.1x10^3$
April (2) 2009	$66x10^3$	39	$46.3x10^3$	27	$57.9x10^3$	34	$170.2x10^3$

During these storm events three molecules of pesticide with different degree of solubility investigated.

Our findings show the existence of a noticeable relationship of linuron in unfiltered water with DOC, TSM and POC but stronger relation was with DOC as it was illustrated by Taghavi et al. (2010). Linuron and DOC show a good relationship with the proportion of subsurface runoff, (figure 63). The main findings of this research provide a relatively enough evidence to believe that linuron is exported by subsurface water and a high degree of linuron and DOC concentration during falling limb of hydrograph. It is worth adding TSM and POC show a significant relation with the proportion of subsurface runoff. This results show, on the one hand, the important role of controlling factors for transporting of linuron, and on the other hand, the important role of the proportion of subsurface water in transporting of linuron and DOC in the small Auradé catchment.

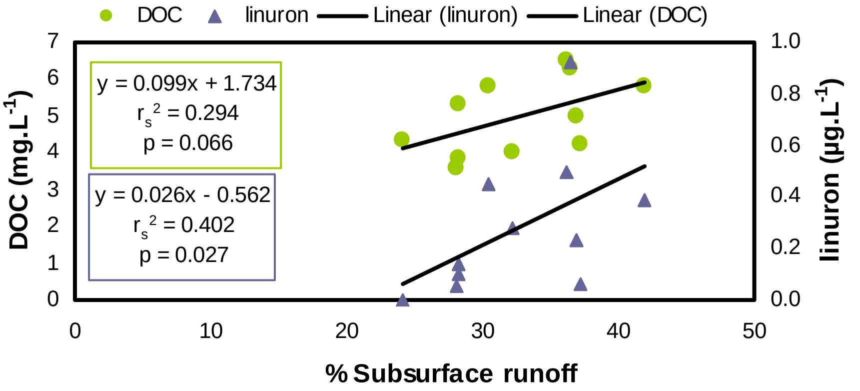


Figure 63- Relationships between linuron and DOC with the proportion of subsurface runoff.

Linuron, as representative of moderately soluble molecule, shows a good relationship with DOC (figure 64). And, this is in contrast to what it has been observed in Save river. However, its relation is also significant with TSM and POC with the value of Pearson coefficient (r^2 = 0.503, p < 0.01 and r^2 = 0.462, p < 0.01) respectively for TSM and POC. Our findings revealed that the interaction of moderately souluble molecules with dissolved and particulate fractions depend on the abundance of these parameters in the environment.

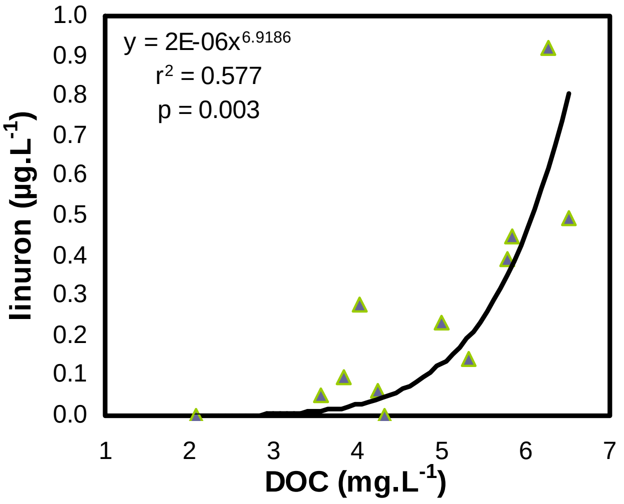


Figure 64- Relationship between metolachlor and DOC contents in filtered water during storm of April 2008 for the Auradé chachment.

Aclonifen didn't show any connection with discharge of different stream flows, however there is a significant relation between aclonifen and concentration of TSM and POC. Moreover, the existence of a good relationship between TSM, and POC with the proportion of subsurface water, could perhaps explain, the higher degree of concentration of this molecule during falling limb of hydrograph (figure 65).

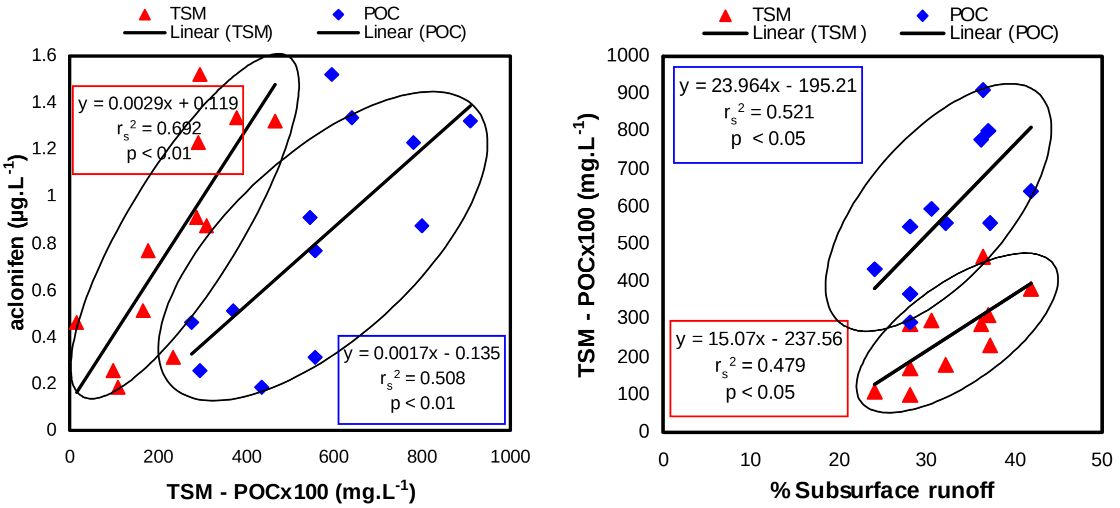


Figure 65- Relationships between aclonifen concentration, TSM and POC (left), and the relationship between TSM and POC with the proportion of subsurface water (right).

The relationship between metolachlor, as a soluble molecule, with controlling factors and discharge of stream flow was analyzed in filtered water. The results show a good relationship between the concentration of metolachlor and the contribution of subsurface water (figure 66), as it has been already observed for Save river. However, the concentration of metolachlor remains within the authorised limit.

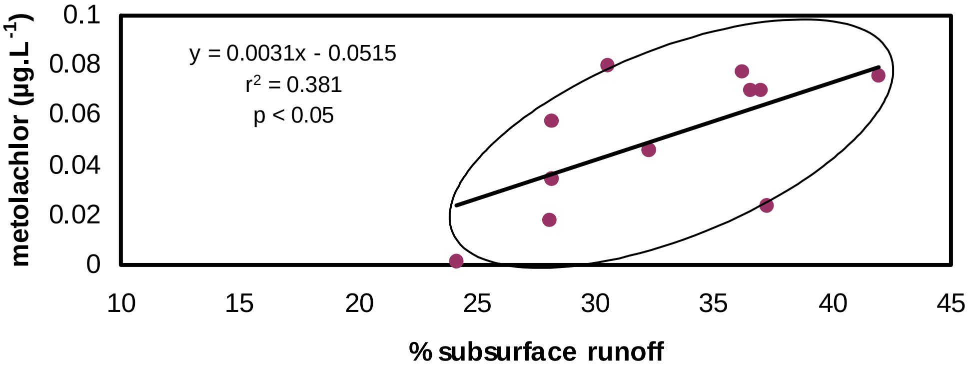


Figure 66- Relationship between the proportion of subsurface water and metolachlor during storm of May 2008 in Aurade catchment.

In Auradé catchmens during storm of May 2008, concentration of metolachlor shows a good relationship with DOC (figure 67), as we observed earlierin Save river during storm of April 2008.

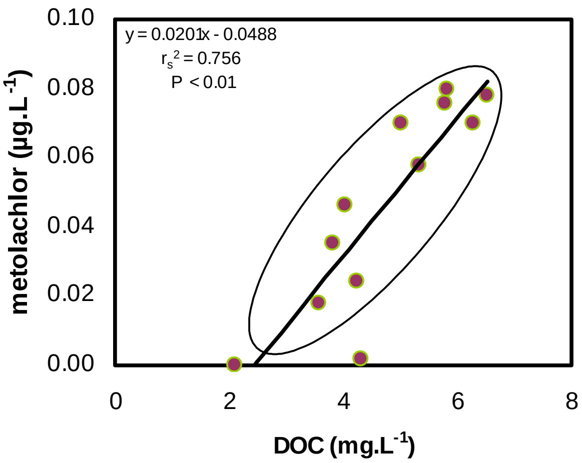


Figure 67- Relationships between metolachlor concentration, and DOC during storm of May 2008 in Auradé catchment.

Summary

The first part of this chapter focused on hydrograph separation to understand the contribution of each stream flow component. The relatinships between each stream component and total water discharge indicate that how each reservoir is replenished or drained. As an example the relationship between the contributions (%) of the groundwater discharge versus total river discharge clearly shows that when the river discharge increases the relative contribution of ground water decreases in both catchments. In the case of subsurface runoff a bell-shap graph which reflects the slow drainage of water in the soil was observed in Save catchment, however in Auradé this phenomenon is less clear. Our observation find a similar pattern for surface runoff, that is to say, as the total river discharge increases so does the surface runoff. In the second part the relationships between pesticides concentration and their controlling factors (TSM, POC and DOC) with total discharge highlighted hysteresis patterns, that indicate different role of each stream flow component in transportiong of pesticides and their controlling factors. In fact this relationship shows different concentration of these elements in rising and falling limb of storm hydrograph for a given river discharge.

In the third part, by using hydrograph separation, we obtained the discharge of each stream flow component. Then the relation between each component and the concentration of pesticides and of controlling allow to better underestand the main routing of transportation of each parameter.

Our findings in Save catchment revealed the role of surface runoff in transport of low to moderatly low soluble molecules and also particulate fractions (TSM, POC). Whereas subsurface flow is responsible for transporting soluble elements such as metolachlor and DOC. However, in Auradé catchment, the water course for molecule transport is not the same as in Save catchment. Our findings in Auradé catchment revealed the important role of the proportion of subsurface flow in transporting of pesticides and their controlling factors.

In addition, the relationships between molecules of pesticides and their controlling factors highlighted the role of particulate fractions (TSM, POC) in transporting of low to moderatly soluble molecules and dissolved organic fraction (DOC) for soluble molecule.

Chapter V

Pesticide riverine fluxes and distribution between dissolved and particulate fractions

Chapter V

Pesticide riverine fluxes and distribution between dissolved and particulate fractions

Introduction

The first part of this chapter out lines in brief, the technique for flux calculation. In the second part, the flux of pesticides and controlling factors (DOC-TSM) are quantified. In the third part the flux of pesticides and volume of water were investigated and the important role of the volume of water in transporting of pesticide is dealt with. The flux of pesticide in Save and Auradé catchments and specific flux calculation will be compaired in the following part. Subsequently, the distribution of pesticides between dissolved and particulate fluxes (K_d) will be assessed and compaired with the obtained-water partitioning (K_{OW}) extrated from literature values. Finally, the relationship between partition coefficient (K_d) in Save and Auradé catchments with total suspended matter (TSM) as a controlling factor was investigated.

1 Flux Calculations

The flux is defined as the mass of the compound transported in the river at each sampling point during a specified time period. The fluxes of each pesticide and controlling factors, TSM and DOC are calculated as the product of the compound concentration and river discharge at each sampling time. For each sampling interval (i to i+1), the flux is the product of discharge weighted concentration C (Ci to i+1= (CiQi+Ci+1Qi+1)/(Qi+Qi+1)) , river discharge (Q) between i and i+1 and the volume of water discharged between i-i+1 is shown like Vi-i+1. The storm event fluxes and the annual fluxes are calculated by summing the fluxes of the different intervals (i to n). Hourly mean discharge values were available for all sampling points for the whole samplings period. The flux of sampling point was then summed to give the total load for whole of the sampling periods and also each storm event.

$$F_{\mathrm{Total.annual}} = \sum_{i=1}^{n} \overline{C}_{i-i+1} \times V_{i-i+1} \qquad \textbf{Eq.2}$$

In flux calculation, in the case of pesticide, not detected pesticides were assigned a value of zero for the load calculations. This means that loads percentage may have been underestimated, when pesticide is present in the water at a concentration just below the limit of detection.

2 DOC and TSM fluxes

The hydrological flux of organic carbon in rivers is an important element of the riverine ecosystems (Robertson et al., 1996; Lovett and Price, 1999). Recent studies on river ecosystems show that river discharge, vegetation productivity and soil organic carbon in the catchment are the major elements which have a marked impact on the fluxes of organic carbon in streams and rivers.

Hinton et al. (1997) point out that storm is responsible for 57 to 68 % of DOC export in the Autumn and 29% to 40% of DOC export in the Spring.

Grieve, (1984); Hope et al. (1994) Boyer et al. (1996,1997) Hinton et al. (1997) and Clark et al. (2007), have all observed that dissolved organic carbon (DOC) fluxes in freshwater increased during storm events. Studies conducted by Buffam et al. (2001) and Inamdar et al. (2006) have shown a large proportion (36 to 50%) of the annual DOC export occurs during a short span of time when intensity of rainfall is high and it occupies 4 to 24 % of the observation time.

Zhang et al. (2009) have reported in their investigations that organic carbon transport exhibits also seasonal variations and almost 90% of the total organic carbon is displaced in the flood season from April to September though 68% of water discharge are transported during this period. However, this study indicates that flood period is responsible for the transport of 95% of particulate organic carbon and more than 97% of suspended sediments.

Bourrin et al. (2008), has reported rising flood events typically exhibit increases in sediment load. In a three-year survey on the Rhone River, Ollivier et al. (2010) concluded that over 80% of TSM (SPM) flux is discharged at the time when the river flooded.

In our research, 64% of the annual volume of the water discharged and nearly 71% of the annual Dissolved Organic Carbon (DOC) flux and 94% of the annual Total Suspended Matter (TSM) flux were transported throughout the sampling exercise periods of flood events, in annexes IV (a).

In Save catchment, the maximum fluxes of DOC are attributed to the storms of June and January with the value of 20 and 26 % of the total annual flux, respectively. Storms of March, April, and December, represent 5, 5.7, and 6.2 percent (%) respectively of the total loads during storm events.

In the case of TSM, the maximum of TSM flux attributed to the storm of June 2008 and that of January 2009 valued 61 and 21 percent respectively. The consequential mass of TSM observed could be attributed to the intense and highly erosive rainfall and runoff during the two episodes of 2008 and 2009. The conclusion of a study on dynamics of suspended sediment transport carried out by Oeurng et al. (2009) is perfectly in line with the results of our research suggesting the importante load of TSM during the storm of June 2008 and January 2009.

Storms of March 2008, April 2008, and December 2008 were only representing 1.84, 7.65 and 2.6 percent (%) of the whole storm periods.

3 Pesticide fluxes

During entire investigation period, 65 and 121 water samples were taken in Save and Auradé catchments respectively in order to determine the total pesticide flux.

Different evolution profile emerged as the result of the displacement of different family of pesticide and this is because their application periods did not coincide at the same time. Pesticide transfer is largely depending on how they are conveyed and, especially their interactions with the environment. In fact, the relative importance of pesticide transport dissolved in water or adsorbed onto suspended solids has been investigated by several authors (Pereira and Rostad, 1990; Barriuso et al., 1996; Clark et al., 1991; Gomme et al., 1991; Brown et al., 1995; Gril et al. 1999; Grebil et al. 2001; Louchart et al., 2001). According to the abondance of DOC and TSM the concentration of pesticide can be very contrasting (Wu et al. 1983; Garmouma et al. 1997; Lecomte et al. 1997; Garmouma et al. 1998; Kreuger, 1998; Lecomte, 1999; Gouy et al. 2000; Hyer et al, 2001).

According to our research the presence of pesticide was unevenly distributed throughout the investigation periods. Our results also show the relative importance of flood events for the total fluxes of pesticide during the whole study period.

The quantity of fluxes for each molecule of pesticide fluxes per storm event, as well as the cumulative fluxes during all storm events and during baseflows in unfiltered and filtered water was shown in annexe IV (a,b).

The total flux of each pesticide at each storm event is compared with the total annual flux in the drainage basin and is expressed as a percentage for each pesticide transported during storm events, annexes IV (a,b).

The percentage of pesticide flux indicates the significant role of storm events in the transport of pesticide. Over 60% (except DEA and atrazine) of studied molecules were transported during these periods and the percentage of pesticides in base flow remains several times less in storm flow. However, this disparity is linked to the molecules chemical substance. We should emphasis in the case of atrazine and DEA the difference in flux value during stormwater and baseflow is minor importance. 37.9 and 21.2 % of annual load of atrazine and DEA was transported in particulate phase. This observation shows that the transport of main bulk of these molecules occur in dissolved phase. This finding is in accordance to the previous studies. Squillance and Thurman (1992) reported that almost the totality of atrazine might be carried under the dissolved form in aquatic environments. Goolsby and Pereira, (1996) pointed out, compounds such as atrazine, with K_{oc} value less than 500, tend to be transported primarily in the dissolved phase.

The previous studies indicate that pesticide losses are related to some phenomenons (Squillace and Thurman, 1992; Brown et al., 1995 and Lennartz et al., 1997) appear, generally, close to the application period. The characteristics of rainfall, runoff volume and storm events, have a great impact on pesticide losses (Rohde et al., 1980; Muller et al., 2003).

The bulk of annual loss of pesticide (over 65%, 70% and 90%) is found in association with water transfer by surface runoff; number of studies concluded (Squillace and Thurman, 1992; Ng and Clegg, 1997, Müller et al., 2003,). Louchart et al. (2001) have provided an example in the Mediterranean vineyard. These authors observed that the degree of pesticide contamination varies according to the storm period and baseflow.

Müller et al. (2002) show that the concentration of pesticides is higher at the time of direct flow than at the base flow and the reason given for this pattern is that soil becomes a «filter» for the molecules.

In sum, the findings of our research showing the variation between the flux of pesticides during stormwater and baseflow could be explained as follows: pesticide flux during the time of baseflow appears to be insignificant comparing with the amount of loss of pesticide during the stormwater, and this pattern occurs despite the relatively important contribution of baseflow to the annual runoff (36.1%). This disparity could be the result of the much higher pesticide concentration during the stormwater than during base flux.

The small loss during the baseflow suggests that adsorption and /or degradation occur in the aquifer.

Previous studies came to the same conclusion, i.e. out of the flooding period; groundwater current is the principal means of pesticide transportation. During this period –no flooding- the flux of pesticide is low for the following reasons: (Attaway et al;, 1982; Larson et al., 2001; Louchart et al., 2001):

- mixture of new water with old water of the catchments moved by storm events,
- mixture of water from different layers of soil, already low contaminated by pesticides.

The findings of our study show that the total flux of pesticide in particulate or dissolved phases depends on the characteristic of the molecules. Which explain the impact of pesticide properties on the pesticide concentration dissolved in runoff and adsorbed onto eroded sediment. Belamie et al. (1997) underline the difficulty to assess the flux of pesticide in any form (particulate or dissolved) based on the solubility of the pesticide and the rate of TSM in natural conditions. However; Muller et al. (2006), emphasis on the minor importance of herbicide properties for total loads in the runoff.

Concentration of pesticide in dissolved form is by far more important than in adsorbed form, except when the rate of erosion is high, as concluded by Wauchope (1978). In contrast, Hall et al. (1974) and Leonard et al. (1979) came to the conclusion that the concentration of pesticide adsorbed onto particulate fraction could have a higher degree of concentration than dissolved. Brown et al. (1995) suggested that the greater part of the pesticide load is carried as dissolved phase except for the low water soluble pesticide such as trifluralin, movement on sediment was shown to be the dominant mode of transport. Kreuger, (1998) observed the same pattern for fenpropimorph (another low water soluble and relatively persistent pesticide) that its movement was associated with sediment during intense rainfall.

Annexe IV (c), presents the percentage of pesticide in particulate fractions during the study period. From the results in annexe IV (c), we can see that for low soluble molecules (epoxiconazole, tebuconazole, fenpropimorph, trifluralin, aclonifen), with solubility < 40 ($mg.L^{-1}$) more than 50% of annual transport can be attributed to particulate phases. However, transport of pesticide by dissolved fraction is proved to be a dominant factor for soluble molecules such as metolachlor and alachlor.

Regarding the results of Auradé catchment, the flux of pesticide was calculated during 4 storm events, for the period of 2008-2009. The findings reveal that the dominant molecules are almost similar to those of Save watershed, although no clear evidence can be provided for storm and base flow due to shortage of data for all of the storm events in this catchment.

Annexe IV (d) reveals quantity of molecules during the period of investigation in unfiltered (a) and filtered water (b) in Auradé catchment.

The amount of pesticide transported did not decrease from one event to the other and differences in the patterns of pesticide's fluxes result from their different uses. And, for some pesticides the largest transport was recorded with the largest amount of water. In Save watershed the storm of January 2009 (5) was an exceptional event, during the whole study period, when 30.5% of volume of water and more than 50% of chlorotoluron and trifluralin, fenpropimorph and tebuconazole transported during this episode. The storm of June (3) was recorded as a complex event with the volume of water around 13.2%, which is responsible for the transport of more than 50% of metolachlor, aclonifen and cyproconazole in unfiltered water. In the case of filtered water, the result of fluxes was illustereted in annexe IV (b).

The relation between flux of pesticide and volume of water during the storm event is positively correlated for some molecules both in unfiltered and filtered water. The equition of the relationship between the flux of pesticide (g) and volume of water (m^3) for the cited molecules at the Save catchment is illustrated in the following table XIV.

Table XIV- Equations between the amount of pesticides transported (Y in g) and volume of water (X in m^3) for some molecules in unfiltered and filtered water in Save Catchment.

Pesticides	Unfiltered water	Filtered water
DEA	$y = 3E\text{-}05x - 211.57$ $r^2 = 0.954$	$y = 2E\text{-}05x - 76.67$ $r^2 = 0.951$
atrazine	$y = 262.58Ln(x) - 4140.8$ $r^2 = 0.878$	–
chlorotuloron	$y = 1880.3e^{4E\text{-}08x}$ $r^2 = 0.824$	$y = 1120.1e^{4E\text{-}08x}$ $r^2 = 0.8285$
alachlor	$y = 293.18Ln(x) - 4704.9$ $r^2 = 0.869$	–
trifluralin	$y = 0.0003x - 4850.4$ $r^2 = 0.969$	–
fenpropimorph	$y = 7E\text{-}06x - 40.97$ $r^2 = 0.949$	–
tebuconazole	$y = 0.0006x - 6048$ $r^2 = 0.989$	–

As an example, the relationship between volume of water and flux of pesticide was depicted in figure 68.

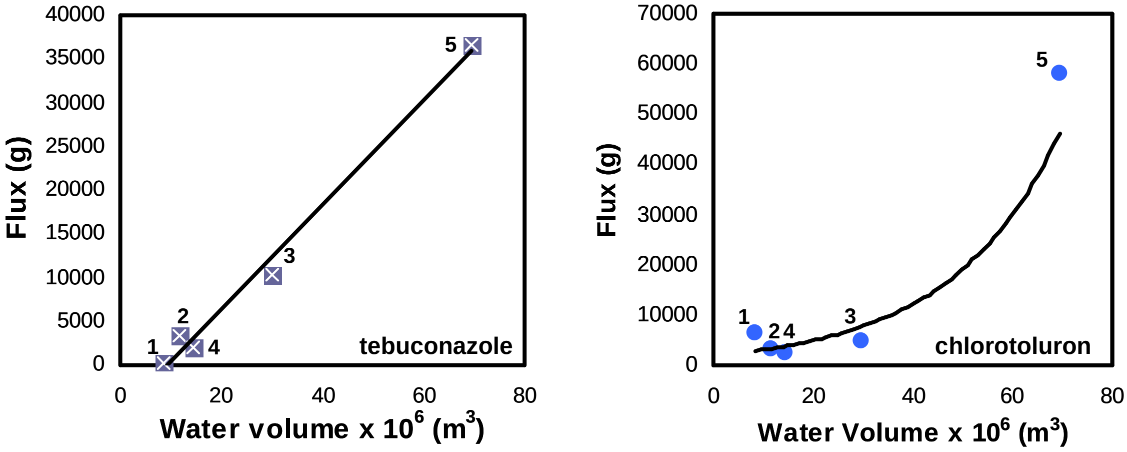


Figure 68- Relationships between volume of water and pesticides fluxes during 5 storm events in the Save river.

In Auradé catchment the relationship between flux and volume of water during each storm events was also plotted. The equations established, show there is a good relationship between the amount of pesticide transported and the volume of water in unfiltered water. In filtered water this relation was also observed in the case of DEA, atrazine, chlorotuluron, fenpropimorph, tebuconazole, cyproconazole and epoxiconazole. The following equations in the table XV below refers to the existence of a good relationship between the amount of pesticides transported and the volume of water in unfiltered and filtered water.

Table XV- Relationships between the amount of pesticides transported (Y in g) and the volume of water (X in m^3) in Auradé catchment.

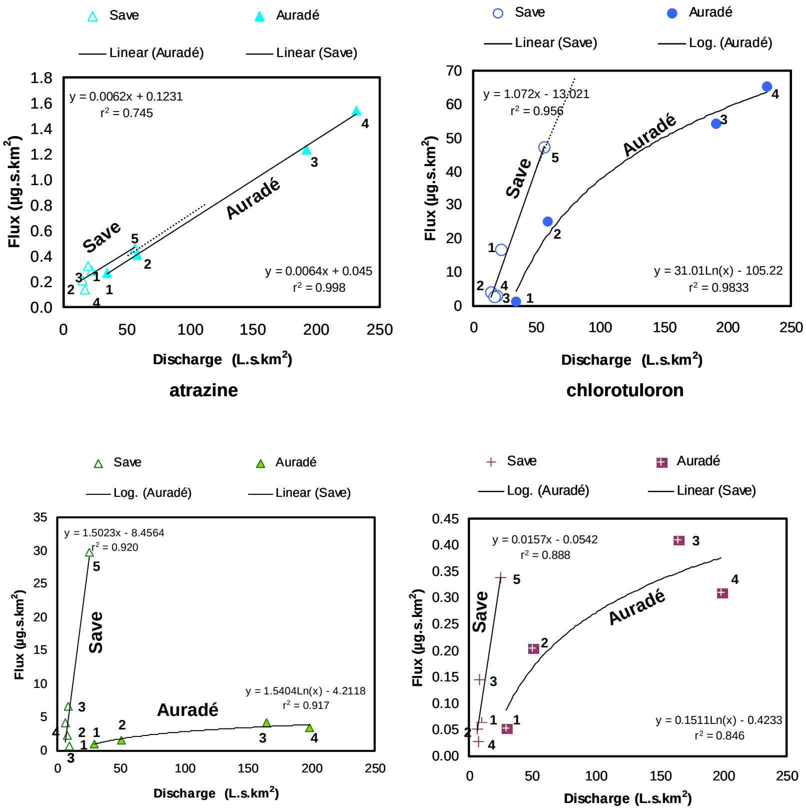
Pesticides	Unfiltered water	Filtered water
DEA	$y = 0.6638e^{6E-06x}$ $r^2 = 0.823$	$y = 0.5597e^{6E-06x}$ $r^2 = 0.842$
atrazine	$y = 7E-06x + 0.053$ $r^2 = 0.927$	$y = 6E-06x + 0.039$ $r^2 = 0.912$
chlorotuluron	$y = 0.0003x - 0.209$ $r^2 = 0.933$	$y = 0.0002x - 1.784$ $r^2 = 0.916$
fenpropimorph	$y = 8E-07x + 0.051$ $r^2 = 0.918$	$y = 2E-06x - 0.044$ $r^2 = 0.874$
tebuconazole	$y = 2E-05x + 0.463$ $r^2 = 0.993$	-
cyproconazole	$y = 5E-06x - 0.002$ $r^2 = 0.998$	$y = 4E-06x + 0.005$ $r^2 = 0.955$
epoxiconazole	$y = 2E-05x + 0.011$ $r^2 = 0.987$	–

4 Specific fluxes and comparioson between Auradé and Save catchments

The degree of pesticide load is a right indicator to measure pollution caused by pesticides and this enable us to establish pollution rate for different catchment, especially if they are expressed as a fraction of the pesticide applied. Moreover, the comparisons of normalized loads are critical to the layout of the studies (e.g. variance in the number of pesticides analysed and length of investigation time).

In order to have the yield (µg.s.km^2), the load of each pesticide was divided by the surface of the cultivated area of the watershed. For Save catchment, the cultivated area included only areas planted in row crops (corn, winter wheat and sunflower) is about 490.79 km^2. For Auradé catchment where the cultures are sunflower and winter wheat in rotation, this area is 2.82 km^2. By comparing the river flux of pesticide in Save and Auradé catchment, we can understand the amount of the pesticide transfer. The most important finding of this research shows that the molecules utilised recently in these catchments did not follow the similar pathways as those of the old one (atrazine).

The results of specific fluxes obtained in Save and Auradé catchments indicate a higher pesticides concentration in Save catchment than in Auradé for a given discharge (figure 69).



atrazine

chlorotuloron

tebuconazole

fenpropimorph

Figure 69-Relationships between specific flux of pesticides and specific water discharge in both catchments, Save and Auradé, during storm events.

The only reason which could substantiate this observation is the use of larger amount of pesticides per unit area during study period for Save catchment; however no data on the exact quantity of pesticides applied in this catchment is available.

The study conducted by Clark, (1997) about two pesticide molecules (EPTCV, atrazine) indicate, watershed size may be an important factor in assessing pesticide fluxes from watershed, and subbassin size did not appear to reduce the percentage of the total annual application of EPTC and atrazine transported from subbasins.

5 Partitioning between dissolved and particulate phases

5.1 Partition coefficients

In the last two decades the role of the n-octanol /water partition coefficient (k_{ow}) for organic compounds has become of paramount importance in predictive environmental studies. This physico-chemical parameter is used in evaluative models for the prediction of distribution among environmental compartments (Cohen et al., 1990; Mackay, 1991) in equations for estimating bioaccumulation in animal and plants (Veith et al., 1979; Briggs et al., 1981) and in predicting the toxic effects of a substance (Calamari and Vighi, 1990). We believe, little is currently known about the relationship between K_{ow} values extracted from the literature and K_d calculated for each molecule from field measurements especially during storm flow. K_d reflects the real distribution of pesticides between dissolved and particulate fractions for a given catchment.

5.1.1 Sorption isotherms (K_d) and sorption coefficients (K_{oc})

Despite limitation of $\mathbf{K_{oc}}$ approach, it is currently the most widely used technique which is quite relevant to predicting the sorption of organic compounds to soils and sediments. Muller et al. (2006) concluded that pesticide properties have a dominant role in the concentration of pesticides dissolved in water or adsorbed onto eroded sediment. Cooke et al. (2004) and Schäfer et al. (2008) also reported the partition coefficients (k_d values) is depending on specific characteristics of soil, just the same as the physico-chemical characteristics of the pesticide.

Most studies carried out on the fate of pesticides in runoff are being dealt with sorption of pesticide to the whole of soil materials. Recently, binding of pesticides to different size fractions has received increasing attention, in particular for pesticides with high hydrophobicity (Gao et al., 1998; De Jonge et al., 2000; Leonard et al., 2001; Riise et al., 2001; Wu et al., 2004). The influence of dissolved organic matter (DOM), a mobile sorbent, on the distribution and transport of non-ionic organic contaminants in natural media has also attracted much attention (Lee et al., 1990; Totsche et al., 1997; Gao et al., 1998; Spark and Swift, 2002).

This is also true for the sorption capacity of a soil to some kind of pesticide which can be quantified by the distribution coefficient of the chemical between aqueous and solid phases (K_d value), often directly related to the content of organic matter in the sample.

$$\mathbf{K_{oc} = K_d / \mathit{f}_{oc}}$$

Where OC is the organic carbon content (mgC. g^{-1}) and K_{oc} is a characteristic for the actual pesticide and K_d is normalized to the weight fraction of organic carbon (e.g. Chiou et al., 1979; Kile et al., 1999). However, Calvet et al. (1981) have mentioned a good relationship between the K_d and the quantity of organic matter obtained when we have a wide range of value.

This is why; our special emphasis was put on the relationship between log K_d and log K_{ow}, for predicting the distribution of molecules in different phases without particulate attention on quantity of organic carbon since in our study area the particulate organic carbon content is very low (2-3% on average).

5.1.2 K_d and K_{ow} relation during storm period in Save and Auradé catchment

In Save watershed the K_d value calculated for all of the storm events based on flux value during these periods, and according to definition of K_d by Taghavi et al. (2010) where K_d is the ratio between dissolved and particulate pesticide concentration.

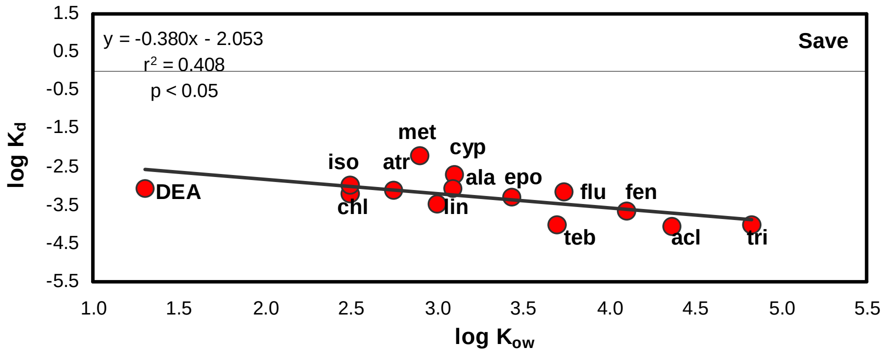


Figure 70- Relation between log K_d and log K_{ow} during storm periods in Save catchment. K_d is calculated for pesticide fluxes export during storm events.

The equation given in figure (70) is characteristic of a river such as the Save with average of variables such as TSM 349 mg.L^{-1}, DOC of 4.2 mg.L^{-1}, %POC 3.2%, as well as pH 8.2 and EC of 482 µs.cm^{-1} during the storm periods.

In the case of each storm water separately, the best relationship between the log K_{ow} and log K_d observed during storm of June 2008. However, storms of April, December in 2008 and January in 2009 show no significant relationship between log K_{ow} and log K_d. It is worth noting, storm of March was excluded in our study due to insufficient data especially during the peak of storm.

As an example in Save catchment, figure 71 depicted the relationship between log K_{ow} and log K_d during storm of June 2008.

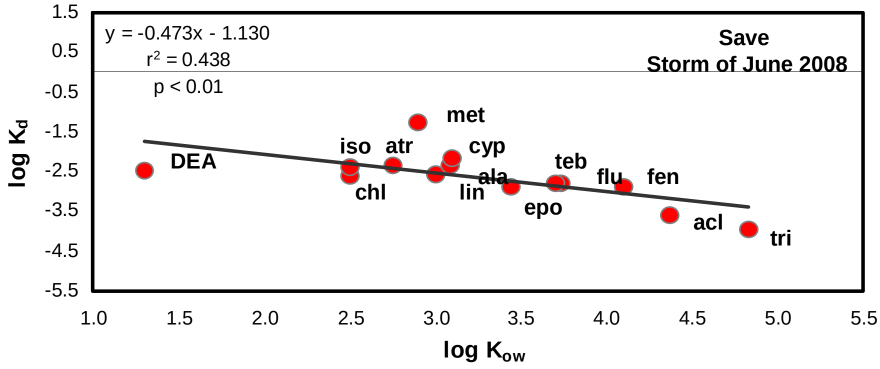


Figure 71- Relationship between log K_{ow} and log K_d during storm of June 2008 in Save catchment.

In Auradé catchment, the best relationship between log K_{ow} and log K_d for all of the storm events was obtained when we calculated the value of K_d by arithmetic means of individual values obtained for each sample (figure 72).

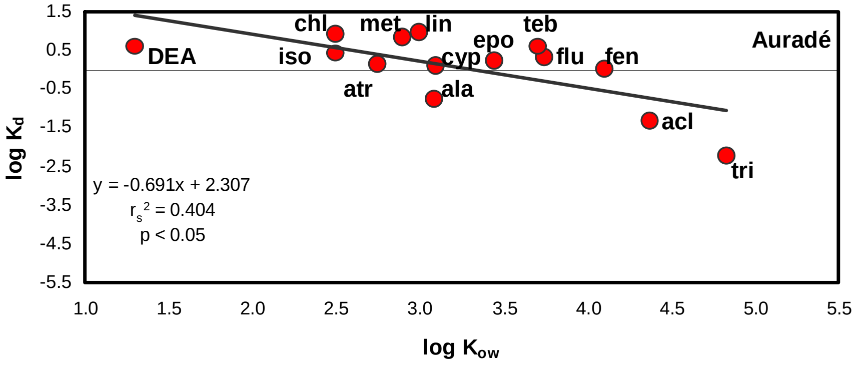


Figure 72- Relationship between log K_d and log K_{ow} during storm period (2008-2009) in Auradé catchment.

The equation obtained in Auradé catchment during storm flow is characterized by average of concentration for TSM 432 mg.L^{-1}, DOC 5 mg.L^{-1} and %POC 2.09, as well as pH 8.2 and EC 752 µs.cm^{-1}.

In Auradé catchment the best relationship between log k_d and log K_{ow} for each storm water was obtained when we weighted (normalized) the value of K_d by discharge value. The best correlation was observed during storm of April (1) in 2009 (figure 73), although the value of coefficient of correlation is significant (r^2= 0.330).

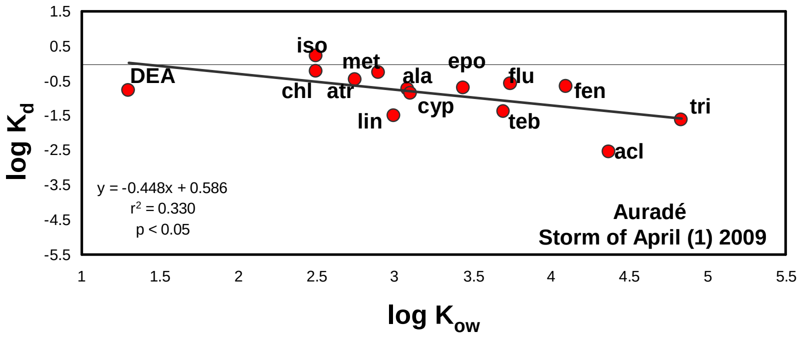


Figure 73- Relationship between log K_{ow} and log K_d during storm of April 2009 (1) in Auradé catchment.

Concerning storm of May and April 2008 and April (2) 2009, no relationship between log K_{ow} and log K_d was registered.

The findings of our research at the timing of storms in two catchments show that:

(i) the value of log K_{ow} grows in inverse proportion to the value of K_d, ($C_{\text{dissolved}}/C_{\text{particulate}}$) (ii) the scale of this disparity between dissolved and particulate phases is not within the same range at two cathchments, even if the slope of relationships to K_d- K_{ow} are very closed (iii) the difference between the value of K_d in Save and Auradé catchments could be explained by the timing period of storm events.

The storm at Auradé catchment, known as flashy storm, takes place in a short span of time (3 days in average). The relative short time of action of "Flashy storm" may prevent the pesticide molecules to fully interact with sorbent such as dissolved organic carbon (DOC) and total suspended matter (TSM).

The average time of storms is extended to 22 days at Save watershed. And, this relatively longer period of time leaves enough room for pesticide molecules interaction with its environment. The result of the study conducted by Selim and Zhu, (2005), clearly exhibits an increase on the value of distribution coefficient (K_d) with reaction time.

5.2 Relationship between log K_{ow} and % of pesticide in suspended matter

Percentage of particulate fractions during all of the storm events was estimated as followes:

$$\% \text{ particulate} = \frac{100\,(C_{\text{unfiltered}} - C_{\text{filtered}})}{C_{\text{unfiltered}}} \qquad \textbf{Eq.3}$$

In Save watershed during a whole period of storm water the percentage of pesticide transported by particulate fractions calculated by flux value in unfiltered and filtered water.

In fact, the best relationship between log K_{ow} and percentage in suspended matter observed when we calculated the percentage of particulate fraction by the flux value (F).

$$\% \text{ particulate} = \frac{100\,(F_{\text{unfiltered}} - F_{\text{filtered}})}{F_{\text{unfiltered}}} \qquad \textbf{Eq.4}$$

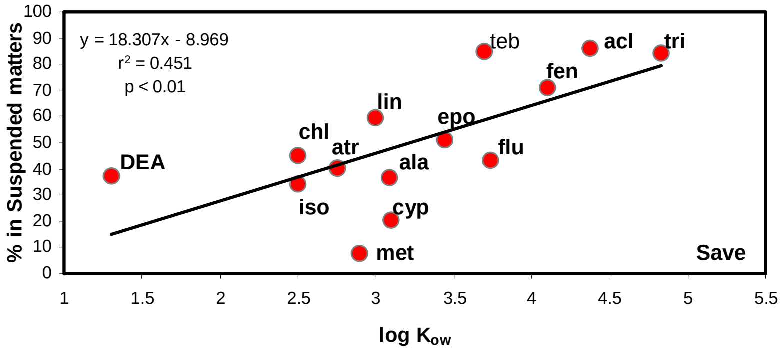


Figure 74- Relationship between log K_{ow} and percentage of pesticide in suspended matter in Save catchment during storm events.

Figure 74 shows that molecules with the highest K_{ow}, such as trifluralin, aclonifen, fenpropimorph and teboconazole are mainly exported with particulate fractions (70 to 90 %). Other molecules (isoproturon, linuron, flusilazol, chlorotuloron, atrazine, epoxiconazole, alachlor, cyproconazole) show a contribution of particulate fraction between 20 to 60%. Metolachlor as a representative of the highest soluble molecules, show a contribution of nearly 10% in particulate fraction. DEA represent nearly 40% of exportation with particulate fractions.

In Auradé catchment the best relationship was observed when we calculated the percentage value of particulate fractions during storm events by doing an arithmetic means of values during a whole period of time (as was done for k_d value).

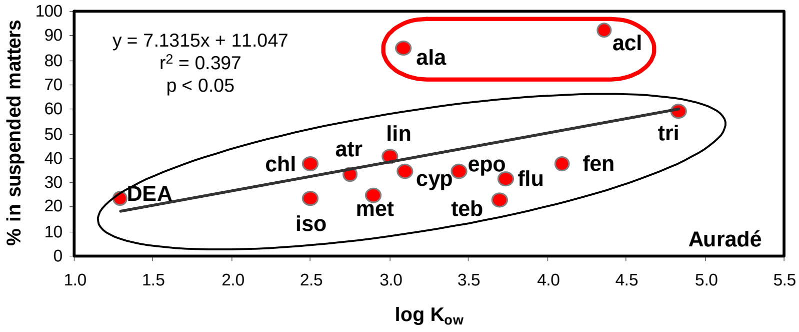


Figure 75- Relationship between log K_{ow} and percentage of pesticide in suspended matter in Auradé catchment during storm events.

In Auradé catchment, the relationship between log K_{ow} and percentage in suspended matter is less obvious and the reason is perhaps due to the lack of sufficient data for all of the storm events. However, a positive relationship between log K_{ow} and percentage of particulate fraction is clearly established, even if alachlor and aclonifen present higher % valus compared to their K_{ow} (figure 75).

The relationship between the value of K_{ow} and percentage in suspended matter was also calculated during each storm event by using the values of flux in two catchments (table XVI). In Save watershed a good relationship between log K_{ow} and percentage of pesticide in suspended matter was observed during storm of June and January. Since, storm of January is an exceptional event in term of discharge; therefore we focus our attention upon the results of June event in 2008. In Auradé catchment, two storm events illustrate a significative relationship between log K_{ow} and percentage in suspended matters. But storm of April (1) in 2009 was in centre of our attention, since we had more sampling points during this event and therefore more reliable estimations.

Table XVI- Relationship between percentage of particulate fractions (%PF) and the K_{ow} values during the each storms period in Save and Auradé catchments.

Catchments and storm periods	**Equation** (y = % PF X = K_{ow})	r^2	**P-value**
Save			
April	y = 14.315x - 6.408	$r^2 = 0.150$	> 0.05
* June	y = 20.361x - 21.24	$r^2 = 0.538$	< 0.01
December	$y = 6.287e^{0.4698x}$	$r^2 = 0.216$	> 0.05
January	y = 12.125x + 25.561	$r^2 = 0.426$	< 0.05
Auradé			
April	$y = 15.971e^{0.2771x}$	$r_s^2 = 0.637$	< 0.05
May	$y = 4.494e^{0.590x}$	$r^2 = 0.384$	>0.05
* April (1)	y = 9.185x + 3.406	$r^2 = 0.421$	< 0.05
April(2)	y = 9.623x - 6.156	$r^2 = 0.293$	> 0.05

* Storm selected for detail study (see figures 75 and 76).

The results of June (2008) storm show a significant relationship between % PF (particulate fractions) and log K_{ow} in Save catchment. For this event, we can distinguish the contribution of molecules in three categories, (figure 76):

- first, for the molecules with the highest value of log K_{ow} (aclonifen and trifluralin), the percentage of particulate fraction increases up to 85% (87% for aclonifen and 94% for trifluralin).
- second, for some of the molecules with log K_{ow} between (3.4-4) such as, teboconazole, fluzilazole, fenpropimorph and epoxiconazole, the contribution of particulate fraction remains between 50 to 60 %.
- third, for molecules with lower log K_{ow} (2.5-3.1) such as, chlortoloron, linuron, isoproturon, atrazine, alachlor, and cyproconazole, the % of particulate fractions range between 20 and 45 %.

Finally, for metolacholor which has also middle log K_{ow} value the contribution of particulate fraction is less than 10%. This result might be due to the high solubility of metolachlor (S_w= 488 mg.L^{-1}). However, DEA with the low value of K_{ow} (K_{ow} = 1.3) represent almost 40% of exportation in particulate phase, might be due to the low value of solubility for this molecule (S_w = 2.7 mg.L^{-1}).

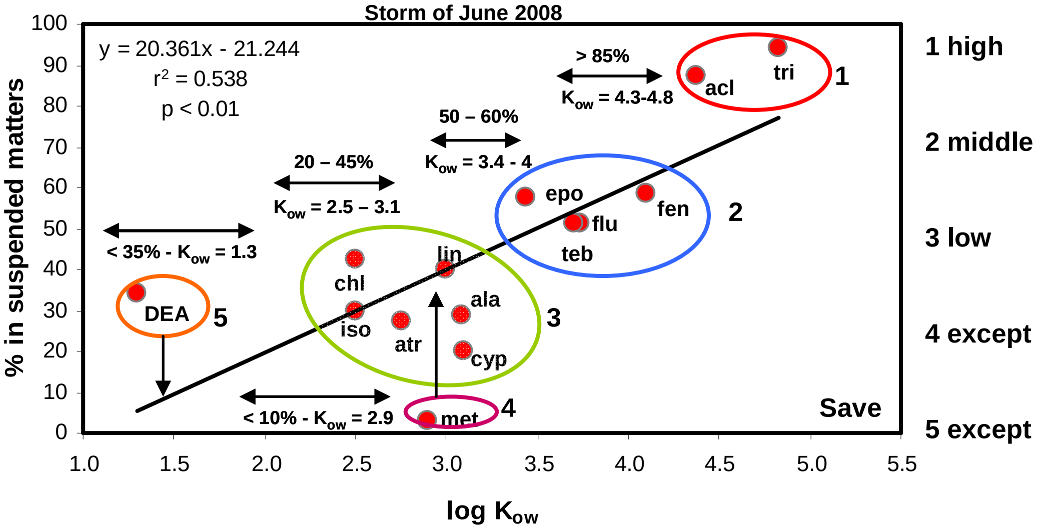


Figure 76- Relationship between % particulate fraction (PF) and log K_{ow} in Save catchment during storm of June 2008.

The storm of April (1) 2009 in Auradé catchment shows a positive relationship between the percentage of particulate suspended matters and the log K_{ow} values. The alterations of concentration in suspended matter vary between 10 to 55 %. However, except DEA, 3 groups can be distinguished, (figure 77):

- first group (trifluralin, aclonifen and tebuconazole) with high log K_{ow}, high-middle % PF (45- 55%)

- second group (epoxoconazole, cyproconazole, fluzilazole, linuron, alachlor and metolachlor) with medium log K_{ow} and middle – low % PF (20-40%)
- thired group (atrazine, isoproturon and chlorotoluron) with low log K_{ow} values and low % PF (up to 20%).

In the case of DEA, the contribution of particulate fractions remains between 30-40% in Auradé catchment as we observed earlier in Save river.

In general, our results indicate the percentage value of each molecule in suspended matter compare to the total molecules, in unfiltered water, alters according to various types of the molecule. In molecules with a high value of K_{ow} a high percentage of particulate fractions have been observed. Moreover, with these findings we can confirm that mobile sediment can serve as a vector for transport of adsorbed contamination, such as hydrophobic organic compounds, that is in line with other literatures (Allan, 1979; Mahler et al., 1999; Sharpe et al., 2004).

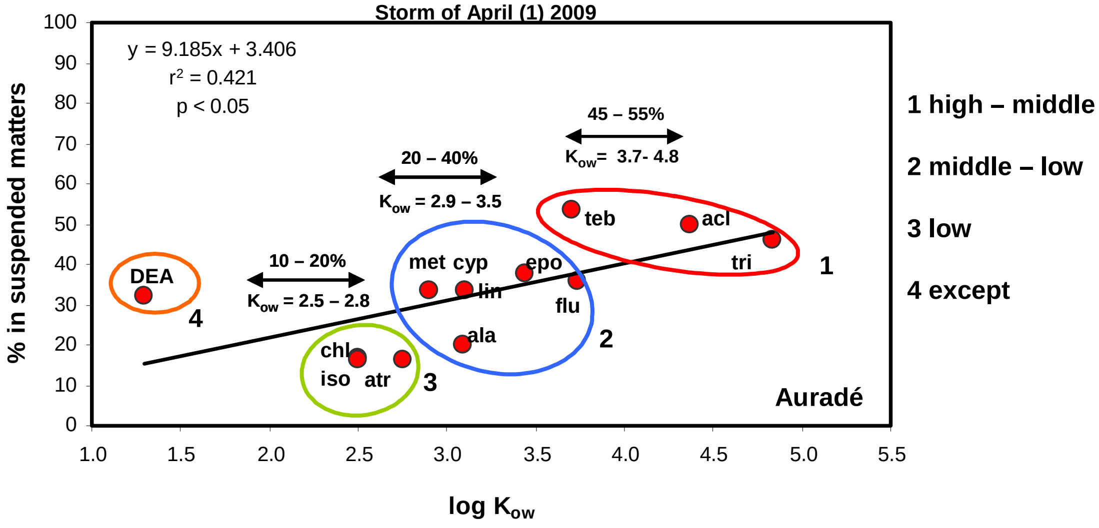


Figure 77- Depicted the relationship between log K_{ow} and log K_d in Save watershed during storm of April (1) in 2009.

6 Relationships between K_d and TSM during storm periods

In aquatic systems, pesticide can exist under a variety of forms, for example as a freely dissolved substance in the water phase or associated with the particulate material. In terms of fate and interactions of pesticides in aquatic environments, thus following up the distribution of pesticides between these various phases is a central issue. In order to better understand and to predict this partitioning between solute and particulate fractions, it is crucial to consider the role of the controlling parameters such as total suspended matter (TSM), dissolved organic carbon (DOC), in the repartition of pesticide molecules into particulate and dissolved phases.

Fluvial sediments are complexe mixture of inorganic compounds (clay minerals, carbonate, manganese and iron oxides…) and organic matters that have a large capacity to adsorbed organic pollutant like pesticides. Dissolved organic carbon (DOC) has an effect on the distribution of pesticides between dissolved and particulate phases. DOC could enhance the solubility of pesticides and by doing so reducing the concentration onto the solid phase as shown for the Montoussé catchment during the flood event of March 2006 (Taghavi et al., 2010). Existence of DOC makes a compound to appear more soluble in water and reduces the total particulate amount (Chiou et al., 1984; Carter and Suffet, 1985; Gschwend and Wu, 1985; Gao et al., 1998). Both of these type of parameters offer sites which may be favorable to the association of pesticides with such a controlling factor.

The adsorption/desorption of pesticides depend also on the pH (Roy and Krapac, 1994; Gao et al. 1998). However, in this study, pH and conductivity seem to have no influence on the K_d values, probably because pH and conductivity remain high and relatively low variable in such a carbonate environment (pH= 8.2 ± 0.2 and 8.2 ± 0.17 and conductivity= 482 ± 190 and 752 ± 158 ($\mu s.cm^{-1}$) respectively, for Save and Auradé catchments).

In the case of DOC, no good relationship between DOC concentration and K_d values could be determined, except for storm of March 2006 in the Montoussé catchment (Taghavi et al., 2010). However, a good relationship was revealed for aclonifen between average TSM concentration of the average partition coefficient (K_d) calculated on the basis of the flux values for each whole storm event on both sites, Auradé and Save catchments (figure 78). For a given concentration of TSM, the latter interaction showed a higher aclonifen K_d value for Auradé than for Save catchment since the storm events in Auradé catchment are flashy, and last a short time (3 days on average, but some hours for the rising water period), the molecules of pesticides are exported rapidly by the runoff and there is not enough time to have an equilibrium between dissolved and particulate phases.

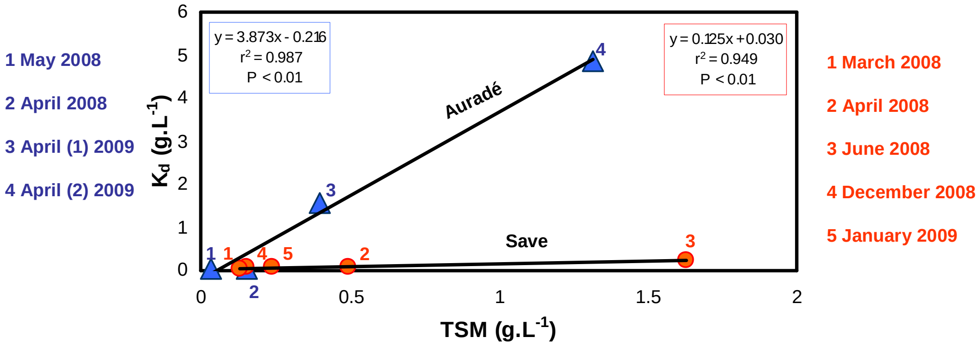


Figure 78- Relationship between total suspended matter (TSM) and partition coefficient (K_d) in Save and Auradé catchments for aclonifen during investigated storms in 2008-2009.

For the Save catchment, a good relationship could be obtained for some pesticides between the partition coefficient (K_d) and the concentration of TSM, both calculated on the basis of the flux values during the whole stormflow period. Table XVII shows the significant relationships obtained for the studied molecules of pesticides.

Table XVII- Equations of the relationships between the TSM concentration (X in g.L^{-1}) in (g) and the partition coefficient K_d (Y in g.L^{-1}) for 6 molecules of pesticides.

Pesticides	Equations (Y= aX+b)		r^2 and p-value
	Y= K_d	X= TSM	
DEA	Y= **1.86**+0.112		0.960 - < 0.01
isoproturon	Y= **2.52**x-0.334		0.976 - < 0.01
chlorotuluron	Y= **1.37**x+0.067		0.940 - < 0.01
linuron	Y= **1.42**x-0.021		0.756 - < 0.05
tebuconazole	Y= **1.024**x-0.180		0.912 - < 0.05
aclonifen	Y= **0.125**x+0.030		0.945 - < 0.01

The slope (a) of the relationship between K_d and TSM represents the ratio of the concentration of the pesticide between dissolved and particulate fractions ($C_{filtered}$/ ($C_{nonfiltered}$ – $C_{filtered}$)). A good relationship between this slope and K_{ow} (pararameter of lipophily) extracted from the literature can be determined for 6 molecules in figure 79. This relationship confirms the role of the particulate fraction in the transportation of low soluble molecules with high value of K_{ow}. So an increase in the K_{ow} values will correspond to an increase of the concentration of the molecule in particulate phases leading to a decrease of the K_d, ratio between dissolved and particulate concentration of each pesticide.

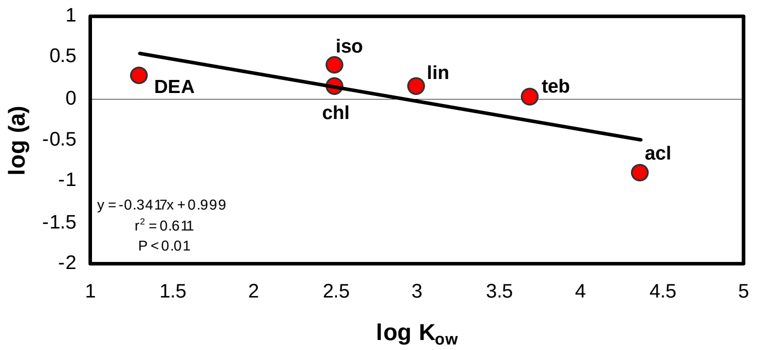


Figure 79- Relationship between the slope a of the relationship K_d = aTSM + b and K_{ow} value for six molecules in the Save catchment during the storm events.

Based on instantaneous samples during storm periods, it can be observed for two molecules of pesticide (aclonifen and chlorotuluron) a good relationship between K_d value calculated for each sampling and TSM concentrations (figure 80). Nevertheless, in the case of aclonifen, two samples are out of the cluster of points and correspond to storm events, that is to say the peak-flow of April 2008 and first peak of June 2008.

As seen in figure 80, the magnitude of K_d value for aclonifen and chlorotuluron is significantly different. The higher values of K_d for chlorotoluron could be explained by the higher solubility of this molecule (see table V). Therefore, we have more concentration of chlorotoluron in dissolved phase than in particulate one.

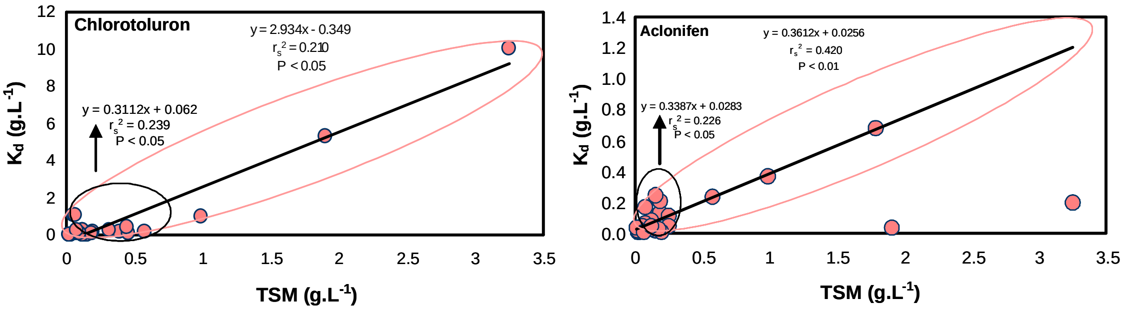


Figure 80- Relationships the K_d value of chlorotoluron (left) or aclonifen (right) and TSM concentration for instantaneous samples collected during the storm periods in the Save catchment.

Different magnitudes of K_d value were also observed by Cooke et al. (2004) in the case of isoproturon and trifluralin, which have relatively similar characteristic with the molecules which have been investigated in our study.

6.1 Relationships between K_d and water discharge (Q_T) during storm of April 2008 in Save catchment.

The interaction between K_d and river water discharge indicates different distribution of molecule in dissolved and particulate phases. For the reasons that we said earlier we focus our attention on the storms of April 2008 for the Save and May 2008 for Auradé catchments. Clockwise hysteresis observed in the case of tebuconazole during storm of April 2008 in Save catchment (figure 81). This result shows that in rising limb of this storm, tebuconazole transport rapidly by surface runoff in dissolved phase since we have higher K_d value. Then after as time goes in falling limb the contribution of particulate phase increase and tebuconazole have enough time to interact with particulate fractions and consequently K_d values decrease.

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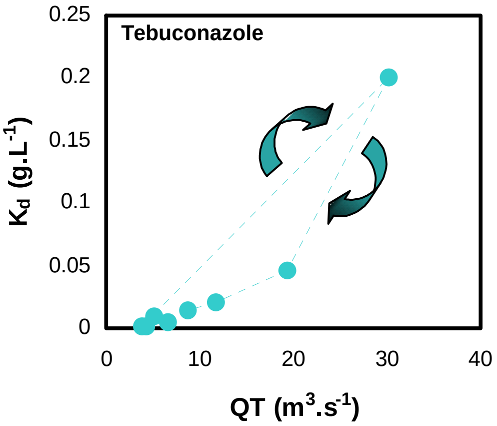

Figure 81- Relationship between tebuconazole K_d (g.L^{-1}) and river discharge (m^3.s^{-1}) during storm of April 2008 in the Save catchment, showing a clockwise hysteresis pattern.

However in the case of Auradé catchment, no hysteresis between K_d values and river discharge could be observed, mainly because of the flushy flood flow in this small catchment which is a limiting factor for the interaction of pesticide molecules between dissolved and particulate fractions.

Summary

The dataset presented in this chapter provides a detailed account of the trends of 14 molecules of the pesticide and also DOC and TSM in surface water during storm and base flow.

Over 60% flux of pesticide is attributed to storm waters and total loads of DOC and TSM reach more than 70% during storm events.

The relationship between the flux of pesticide and volume of water depicted is positively correlated for some of the pesticides in both catchments.

This chapter has also served to underline the differences between fluxes of each pesticide in two nested watersheds of different size. It could be shown that the specific flux of pesticides is more important in the case of Save river and this could be due to the more consumption of pesticides in this agricultural catchment.

The pesticide distribution (K_d) between dissolved and particulate phases could be related to the value of K_{ow} extracted from literature. This result is relatively important and could be used latter in modeling approaches. Our findings indicate clearly the role of TSM in partitioning of pesticides into particulate and dissolved fractions. The different magnitudes of K_d values depend on the characteristics of pesticides such as their solubility, in accordance with the study conducted by Cooke et al. (2004).

The result of hysteresis pattern between K_d and river water discharge during storm of April 2008 in Save catchment highlighted the different distribution of pesticides into dissolved and particulate fractions during rising and falling periods of stormflow, showing higher value of K_d in rising limb. This pattern explains that during rising limb the pesticides wash rapidly in dissolved fraction and runoff may facilitate pesticide's transport, and then as the time goes it can be adsorbed onto particulate fractions.

General Conclusion

General Conclusion

There can be no doubt about pesticides displacement from agricultural lands into stream waters. Experimental and observational approaches carried out in this study consist in monitoring of pesticide concentration and the mechanisms of pesticide transport from agricultural soils into river in a short span of time at two different size nested catchments: Montoussé catchment at Auradé (3.28 Km^2) and Save catchment at Larra (1110 Km^2).

Spatial and temporal variations were conducted in Auradé catchment, whereas in Save catchment only temporal variations in pesticide concentration was surveyed. In a two-year sampling campaign carried out in Auradé catchment, no spatial variation in pesticide concentration was registered. And this could be explained by the nature of the crops (wheat and sunflower in rotation) since this practice has not been changed for the last few decades.

Temporal intensive measurements during two years in Auradé and one year in Save catchment have shown that the water flow in Save and Auradé catchments are strongly influenced by raining period and the highest concentration corresponds to pesticide application periods. The temporal variations of pesticide show that:

- during low flow periods, in general, the concentration of pesticide remains below the threshold levels of drinking water consumption (0.1µg.L^{-1}).
- subsequent to precipitation, the concentration of some pesticides indicate during strom flow periods, concentration values higher than 0.1 µg.L^{-1} and even higher than 1 µg.L^{-1}.

Our findings revealed the role of stormwater in transporting of the parameters like TSM and DOC which are controlling pesticide transport leading to fluctuation of concentration level. However, in the absence of stormy periods, the level of concentration of the controlling factors (TSM- DOC) remained nearly invariable. pH and EC didn't show any significant variation during the whole observation period.

To have a good and clear understanding about the mechanism of pesticides transport during stormwater, storm hydrograph separation and hysteresis patterns have been dealt with a particular attention. To reach these objectives, a special emphasis was put on one storm event in Save catchment (April 2008), and another one in Auradé catchment (May 2008). The reason of selecting these two storm events is due to coincidence of these periods with application period and moreover, our sampling points are nearly covered all the storm phases (rising and falling limbs).

A closer look at the data obtained during our investigation indicates:

- low soluble molecules of pesticide have shown a good relationship with the total suspended matters (TSM) and particulate organic carbon (POC).
- there is a good relationship between dissolved organic carbon (DOC) and particulate fractions (TSM and POC) and moderately soluble pesticide molecules. And, the distribution of pesticide molecules between dissolved and particulate fractions depends on relative abundance of these parameters in aquatic systems.
- soluble molecules have shown a significant interaction with dissolved organic carbon (DOC).

Particulate transport of pesticide depends, to a great extent, on the affinity of pesticides to suspended particles that are closely related to the hydrophobicity of the pesticide and the contents of organic matter in the suspended material. In addition, dissolved transport of pesticide depends on the characteristics of molecules, on the one hand, and also on the amount of Dissolved Organic Carbon which is regarded as the main sorbent for hydrophilic pesticides.

The results of hysteresis pattern with regard to relationship between pesticide concentration and river discharge indicate:

- clockwise hysteresis, with more contribution of surface water for low to moderately low soluble molecules, shows higher concentration of elements (such as low soluble molecules of pesticides and particulate fractions) in rising limb of hydrograph.
- anticlockwise hysteresis, with higher concentration of soluble pesticides and dissolved organic fraction in falling limb of hydrograph.

The hysteresis patterns are characterizing the general nature and complex behaviour of pesticides and their controlling factors in particulate and dissolved fractions with water discharge for the different hydrological stages of the hydrograph. The contribution of storm flow components have been studied by storm hydrograph separation using the principle of an exponential method estabilished by (Maillet, 1905; Barnes, 1039) that enable us to highlight:

- the role of surface runoff discharge in transporting of low to moderately low soluble molecules and particulate fractions, particularly during the rising period.
- the displacement of dissolved organic carbon and soluble pesticide molecules by subsurface runoff discharge during the falling period (recession period).

Overall, our findings also demonstrated that both surface and subsurface runoffs are the effective mechanisms of pesticides and their controlling factors transport during storm events.

Reviewing the experimental results of Save and Auradé catchments clearly illustrate the predominant role of the controlling factors in pesticides concentration. In Auradé catchment, for example, during storm of May 2008, aclonifen and linuron show an anticlockwise hysteresis with more contribution of subsurface water than surface runoff, particularly during the falling period. A similar pattern was registered for total suspended matter (TSM), Particulate Organic Carbon (POC) and Dissolved Organic Carbon (DOC) during this period. This observation illustrates that interaction between pesticides and their controlling factors could play a more important role in pesticides transport than the contribution of river discharge during storm of May 2008 in small catchments such as Auradé due to its flashy hydrograph with a rapid rising limb and more contribution of subsurface runoff in transporting of pesticides and their controlling factors.

However, in Save catchment, our findings present, on the one hand the role of superficial flows and controlling factors in pesticides transport and on the other hand the role of each streamflow component was highlighted. As an example during storm of April (2008) , our results revealed the role of proportion of surface runoff in transporting of pesticides and particulate parameters such as TSM and POC. Subsurface flow appears to be responsible for displacement of soluble molecules and dissolved parameters such as DOC. In addition, TSM and POC show good relationships with aclonifen and linuron as low and moderately soluble molecule respectively. Whereas, DOC has a significant relationship with metolachlor as a soluble molecule

The results of flux values highlight:

- the important role of storm events in transporting of pesticides with the contribution of more than 60% according to molecules, to the total annual river fluxes.
- more than 70% for DOC and 90% of TSM are transported during these events.

The comparison between fluxes of pesticides in Auradé and Save catchments by calculating specific flux indicate higher values for large catchments like Save. The later results indicate an average concentration of pesticides in Save catchment in comparison to Auradé for a given amount of river discharge. The only explanation for the higher specific fluxes of pesticides with high concentration in Save catchment could be found in the larger amount of pesticides consumption in this period of observation for Save catchment.

The distribution of pesticides between dissolved and particulate fractions (K_d) shows that:

- it depends on pesticide's properties, particularly their solubility and their octanol-water partitioning coefficient (K_{ow}).
- there is a good negative relationship between log K_d and log K_{ow} , showing that when K_{ow} increases, the contribution of particulate phases will increase too, and pesticides molecules have more affinity to be adsorbed onto suspended matters.
- it can also be observed significant relationships between the percentage of pesticides in particulate fractions and log K_{ow}. This model enables us to estimate the proportion of pesticides in particulate fractions in the Save and alike catchments with similar physico-chemical characteristics.
- good linear relationships between pesticide partition coefficient (K_d) and TSM, both calculated from flux values for each whole storm event, show higher K_d values for Auradé catchment which means more contribution of dissolved fraction in transporting of pesticides as a result of short duration and flashy storm event in this catchment. The slopes of these relationships appear to be proportional to K_{ow} values for each pesticide molecule.
- K_d value calculated for each instantaneous sample collected during storm events in the Save catchment is well correlated to TSM, particularly for aclonifen and chlorotoluron.
- clockwise hysteresis patterns between K_d calculated for each instantaneous sample and river discharge can be clearly observed during storm event, particularly in the case of tebuconazole. This result exhibits different contributions of dissolved and particulate fractions during rising and falling stages of the storm hydrograph phases. At the time of rising limb of the storm, tebuconazole is transported rapidly by surface runoff in dissolved phase since we have a higher K_d value. Then as time goes by in falling limb, the contribution of particulate phase increases and tebuconazole has enough time to interact with particulate fractions and consequently K_d values decrease.

Conclusion générale

Il n'y a aujourd'hui aucun doute en ce qui concerne le transfert des pesticides des zones agricoles vers les cours d'eau. Les observations et les approches expérimentales développées dans cette étude ont porté sur le monitoring des concentrations en pesticides et sur l'étude des mécanismes qui contrôlent le transport des pesticides des sols agricoles vers les rivières dans un laps de temps très court sur deux bassins versants emboités de taille différente : le Montoussé à Auradé (3.28 Km^2) et la Save à Larra (1110 Km^2).

Les variations spatiales et temporelles des concentrations ont été étudiées sur le bassin d'Auradé alors que sur la Save, seules les variations temporelles ont été appréhendées. Sur le bassin d'Auradé au cours des deux années d'échantillonnage, les concentrations en pesticides varient peu dans l'espace d'une station à l'autre. Ce résultat peut être expliqué par les pratiques culturales (blé/tournesol en rotation) qui n'ont pas changé au cours des dernières décennies.

Les mesures intensives que nous avons réalisées pendant deux ans sur le petit bassin expérimental d'Auradé et pendant une année sur le bassin versant de la Save montrent que les écoulements fluviaux sont directement contrôlés par les pluies, notamment en périodes de crue, et les concentrations en pesticides les plus élevées correspondent aux périodes de crues et aux périodes de traitements phytosanitaires. Les variations temporaires des concentrations en pesticides montrent que :

- durant les périodes de basses eaux, les concentrations en pesticides restent généralement en dessous des limites autorisées pour la consommation d'eau potable ($0.1 \mu g.L^{-1}$)
- à la suite de précipitations intenses et durant les périodes de crue, les concentrations de certains pesticides augmentent et montrent des valeurs supérieures à $0.1 \mu g.L^{-1}$, parfois même supérieures à $1 \mu g.L^{-1}$.

Notre étude met bien en évidence le rôle des épisodes de crues dans le transport des matières en suspension (MES) et du carbone organique dissous (COD), paramètres qui contrôlent le transport des pesticides et conduisent à des variations de concentrations. Cependant, en dehors des périodes de crue, le niveau de concentration de ces paramètres (MES et COD) reste pratiquement invariable. Le pH et la conductivité ne présentent aucune variation significative durant toute la période d'observation.

Pour mieux comprendre les mécanismes de transport des pesticides pendant les crues, la séparation des composantes de l'écoulement fluvial sur les hydrogrammes de crue et les modèles d'hystérésis sur les relations concentration-débit ont été traités avec une attention particulière dans cette étude. Pour atteindre ces objectifs, nous nous sommes focalisés sur des épisodes de crues caractéristiques de chaque bassin versant : crue d'avril 2008 sur le bassin de la Save et crue de mai 2008 sur le bassin d'Auradé. Ces deux crues ont été sélectionnées aussi parce qu'elles correspondaient à des périodes de traitement phytosanitaire et parce que les échantillonnages réalisés étaient complets, intégrant aussi bien la montée et le pic de crue que la descente de crue.

Une analyse détaillée des données obtenues au cours de nos investigations montrent que:

- les concentrations en pesticides peu solubles présentent de bonnes relations avec les teneurs en MES et les concentrations en carbone organique particulaire (COP),
- les teneurs en pesticides moyennement solubles sont très bien corrélées aux teneurs en COD, COP et MES et la distribution de ces pesticides entre les phases dissoutes et particulaires dépend de l'abondance relative de ces paramètres dans les systèmes aquatiques,
- les molécules les plus solubles montrent de fortes interactions avec le COD.

Le transport en suspension des pesticides dépend en grande partie de leur affinité pour les particules, affinité qui est étroitement reliée à leur hydrophobicité et aux teneurs en matières organiques dans les matières en suspension. En revanche, le transport en solution des pesticides est étroitement associé aux caractéristiques des molécules et aux teneurs en COD qui est l'un des principaux agents sorbents.

Les hystérésis que nous avons pu mettre en évidence sur les relations entre les concentrations en pesticides et les débits des cours d'eau présentent deux modèles:

- des hystérésis dextres (sens des aiguilles d'une montre) pour les molécules peu ou moyennement solubles et les fractions particulaires, montrant des concentrations en pesticides, MES et COP plus élevées durant la montée de crue
- des hytérésis senestres (sens inverse des aiguilles d'une montre) pour les pesticides les plus solubles et le COD, montrant des concentrations plus élevées en descente de crue.

Ces modèles d'hystérésis permettent de caractériser la nature et le devenir complexe des pesticides et de leurs facteurs de contrôle dans les fractions particulaires et dissoutes en fonction des variations de débits au cours des différents phases hydrologiques d'une crue. Ainsi la séparation des composantes de l'écoulement fluvial que nous avons pu réaliser par découpage des hydrogrammes de crue en suivant le principe d'une décroissance exponentielle des débits en période de récession (Maillet, 1905 ; Barnes, 1939) , nous a permis de mettre en évidence:

- le rôle du ruissellement superficiel dans le transport des fractions particulaires et des pesticides peu ou moyennement solubles, en particulier durant la montée de crue
- la mobilisation du COD et des pesticides les plus solubles par le ruissellement hypodermique durant la descente de crue (période de récession)

Plus généralement, nos résultats démontrent bien que les écoulements de surface (ruissellement superficiel et écoulement hypodermique) sont les principaux écoulements responsables du transfert des pesticides et de leurs facteurs de contrôle (MES, COP et COD) des sols vers les eaux de surface durant les épisodes de crue.

Les résultats obtenus aussi bien sur le bassin d'Auradé que sur celui de la Save illustrent clairement le rôle prédominant des facteurs de contrôle sur les teneurs en pesticides dans les cours d'eau. Sur le bassin d'Auradé, au cours de la crue de mai 2008 par exemple, l'aclonifène et le linuron présentent un hystérésis senestre avec une contribution de l'écoulement hypodermique plus forte que celle du ruissellement superficiel, notamment en descente de crue. Une évolution similaire a pu être observée pour les MES, le COP et le COD au cours de cette crue. Ces résultats montrent que sur un petit basin versant comme celui d'Auradé, les interactions entre les pesticides et leurs facteurs de contrôle (MES, COP et COD) jouent un rôle plus important dans le transport des pesticides que la contribution des débits du ruisseaux.

Cependant dans le bassin versant de la Save, nos résultats montrent d'une part le rôle des écoulements de surface et des facteurs de contrôle sur le transport des pesticides et d'autre part, le rôle de chaque composante de l'écoulement fluvial. Par exemple lors de la crue d'avril 2008, les résultats mettent en évidence le rôle de la contribution du ruissellement superficiel sur le transfert des pesticides et des phases particulaires comme les MES et le COP. L'écoulement hypodermique apparait comme responsable du transfert des pesticides solubles et des paramètres dissous comme le COD. De plus, les MES et COP montrent de bonnes relations avec les concentrations en aclonifène et linuron, pesticides respectivement peu et modérément solubles. En revanche le COD présente une relation significative avec le métolachlore, molécule très soluble.

En ce qui concerne les flux, les principaux résultats que nous avons obtenus montrent :

- aussi et confirment le rôle important des épisodes de crue dans l'exportation des pesticides avec une contribution de plus de 60% au flux total annuel évacué par la rivière suivant les molécules

- que plus de 70% du flux de COD et près de 90% du flux de MES sont exportés par la rivière durant ces périodes de crue
- que les flux spécifiques (flux par unité de surface) de pesticides exportés sur le bassin d'Auradé sont plus faibles pour un même débit spécifique que ceux évacués sur le bassin de la Save, montrant ainsi que les concentrations moyennes en pesticides sont en général plus élevées sur le bassin de la Save que sur celui d'Auradé, dues à des traitements phytosanitaires plus importants sur le bassin de la Save que sur le bassin expérimental d'Auradé où les agriculteurs pratiquent des traitements raisonnés en fonction de l'état des cultures et des conditions climatiques.

La distribution des pesticides entre les phases dissoutes et particulaires (K_d) montre que :

- ce fractionnement dépend des propriétés physico-chimiques des pesticides, en particulier leur solubilité et leur coefficient de partage octanol-eau (K_{ow}).
- il y a une bonne relation négative entre log K_d et log K_{ow} montrant que quand K_{ow} augmente la contribution des phases particulaires augmentent aussi et les pesticides voient leur adsorption sur les matières en suspension augmenter.
- l'on peut observer aussi une relation significative entre le pourcentage de pesticides dans les fractions particulaires et le log K_{ow} des différents pesticides, extrait de la littérature. Ce modèle nous permet d'estimer sur un bassin versant comme celui de la Save ou sur un bassin ayant les mêmes caractéristiques physico-chimiques, la proportion de pesticides dans les matières en suspension.
- L'on obtient de bonnes relations linéaires entre le coefficient de partage (K_d) des pesticides et la charge en MES. Tous les deux sont calculés à partir des valeurs de flux pour chaque épisode de crue. On note ainsi des valeurs de K_d plus élevées pour le bassin d'Auradé. Ce résultat peut être attribué à une contribution plus importante des phases dissoutes dans le transport des pesticides au cours de crues « éclair » sur ce petit bassin.
- les valeurs de K_d calculées pour chaque échantillon collecté en périodes de crue sur la Save sont bien corrélées à la charge en suspension (MES), en particulier pour l'aclonifène et le chlorotoluron.
- des hystérésis dextres entre K_d calculées pour chaque échantillon et le débit du cours d'eau peuvent être clairement observées pendant les crues, en particulier pour le tébuconazole. Ce résultat met en évidence des contributions différentes des fractions dissoutes et particulaires durant la montée et la descente de crue. En période de montée de crue, le tébuconazole est transporté rapidement par le

ruissellement superficiel dans les phases dissoutes car on peut observer une plus forte valeur de K_d. Puis en descente de crue, la contribution des phases particulaires augmente, le tébuconazole peut alors interagir avec les particules et les valeurs de K_d diminuent.

Perspective

Pesticides retained in surface soils can be transported laterally with surface runoff or vertically with drainage water and reach surface water and groundwater. In runoff water, both the dissolved and particle bound pesticides are considered as mobile fractions, however, they may have different transport pathway. Understanding the distribution of pesticides between dissolved and particulate fractions is important in assessing their fate and transport within the aquatic ecosystem.

Current interest is focused on understanding the routes of entry of pesticide with different characteristics into surface water especially during storm events when we have different contribution of streamflow components.

To confirm and elaborate our findings we could suggest the following ways in order to develop further our investigations:

- Use of others methods for separating hydrograph of storm events such as chemical tracers and isotopic methods (Ladouche et al 2001; Tardy et al. 2004), since pesticide transport was rarely analyzed from this point of view. All of these methods are aimed at understanding and preventing contamination in the future.

- Pesticide partition between the dissolved and particulate fractions could be measured in the standard laboratory batch in order to compare with the value obtained during our study and to determine the distribution of pesticides between dissolved and particulate fractions in experimental condition.

- Dissolved and particulate organic carbons as well as total suspended matters are the most abundant materials in hydrosystems. Therefore they play an important role in complexation and adsorption reactions and determining the behaviour of pesticides and other organic chemicals in the environment. Understanding the composition and quantity of these elements are crucial factors that worth considering to predict the distribution of pesticides into the different phases.

- To be sure that the pesticide is detected, continuous sampling systems are preferred but due to high sampling costs, alternative sampling systems such as passive devices (POCIS or SPMD) can be used in combination with models.

- Within a broader context, results from this research are critical in modelling the dynamic and distribution of pesticides in dissolved and particulate fractions in small and large agricultural catchments.

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Annexe

Annexe I- Different stream flows discharge during storm events in Save river.

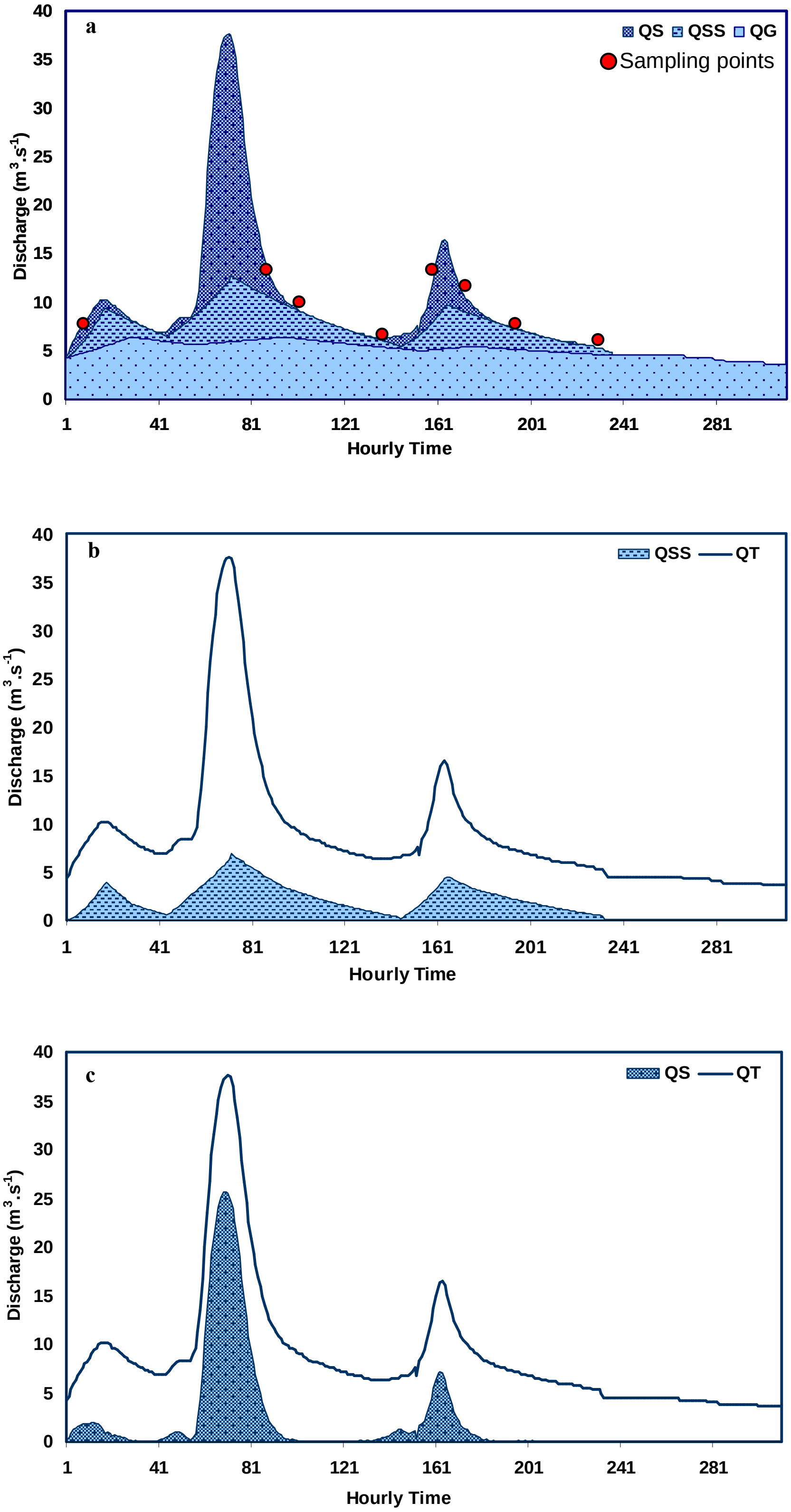
Sampling (stormwater)		Q_T	Q_S		Q_{SS}		Q_G		Q_S+Q_{SS}	
		$m^3.s^{-1}$	$m^3.s^{-1}$	%	$m^3.s^{-1}$	%	$m^3.s^{-1}$	%	$m^3.s^{-1}$	%
March 2008	*1*	**8.18**	**1.46**	**17.9**	**1.84**	**22.5**	**4.87**	**59.5**	**3.3**	**40.3**
	2	**11.2**	**1.09**	**9.7**	**3.83**	**34.2**	**6.28**	**56.1**	**4.92**	**43.9**
	3	**7.97**	**0**	**0**	**2.03**	**25.4**	**5.95**	**74.6**	**2.03**	**25.5**
	4	**6.34**	**0.05**	**0.8**	**0.84**	**13.3**	**5.45**	**85.9**	**0.89**	**14.0**
	5	**12.4**	**4.12**	**33.3**	**3.19**	**25.8**	**5.08**	**41**	**7.31**	**59.0**
	6	**8.99**	**0.53**	**5.9**	**3.09**	**34.4**	**5.36**	**59.7**	**3.62**	**40.3**
	7	**6.54**	**0.07**	**1**	**1.54**	**23.6**	**4.93**	**75.4**	**1.61**	**24.6**
	8	**5.52**	**0.3**	**5.5**	**0.6**	**10.9**	**4.61**	**83.6**	**0.9**	**16.3**
April 2008	*1*	**4.9**	**0.52**	**10.6**	**1.45**	**29.5**	**2.93**	**59.7**	**1.97**	**40.2**
	2	**7.77**	**1.36**	**17.5**	**2.96**	**38.1**	**3.45**	**44.4**	**4.32**	**55.6**
	3	**4.28**	**0.17**	**3.9**	**0.41**	**9.7**	**3.7**	**86.4**	**0.58**	**13.6**
	4	**3.83**	**0**	**0**	**0.71**	**18.6**	**3.12**	**81.5**	**0.71**	**18.5**
	5	**30.2**	**19.56**	**64.8**	**5.98**	**19.8**	**4.66**	**15.4**	**25.54**	**84.6**
	6	**19.44**	**8.32**	**42.8**	**6.22**	**32**	**4.89**	**25.2**	**14.54**	**74.8**
	7	**11.6**	**1.72**	**14.8**	**4.76**	**41**	**5.13**	**44.2**	**6.48**	**55.9**
	8	**8.78**	**0.12**	**1.4**	**3.67**	**41.8**	**4.99**	**56.8**	**3.79**	**43.2**
	9	**6.54**	**0**	**0**	**1.9**	**29**	**4.65**	**71**	**1.9**	**29.1**
	10	**4.49**	**0.13**	**2.9**	**0.29**	**6.4**	**4.07**	**90.6**	**0.42**	**9.4**
	11	**5.1**	**0**	**0**	**1.4**	**27.4**	**3.71**	**72.7**	**1.4**	**27.5**
June 2008	*1*	**1.75**	**0**	**0**	**0.34**	**19.6**	**1.41**	**80.4**	**0.34**	**19.4**
	2	**3.38**	**0.35**	**10.4**	**1.14**	**33.6**	**1.9**	**56**	**1.49**	**44.1**
	3	**10.4**	**3.73**	**35.8**	**4.07**	**39.1**	**2.6**	**25**	**7.8**	**75.0**
	4	**24.44**	**14.05**	**57.5**	**6.52**	**26.7**	**3.87**	**15.8**	**20.57**	**84.2**
	5	**4.69**	**0.41**	**8.8**	**0.4**	**8.5**	**3.88**	**82.7**	**0.81**	**17.3**
	6	**42.59**	**31.44**	**73.8**	**7**	**16.4**	**4.15**	**9.8**	**38.44**	**90.3**
	7	**24.28**	**13.9**	**57.3**	**6.07**	**25**	**4.32**	**17.8**	**19.97**	**82.2**
	8	**12.4**	**3.64**	**29.3**	**4.44**	**35.8**	**4.32**	**34.9**	**8.08**	**65.2**
	9	**7.77**	**0.08**	**1.1**	**3.5**	**45.1**	**4.18**	**53.9**	**3.58**	**46.1**
	10	**6.95**	**0**	**0**	**2.86**	**41.1**	**4.08**	**58.7**	**2.86**	**41.2**
	11	**6.13**	**0**	**0**	**2.3**	**37.5**	**3.83**	**62.5**	**2.3**	**37.5**
December 2008	*1*	**6.13**	**0**	**0**	**0**	**0**	**6.13**	**100**	**0**	**0.0**
	2	**10**	**0.25**	**2.5**	**2.12**	**21.2**	**7.63**	**76.3**	**2.37**	**23.7**
	3	**26.58**	**13.28**	**50**	**5.97**	**22.5**	**7.33**	**27.6**	**19.25**	**72.4**
	4	**16.63**	**2.69**	**16.2**	**6.3**	**37.9**	**7.64**	**46**	**8.99**	**54.1**
	5	**13.54**	**1.61**	**11.9**	**4.21**	**31.1**	**7.72**	**57**	**5.82**	**43.0**
	6	**10.2**	**0**	**0**	**2.77**	**27.1**	**7.51**	**73.6**	**2.77**	**27.2**
	7	**9.59**	**0**	**0**	**2.29**	**23.8**	**7.3**	**76.1**	**2.29**	**23.9**
January 2009	*1*	**9.59**	**0**	**0**	**5.04**	**52.6**	**4.55**	**47.4**	**5.04**	**52.6**
	2	**46.55**	**30.6**	**65.7**	**8.3**	**17.8**	**7.7**	**16.5**	**38.89**	**83.5**
	3	**12.4**	**0**	**0.0**	**2.3**	**18.5**	**10.1**	**81.4**	**2.3**	**18.5**
	4	**23.8**	**12.49**	**52.5**	**2.4**	**9.9**	**9.0**	**37.6**	**14.85**	**62.4**

Annexe II- Different stream flows discharge during storm events in Auradé catchment.

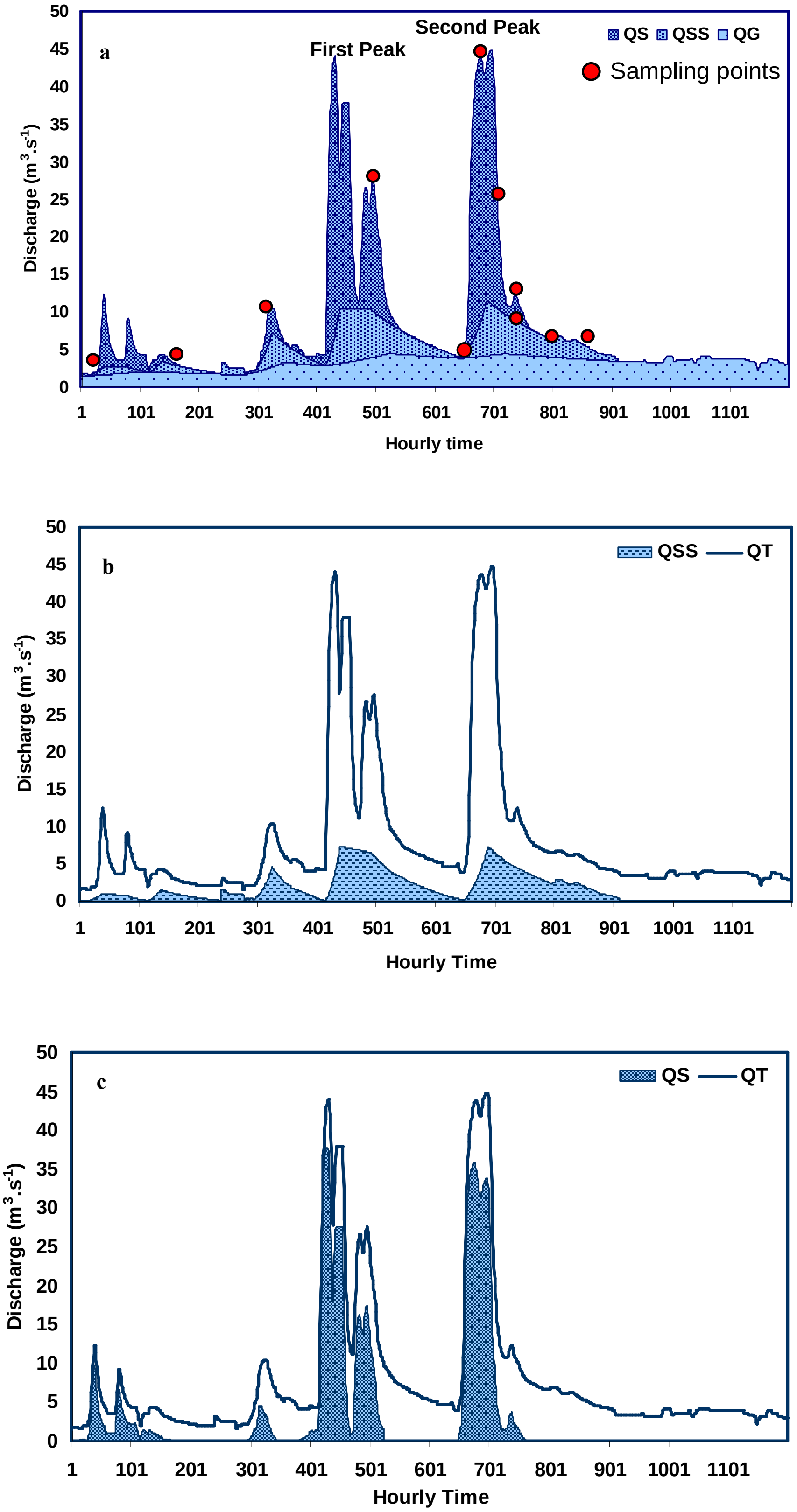
Sampling (stormwater)		QT	QS		QSS		QG		QS+QSS	
		m3.s-1	m3.s-1	%	m3.s-1	%	m3.s-1	%	m3.s-1	%
April 2008	1	6.31	0.00	0.00	0.00	0.00	6.31	100.00	0.00	0.00
	2	37.92	16.31	42.99	14.21	37.48	7.40	19.53	30.52	80.47
	3	32.90	12.28	37.34	12.98	39.46	7.63	23.20	25.26	76.80
	4	24.02	5.22	21.73	10.72	44.60	8.09	33.67	15.94	66.33
	5	20.17	2.88	14.30	8.75	43.39	8.53	42.31	11.63	57.69
	6	13.56	0.91	6.74	3.94	29.06	8.71	64.21	4.85	35.79
May 2008	1	8.80	0.00	0	0.00	0.00	8.80	100.00	0.00	0.0
	2	21.70	10.09	46.50	6.09	28.08	5.51	25.39	16.18	74.6
	3	28.70	13.43	46.79	8.09	28.18	7.17	24.98	21.52	75.0
	4	34.40	13.40	38.95	11.08	32.21	9.91	28.81	24.48	71.2
	5	36.40	10.65	29.26	13.53	37.17	12.19	33.49	24.18	66.4
	6	33.40	9.78	29.28	12.35	36.98	11.27	33.74	22.13	66.3
	7	29.90	8.75	29.26	10.91	36.49	10.22	34.18	19.66	65.8
	8	26.60	7.79	29.29	9.63	36.20	9.18	34.51	17.42	65.5
	9	23.70	4.09	17.26	9.95	41.98	9.65	40.72	14.04	59.2
	10	24.30	9.46	38.93	7.40	30.45	7.42	30.53	16.86	69.4
	11	25.40	10.31	40.59	7.16	28.19	7.76	30.55	17.47	68.8
	12	17.70	5.48	30.96	4.26	24.07	7.94	44.86	9.74	55.0
April (1) 2009	1	58.75	38.64	65.77	2.99	5.09	17.12	29.14	41.63	70.86
	2	80.74	39.28	48.66	22.92	28.39	18.54	22.96	62.20	77.04
	3	106.71	59.94	56.17	27.98	26.22	18.78	17.60	87.93	82.40
	4	209.84	153.80	73.30	36.88	17.57	19.16	9.13	190.68	90.87
	5	253.01	167.56	66.23	64.98	25.68	20.47	8.09	232.54	91.91
	6	147.77	62.31	42.17	60.35	40.84	25.11	16.99	122.66	83.01
	7	136.80	51.35	37.53	60.74	44.40	24.72	18.07	112.08	81.93
	8	52.28	4.79	9.17	25.04	47.91	22.44	42.92	29.84	57.08
	9	37.30	0.00	0.00	15.51	41.58	21.79	58.42	15.51	41.58
April (2) 2009	1	46.20	11.41	24.71	16.52	35.76	18.27	39.54	27.93	60.46
	2	116.50	62.60	53.74	34.86	29.93	19.03	16.34	97.47	83.66
	3	177.60	114.40	64.42	43.88	24.71	19.32	10.88	158.28	89.12
	4	309.90	208.01	67.12	81.69	26.36	20.20	6.52	289.70	93.48
	5	159.20	72.55	45.57	59.53	37.39	27.13	17.04	132.07	82.96
	6	97.60	23.01	23.58	43.68	44.75	30.91	31.67	66.69	68.33
	7	73.00	5.98	8.20	33.49	45.88	33.52	45.92	39.48	54.08
	8	65.60	4.61	7.03	27.74	42.28	33.25	50.69	32.35	49.31
	9	52.30	1.79	3.42	17.79	34.02	32.72	62.56	19.58	37.44
	10	26.30	0.00	0.00	0.00	0.00	26.30	100.00	0.00	0.00

Annexe III- Hydrograph separation for storm events in Save and Auradé catchments during in 2008-2009.

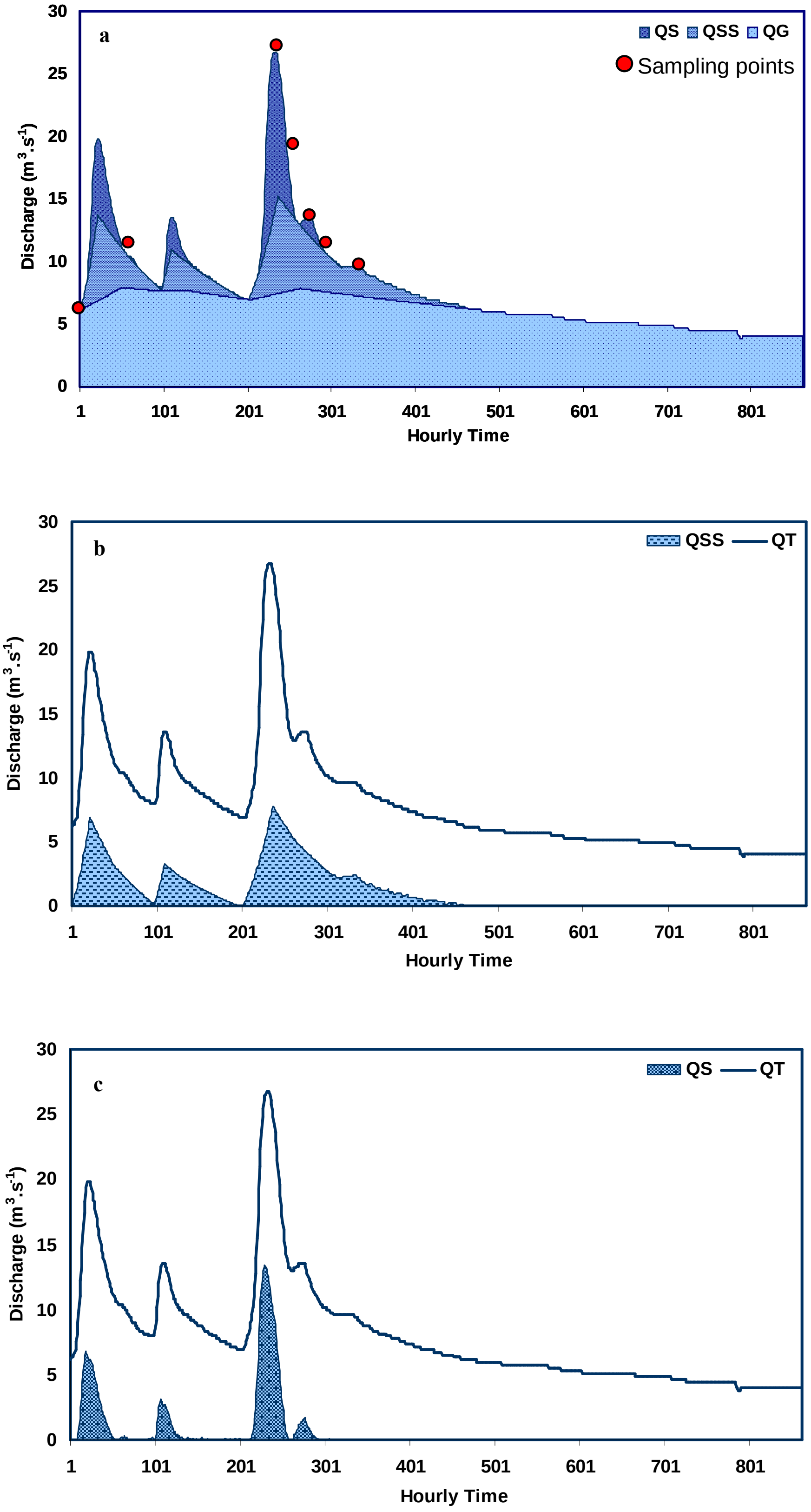
Annexe III (a)- Hydrograph separation for storm of March 2008 in Save river at Larra. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.



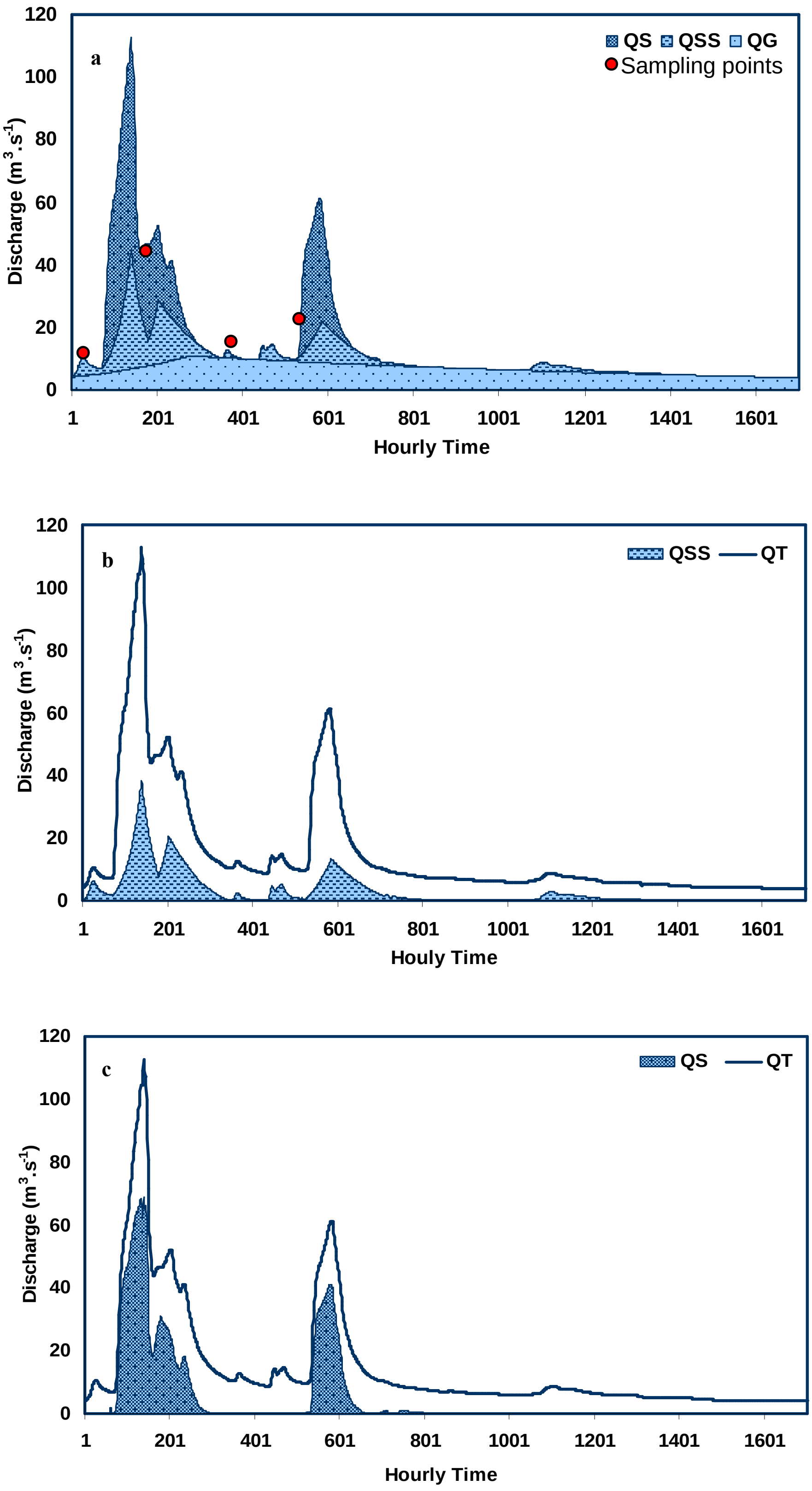
Annexe III (b)- Hydrograph separation for storm of June 2008 in Save river at Larra. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.



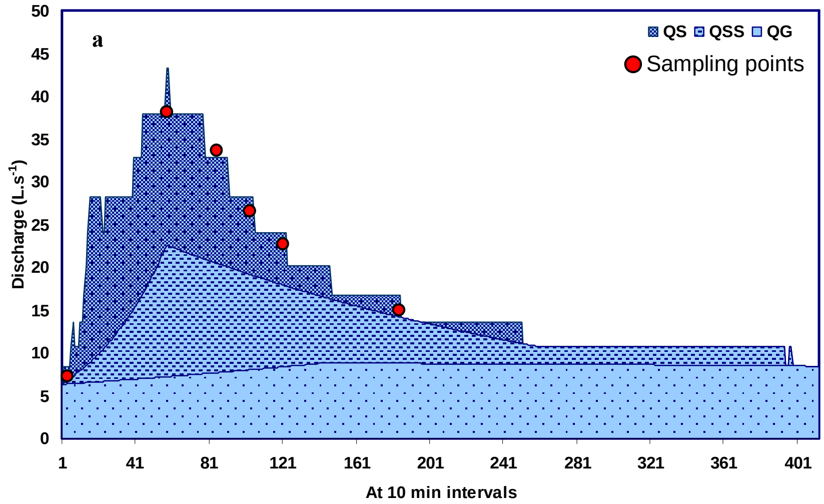
Annexe III (c)- Hydrograph separation for storm of December 2008 in Save river at Larra. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.

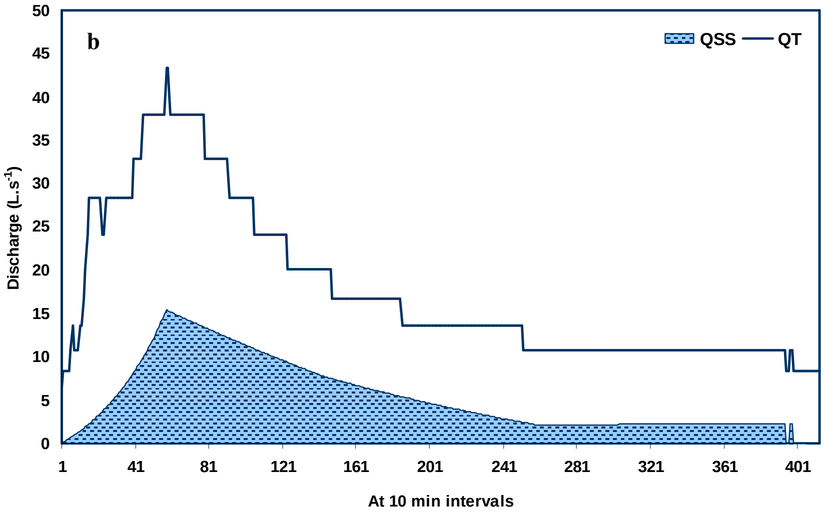


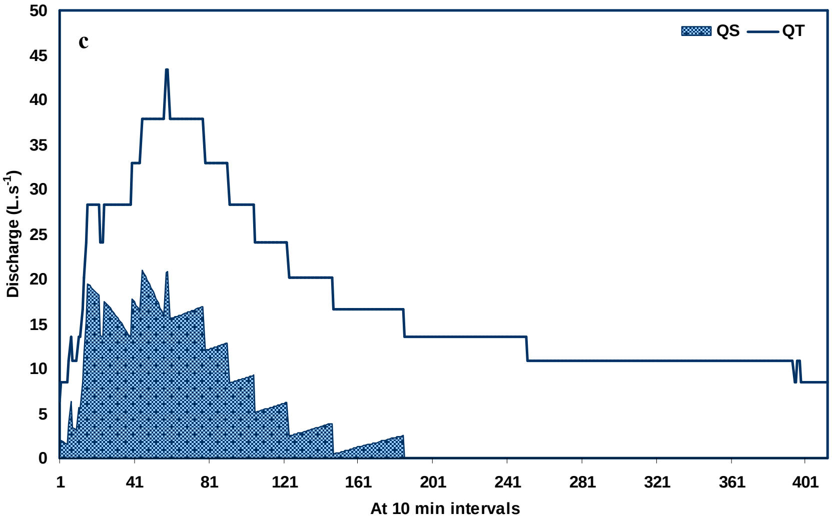
Annexe III (d)- Hydrograph separation for storm of January 2009 in Save river at Larra. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.



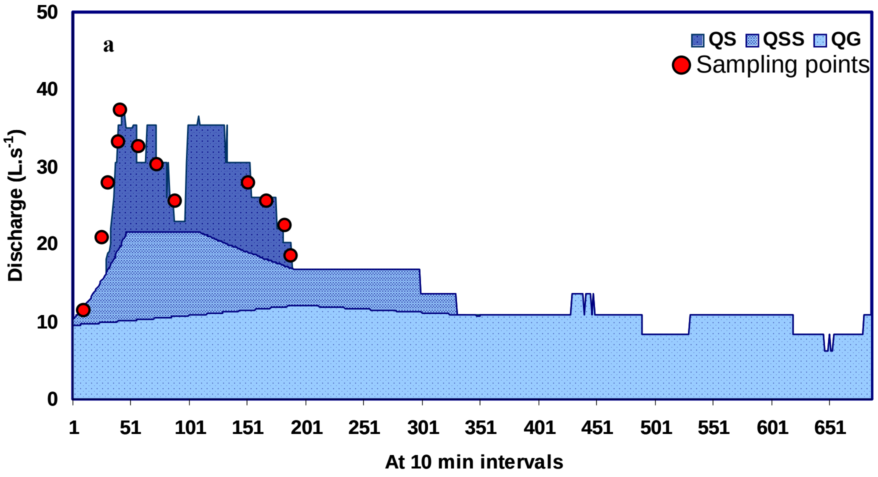
Annexe III (e)- Hydrograph separation for storm of April 2008 in Montoussé river at Auradé. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.

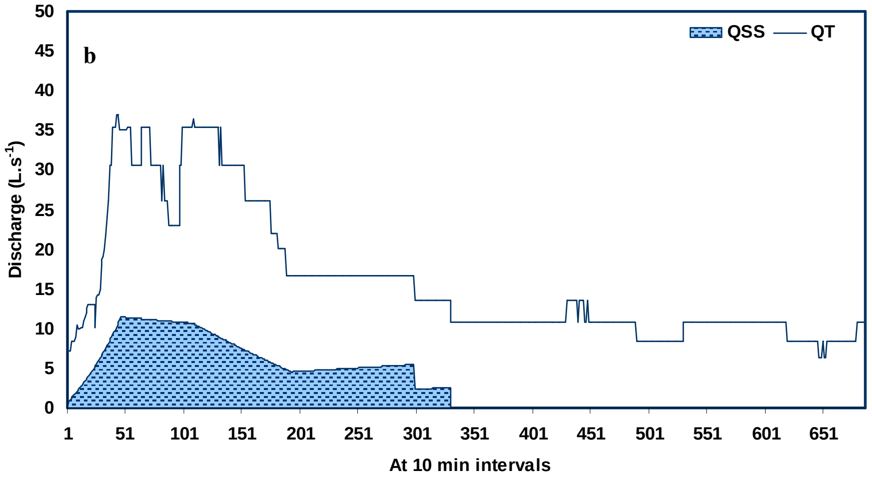


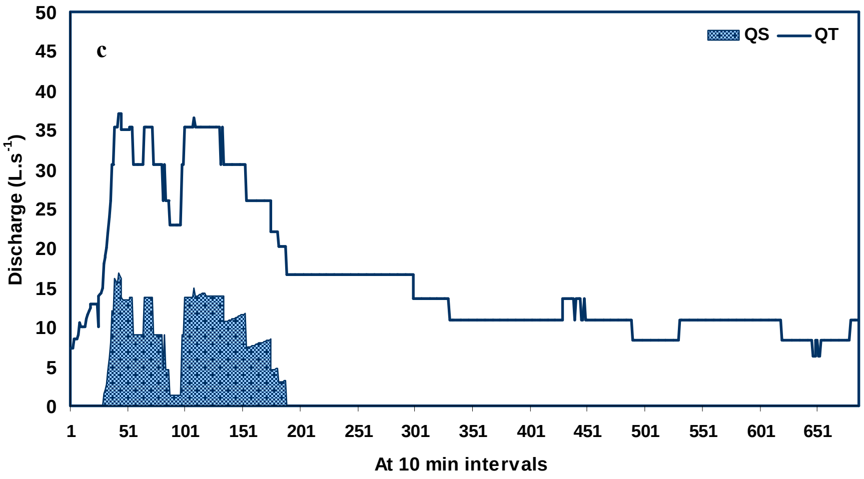




Annexe III (f)- Hydrograph separation for storm of May 2008 in Mntousse river at Auradé. a- volume of each component: QS: surface runoff, QSS: subsurface runoff and QG: Groundwater and red circles: sampling points. b- discharge of subsurface runoff and total discharge. c- discharge of surface runoff and total discharge.







Annexe IV- Fluxes of water, TSM, DOC and different pesticide molecules (g and %) exported in unfiltered, filtered and particulate fractions in Save et Auradé catchments during stormwater and base flux of the hydrological cycle 2008-2009.

Annexe IV (a)- Fluxes of water, TSM, DOC and different pesticide molecules (g and %) exported in unfiltered water by the Save river at Larra during stormwater and base flux of the hydrological cycle 2008-2009.

Storm water	Duration (Day)	DEA	atrazine	chlorotuloron	linuron	isoproturon	metolachlor	alachlor	aclonifen	trifluralin	fenpromiroph	fluzilazole	Cyproconazole	Tebuconazole	epoxoconazole	TSM(tonne)	DOC(tonne)	Volume of water (m3)
March 2008 (1)	9	108	111	6363	6616	667	143	10	576	2	22	50	43	275	30	1529	41	9.9×10^6
April 2008 (2)	19	306	166	3228	6254	850	5015	154	2613	66	41	155	162	3347	155	6369	47	12.8×10^6
June 2008 (3)	37	429	501	4633	15401	5991	16692	467	17799	3285	229	670	2055	10328	1584	51056	164	31.3×10^6
December 2008 (4)	20	303	115	2379	220	2520	269	38	253	64	23	78	63	1997	115	2144	51	16.1×10^6
January 2009 (5)	29	2024	571	57884	1229	517	1605	558	644	20432	417	387	362	36696	710	17189	210	72.3×10^6
Before December 2008 (not study) (6)	28															196	70	8.9×10^6
Stormwater2008-2009	142	3170	1464	74487	29720	10545	23724	1227	21885	23849	732	1340	2685	52625	2594	78483	583	151.3×10^6
Baseflow 2008-2009	223	3323	1004	27122	4744	7266	3050	375	2397	8371	273	640	436	13009	775	4798	238	85.5×10^6
2008-200 (annual)	365	6493	2468	101609	34464	17811	26774	1602	24282	32220	1005	1980	3121	65634	3369	83281	821	236.8×10^6

Storm water	**Duration (Day)**	**DEA**	**atrazine**	**chlorotuloron**	**linuron**	**isoproturon**	**metolachlor**	**alachlor**	**aclonifen**	**trifluralin**	**fenpromiroph**	**fluzilazole**	**Cyproconazole**	**Tebuconazole**	**epoxoconazole**	**TSM (%)**	**DOC (%)**	**Volume of water (%)**
March 2008 (1)	2.5	1.7	4.5	6.26	19.2	3.74	0.53	0.62	2.4	0.00	2.2	2.5	1.4	0.4	0.90	1.84	5	4.2
April 2008 (2)	5	4.7	6.7	3.2	18.1	4.8	18.8	9.6	10.8	0.02	4.07	7.8	5.2	5	4.6	7.65	5.7	5.4
June 2008 (3)	10	6.6	20.2	4.6	44.7	33.7	62.3	29.1	73.3	10.2	22.8	33.8	65.8	15.8	47	61.3	20	13.2
December 2008 (4)	5.5	4.6	4.65	2.34	0.64	14.1	1.0	2.4	1.0	0.2	2.3	3.9	2.0	3.04	3.4	2.6	6.2	6.8
January 2009 (5)	8	31.2	23.1	57	3.6	2.9	6.0	34.9	2.7	63.4	41.5	19.7	11.6	55.9	21	20.6	25.6	30.5
Before December 2008 (not study) (6)	8															0.2	8.5	3.8
Stormwater2008-2009	39	48.8	59.3	73.3	86.2	59.2	88.6	76.6	90.1	74.0	72.8	67.7	86	80.2	77	94.2	71	63.9
Baseflow 2008-2009	61	51.2	40.7	26.7	13.8	40.8	11.4	23.4	9.9	26.0	27.2	32.3	14	19.8	23	5.8	29	36.1
2008-200 (annual)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Annexe IV (b)- Fluxes of water, TSM, DOC and different pesticide molecules (g and %) exported in filtered water by the Save river at Larra during stormwater and base flux of the hydrological cycle 2008-2009.

Storm water	Duration (Day)	DEA	atrazine	chlorotuloron	linuron	isoproturon	metolachlor	alachlor	aclonifen	trifluralin	fenpromiroph	fluzilazole	Cyproconazole	tebuconazole	epoxoconazole	TSM(tonne)	DOC(tonne)	Volume of water (m3)
March 2008 (1)	9	65	88	3333	723	317	85	3	178	1	4	41	21	129	16	1529	41	$9.9x10^6$
April 2008 (2)	19	206	164	2249	1383	453	4591	134	351	13	38	155	162	351	155	6369	47	$12.8x10^6$
June 2008 (3)	37	283	365	2667	9240	4214	16178	332	2254	186	95	327	1642	5043	674	51056	164	$31.3x10^6$
December 2008 (4)	20	257	110	1309	193	1762	212	34	40	36	21	47	2	560	86	2144	51	$16.1x10^6$
January 2009 (5)	29	1167	146	31292	386	183	801	268	155	3451	52	185	314	1754	339	17189	210	$72.3x10^6$
Before December 2008 (not study) (6)	28															196	70	$8.9x10^6$
Stormwater2008-2009	142	1978	873	40850	11924	6928	21849	771	2978	3687	210	755	2141	7837	1270	78483	583	$151.3x10^6$
Baseflow 2008-2009	223	2046	869	22109	1281	2493	1806	269	839	3148	190	399	220	2536	394	4798	238	$85.5x10^6$
2008-200 (annual)	365	4024	1742	62959	13205	9421	23655	1040	3817	6835	400	1154	2361	10373	1664	83281	821	$236.8x10^6$

Storm water	Duration (Day)	DEA	atrazine	chlorotuloron	linuron	isoproturon	metolachlor	alachlor	aclonifen	trifluralin	fenpromiroph	fluzilazole	Cyproconazole	tebuconazole	epoxoconazole	TSM (%)	DOC (%)	Volume of water (%)
March 2008 (1)	2.5	1.6	5.0	5.3	5.5	3.4	0.4	0. 3	4.7	0.01	1	3.55	0.89	1.24	1.0	1.84	5	4.2
April 2008 (2)	5	5.1	9.4	3.6	10.5	4.8	19.4	12.9	9.2	0.2	9.5	13.4	6.9	3.4	9.3	7.65	5.7	5.4
June 2008 (3)	10	7.0	20.9	4.2	70.0	44.7	68.4	31.9	59.05	2.7	23.75	28.3	69.5	48.6	40.5	61.3	20	13.2
December 2008 (4)	5.5	6.4	6.3	2.07	1.5	18.7	0.9	3.2	1.05	0.53	5.25	4.1	0.08	5.4	5.2	2.6	6.2	6.8
January 2009 (5)	8	29.0	8.4	49.7	2.9	1.9	3.4	25.8	4.0	50.5	13	16.0	13.3	17	20.4	20.6	25.6	30.5
Before December 2008 (not study) (6)	8															0.2	8.5	3.8
Stormwater2008-2009	39	49.1	50.1	64.9	90.3	73.5	92.4	74.1	78.1	53.9	42.5	65.4	90.7	75.6	76.3	94.2	71	63.9
Baseflow 2008-2009	61	50.9	49.9	35.1	9.7	26.5	7.6	25.9	22	46.1	57.5	34.6	9.3	24.4	23.7	5.8	29	36.1
2008-200 (annual)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Annexe IV (c)- Percentage of each pesticide in particulate phase ([unfiltered minus filtered water]/ unfiltered).

Stormwater	DEA	atrazine	chlorotuloron	linuron	isoproturon	metolachlor	alachlor	aclonifen	trifluralin	fenpropimorph	fluzilazole	cyproconazole	tebuconazole	epoxiconazole
March 2008 (1)	39.8	20.7	47.6	52.5	89.1	40.6	70.0	69.1	50.0	81.8	18.0	51.2	49.8	46.7
April 2008 (2)	32.7	1.2	30.3	46.7	77.9	8.5	13.0	86.6	80.3	7.3	0.0	0.0	89.5	0.0
June 2008 (3)	34.0	27.1	42.4	29.7	40.0	3.1	28.9	87.3	94.3	58.5	51.2	20.1	51.2	57.4
December 2008 (4)	15.2	4.3	45.0	30.1	12.3	21.2	10.5	84.2	43.8	8.7	39.0	96.8	72.0	25.2
January 2009 (5)	42.3	74.4	45.9	64.6	68.6	50.1	52.0	75.9	83.1	87.5	52.2	13.3	95.2	52.3
Stormwater2008-2009	37.6	40.3	45.2	59.9	34.3	7.9	36.8	86.4	84.5	71.3	43.6	20.3	85.1	51.0
Baseflow 2008-2009	38.4	7.1	18.5	73	65.7	40.8	28.3	65.0	62.4	30.4	37.7	49.5	80.5	49.2
2008-200 (annual)	37.9	21.2	38.0	61.7	47.1	11.6	35.1	84.3	78.8	60.2	41.7	24.4	84.2	50.6

Annexe IV (d)- Fluxes of water, TSM, DOC and different pesticide molecules (gr) exported in unfiltered (a), filtered (b) water and percentage of each pesticide in particulate phase ([unfiltered minus filtered water]/ unfiltered) by the Montousse river at Auradé during stormwater and base flux of the hydrological cycle from June 2007- to June 2009 and March 2008 until March 2009 in common with the Save river.

(a)

Period	Duration (Day)	DEA	atrazine	chlorotuloron	isoproturon	linuron	metolachlor	alachlor	aclonifen	trifluralin	fenpromiroph	fluzilazole	cyproconazole	tebuconazole	epoxoconazole	TSM (tonne)	DOC (tonne)	Volume of water (10^3 m3)
April 2008	3	0.77	0.20	1.07	5.58	5.18	0.24	0.19	0.56	0.06	0.04	0.21	0.11	0.78	0.33	0.60	0.12	$18.3x10^3$
May 2008	2	0.8	0.2	12.3	2.8	4.1	0.8	0.2	15.0	0.1	0.1	0.3	0.1	1.0	0.6	4.1	0.1	$27.1x10^3$
April (I) 2009	4	3.1	1.2	52.9	11.1	21.7	21.2	1.3	30.3	45.6	0.4	1.4	0.9	4.1	3.7	76.1	1	$190.1x10^3$
April (II) 2009	4	1.4	1.5	63.8	6.8	51.0	31.0	2.2	14.5	1.4	0.3	2.2	0.8	3.4	3.8	224.2	1.3	$170.2x10^3$
∑storm water	13	6.1	3.1	130.0	26.3	81.9	53.2	3.8	60.5	47.2	0.8	4.2	2.0	9.1	8.5	305	2.5	$405.7x10^3$
Total for one Year (2008-2009)	365	37.0	7.9	247.2	87.1	71.4	17.6	12.9	104.6	423.5	3.2	6.1	3.1	47.3	8.3	45	6.2	$347.2x10^3$
Total for two years (2007-2009)	730	46.9	16.4	490.4	173.1	196.9	74.8	19.8	167.2	492.2	8.2	13.3	10.1	69.8	21.3	353.4	10.6	$917.4x10^3$

(b)

Period	Duration (Day)	DEA	atrazine	chlorotuloron	isoproturon	linuron	metolachlor	alachlor	aclonifen	trifluralin	fenpromiroph	fluzilazole	cyproconazole	tebuconazole	epoxoconazole	TSM (tonne)	DOC (tonne)	Volume of water (m3)
April 2008	3	0.6	0.13	0.76	4.27	1.22	0.16	0.13	0.29	0.01	0.01	0.13	0.06	0.63	0.19	0.60	0.12	$18.3x10^3$
May 2008	2	0.7	0.2	6.1	2.6	3.7	0.8	0.1	2.7	0.0	0.0	0.2	0.1	0.8	0.6	4.1	0.1	$27.1x10^3$
April (I) 2009	4	2.1	1.0	44.2	9.3	4.5	14.1	0.7	24.2	22.8	0.4	0.9	0.6	1.9	2.3	76.1	1	$190.1x10^3$
April (II) 2009	4	1.1	1.3	26.4	6.8	34.0	29.4	1.4	11.4	0.5	0.2	1.9	0.7	2.0	3.2	224.2	1.3	$170.2x10^3$
∑storm water	13	4.5	2.5	77.5	23.0	43.5	44.4	2.4	38.6	23.3	0.7	3.2	1.5	5.3	6.3	305	2.5	$405.7x10^3$
Total for one Year (2008-2009)	365	27	6	190	58	32	8	5	24	279	1	4	2	19	6	45	6.2	$347.2x10^3$
Total for two years (2007-2009)	730	35	9.5	354	147	110	56	10	70	316	5	10	6	35	15	353.4	10.6	$917.4x10^3$

Annexe V- Scientific production

Annexe V (a)- Taghavi et al. 2010. Intern. J. Environ. Anal. Chem., 90: 390–405.

Intern. J. Environ. Anal. Chem.
Vol. 90, Nos. 3–6, 15 March–15 May 2010, 390–405

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

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

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

1. Introduction

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

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

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

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

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

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

The main objectives of this study are:

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

2. Experimental

2.1 *Study area*

2.1.1 *Location and characteristics*

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

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

2.1.2 *Climate and hydrology*

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

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

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

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

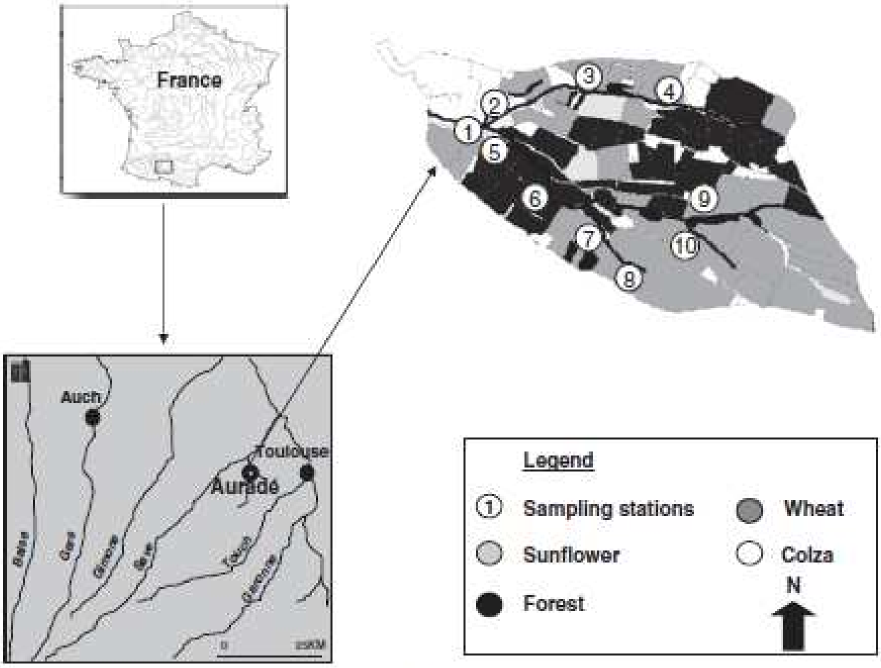

Figure 1. Geographical situation map of the Montoussé experimental catchment at Auradé (Gers, south west France) and location of the sampling stations (1 to 10).

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

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

2.3 *Method of analysis: multi-residue approach*

2.3.1 *Sample analysis*

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

2.3.1.2 *Filtration and extraction of sample*. The water sample was filtered by applying vacuum. The filter used to filtration is a cellulose ester filter (Millipore, 0.45 μm) [28]. Each filter was rinsed with MilliQ water before filtration. Filter blanks were measured and pesticide concentrations were always under the detection limit (0.005 to 0.01 $\mu g\,L^{-1}$ according to the molecules). To extract water samples, the liquid/liquid extraction technique was applied [29], by using a shaker flask (3–4 L with Teflon key) as a means and dichloromethane as a solvent for phase exchange. The total solvent/water ratio was noted as 1 : 6, V/V. Once the extraction performed, dichloromethane was dried on 50 g anhydrous sodium sulphate, and the remaining organic phase was evaporated under vacuum and the dry residue was recuperated with 2 ml of hexane.

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

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

3. Results and discussion

3.1 *Temporal variations during the flood of May 2008*

3.1.1 *DOC, TSM and water discharge fluctuations*

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

Worrall and Burt [31], suggesting that increase in DOC concentration could result from change in hydrology, and Tranvik and Jansson [32], have mentioned a decrease in discharge could result in a change in concentration. However, Werrity [33] established that there is a positive relation between discharge and DOC concentration for UK rivers.

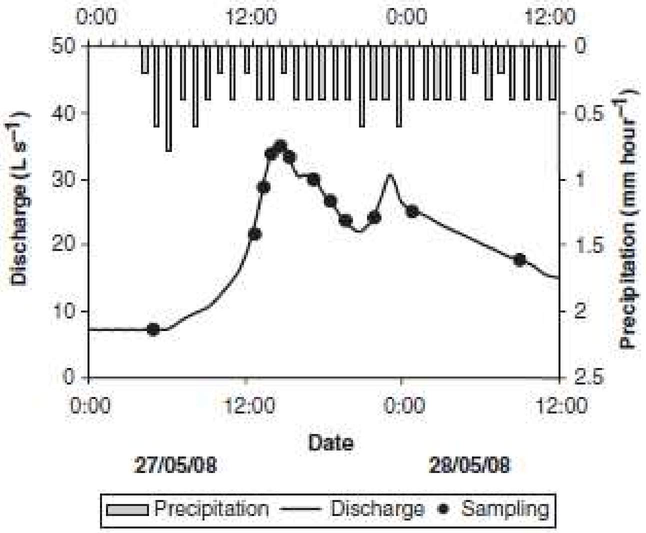

Figure 2. Hourly precipitation and stream discharge measured at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008. Black circles on the hydrogragh represent the sampling periods.

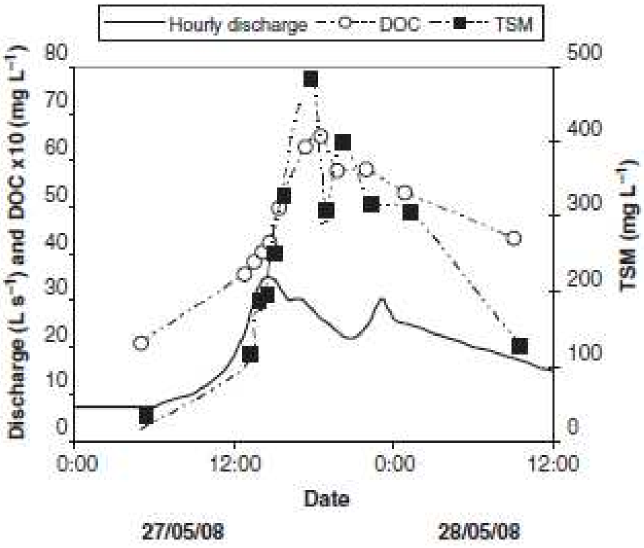

Figure 3. TSM and DOC concentration variations compared to stream discharge fluctuations at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008.

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

In this study we can observe that the concentrations and fluxes of TSM and DOC are higher during the recession phase of which the contribution to the total flood event represents 67% for DOC and 73% for TSM loads. Consequently, for a given discharge

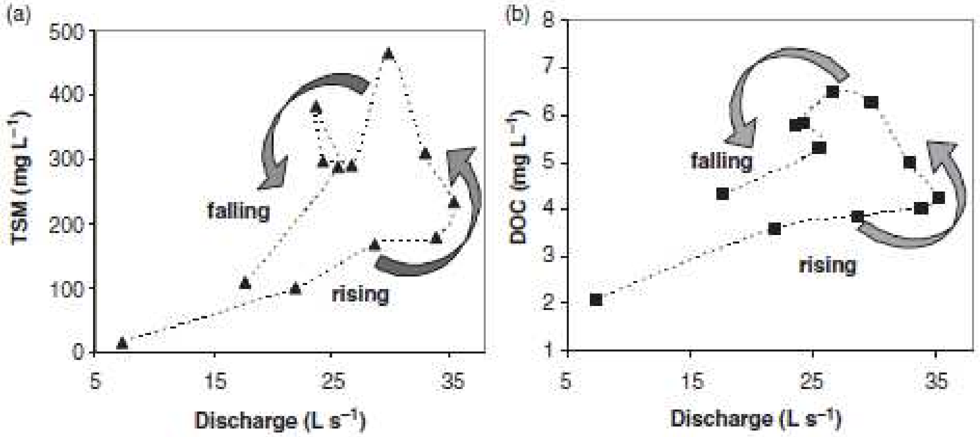

Figure 4. Relationships between TSM (a) or DOC (b) contents and stream discharge at the outlet of the Montoussé catchment during the flood event of May 2008, showing the hysteresis phenomenum between rising and falling limbs of the storm hydrograph.

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

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

3.1.2 *Variations of pesticide concentrations and fluxes*

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

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

As seen in Figure 5, pesticide concentrations in unfiltered waters are higher after the peak discharge during the recession period than during the rising discharge, showing a hysteresis between the two hydrological periods. That means most of the pesticides are mainly exported by the subsurface run-off. This hysteresis phenomenon is illustrated as an

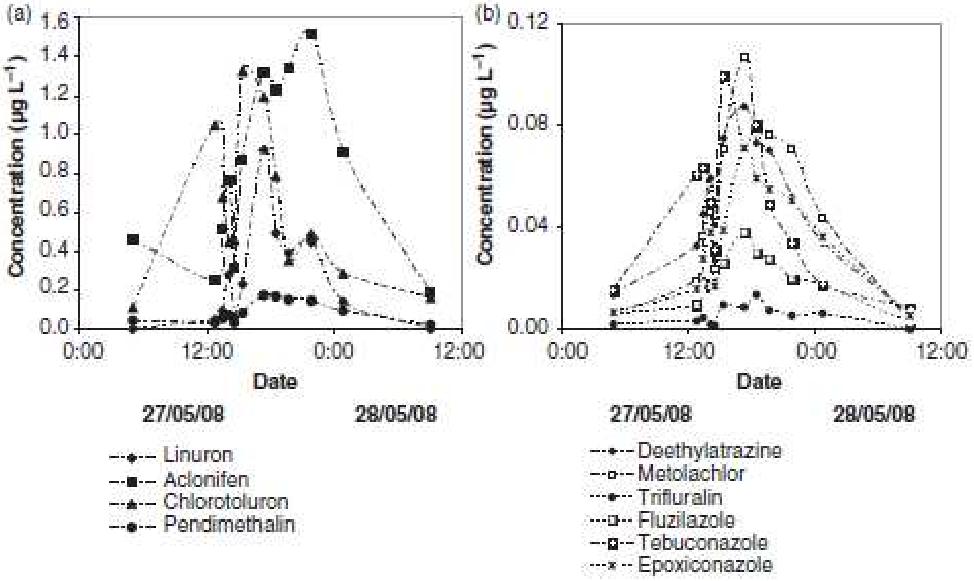

Figure 5. Variations of pesticide concentrations in unfiltered waters at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008. (a) High concentration molecules, (b) low concentration molecules.

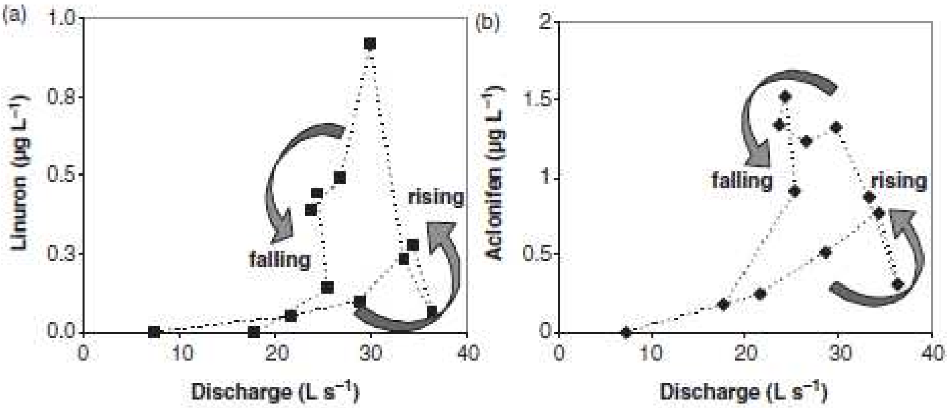

Figure 6. Relationships between linuron (a) or aclonifen (b) concentrations and stream discharge at the outlet of the Montoussé catchment during the flood event of May 2008, showing the hysteresis phenomenum between rising and falling limbs of the storm hydrograph.

example in Figure 6(a) and (b), respectively for linuron and aclonifen which have the highest concentrations during the flood event. As already seen for TSM and DOC, there is a lag of concentration between the rising period and the falling limb of the hydrograph showing higher linuron and aclonifen concentrations during the recession period, when the sub-surface run-off contribution reaches its maximum, than during the rising discharge.

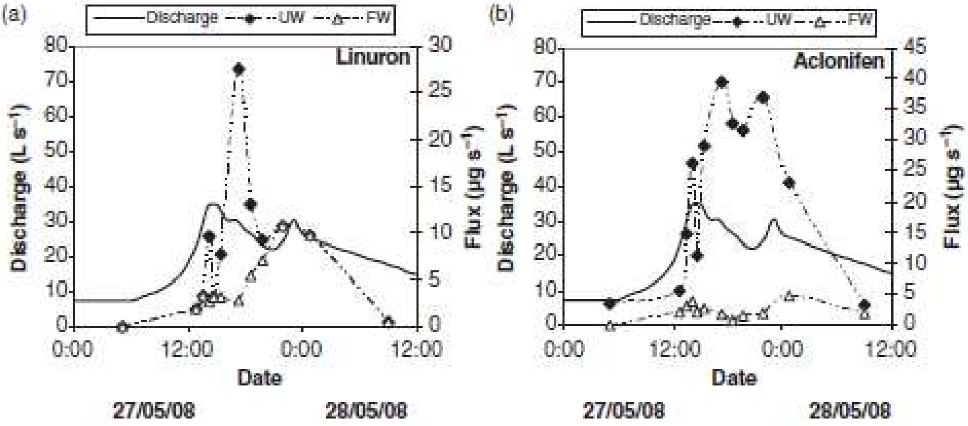

Figure 7. Discharge and variations of linuron (a) and aclonifen (b) fluxes measured in filtered (FW) and unfiltered (UW) waters during the flood flow of May 2008.

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

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

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

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

In the unfiltered water two molecules (aclonifen and DEA) have concentrations between 0.1 and 0.5 µg L^{-1}, and 5 molecules (metobromuron, isoproturon, chlorotoluron,

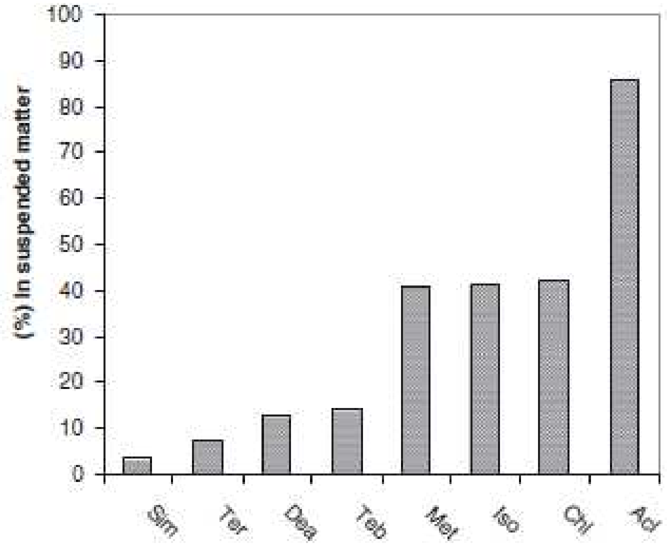

Figure 8. Percentage of particulate fractions (unfiltered minus filtered waters) to the total molecule measured in unfiltered waters during the flood event of March 2006. Average values for the 10 stations.

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

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

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

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

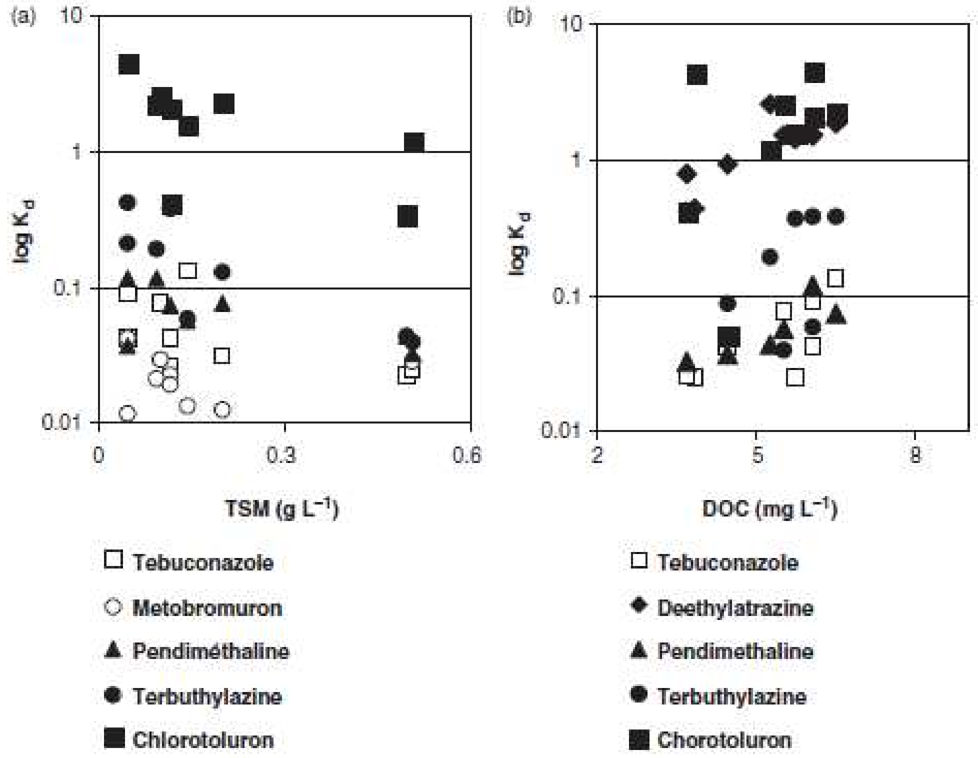

Figure 9. Relationships between the partition coefficient K$_d$ of different pesticides and TSM (a) or DOC (b) concentrations at the outlet of the Montoussé catchment (station 1) during the flood event of March 2006.

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

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

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

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

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

There was a reverse relationship between K$_d$ and TSM concentrations for tebuconazole, metobromuron, pendimethalin, terbuthylazin and chlorotoluron (Figure 9(a)) showing that the adsorption of these molecules onto particulate phases increases with increasing TSM concentrations. On the contrary, for tebuconazole, deethylatrazine, pendimethalin, terbuthylazin and chlorotoluron, K$_d$ values increase with increasing DOC contents,

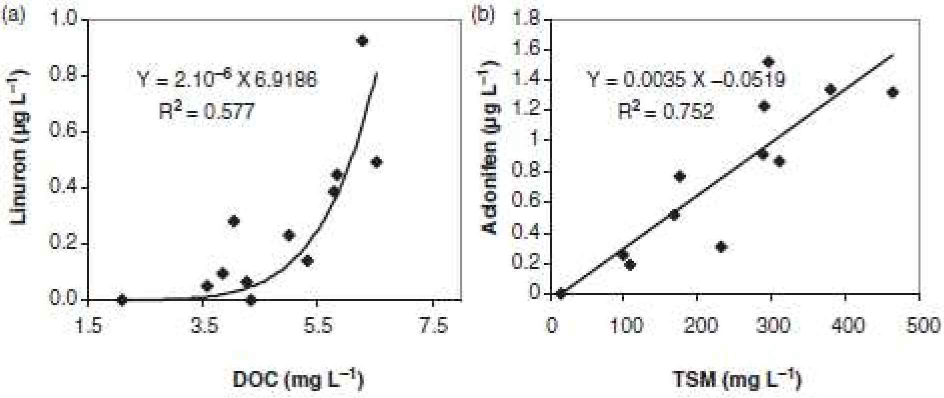

Figure 10. Linuron (unfiltered waters) *versus* DOC concentrations (a) and aclonifen (unfiltered waters) *versus* TSM content (b) at the outlet of the Montoussé catchment (station 1) during the flood event of May 2008.

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

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

$$[\text{linuron}] = 2.10^{-6}\ [\text{DOC}]^{6.9186} \qquad R^2 = 0.577, \quad p < 0.01 \tag{3}$$

$$[\text{aclonifen}] = 0.0035\ [\text{TSM}] - 0.0519 \qquad R^2 = 0.752, \quad p < 0.01 \tag{4}$$

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

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

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

3.4 *Relationship between K_d and K_{ow}*

The octanol-water partition coefficient K_{ow} is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. K_{ow} values for pesticides are generally listed in databases (see, for example, in the pesticide manual [40]).

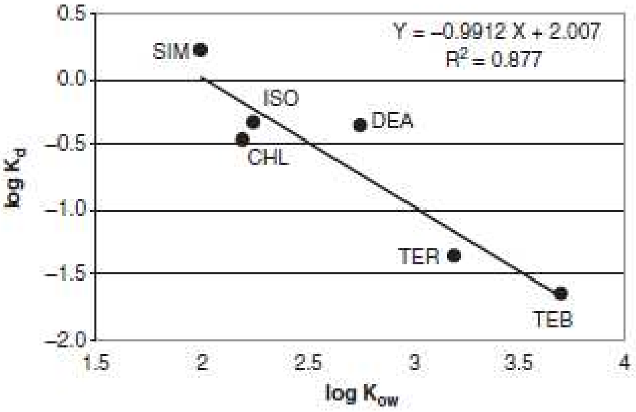

Figure 11. Relationship between log K_d and log K_{ow} during March 2006 flood event at the outlet of the Montoussé catchment (station 1). SIM: simazin, CHL: chlorotoluron, ISO: isoproturon, DEA: deethylatrazine, TER: terbuthylazin, TEB: tebuconazole.

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

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

The equation of this relationship is as follows:

$$\begin{aligned} \log K_d &= -0.9912 \log K_{ow} + 2.007 \\ R^2 &= 0.877, \quad p < 0.01. \end{aligned} \tag{5}$$

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

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

4. Conclusion

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

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

Acknowledgements

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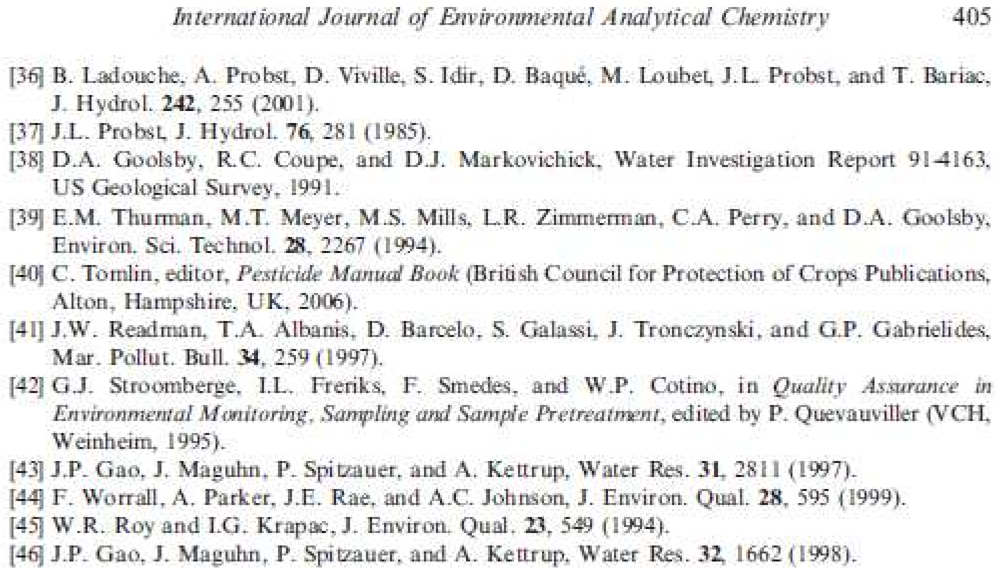

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Annexe V (b)- Taghavi et al. 2010. Knowledge and Management of aquatic ecosystems (KMAE)., In press.

The role of storm flows on concentration of pesticides associated to particulate and dissolved fractions as a threat to aquatic ecosystem

Case study: the agricultural watershed of Save river (South west of France)

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ABSTRACT

Measuring the fluxes of pesticides ran for a year ended in March 2009 in the Save catchment, in the vicinity of Toulouse. Hydrograph separation technique was used to evaluate the respective contribution of stormflow and baseflow in transporting of 12 pesticide molecules. Transport of over 59% of pesticides and their controlling factors such as total suspended matter (TSM), particulate organic carbon (POC) and dissolved organic carbon (DOC) occurred during storm periods. Hysteresis patterns could be observed on the concentration-discharge relationships only for some molecules between rising and falling periods of storm hydrograph. Clockwise hysteresis was noticed for low to moderately soluble pesticide molecules and for particulate fractions that explains the role of surface runoff in pesticide displacement. In contrast, anticlockwise hysteresis was registered for soluble molecules and dissolved fractions, explaining the role of subsurface flows and soil leaching processes. The important role of TSM, POC and DOC in the pesticide transport was clearly established. We also came to the conclusion that the role of stormy periods in pesticide movement and their controlling factors worked as a threat to aquatic ecosystems. And there was a positive relation between riverine TSM, POC, DOC and pesticides according to pesticide properties.

***Key-words**: Pesticide, TSM, DOC, hysteresis patterns, flood flow*

RÉSUMÉ

Les flux de pesticides sont mesurés durant une année hydrologique (2008-2009) sur le bassin versant de la Save, proche de Toulouse. La technique de séparation des hydrogrammes de crue a été utilisée pour évaluer la contribution respective des écoulements de crue et des écoulements de base au transport fluvial de 12 molécules de pesticides. Plus de 59% des flux de pesticides, de matières en suspension (MES), de carbone organique dissous (COD) et particulaire (COP) sont transportés durant les périodes de crue. Des hystérésis peuvent être observées sur les relations concentrations-débits, uniquement pour quelques molécules, entre la montée et la descente de crue. Des hystérésis dextres (sens des aiguilles d'une montre) sont observées pour les molécules peu ou modérément solubles et pour les fractions particulaires montrant le rôle du ruissellement de surface dans le transfert des pesticides. Au contraire, des hystérésis senestres (sens inverse) sont observées pour les molécules solubles et les fractions dissoutes montrant le rôle des écoulements hypodermiques et du lessivage des sols. On a pu établir clairement le rôle important des MES, du COP et du COD dans le transport des pesticides. Les résultats obtenus nous montrent aussi le rôle joué par les épisodes de crue sur les transferts de pesticides et de leurs facteurs de contrôle, représentant un risque potentiel important de contamination des eaux et une menace pour les écosystèmes aquatiques. Des relations positives sont mises en évidence entre les teneurs en MES, COD ou COP et les concentrations en pesticides selon les propriétés physico-chimiques des différents pesticides.

Mot-clé : *Pesticide, MES, COD, hystérésis, crues.*

INTRODUCTION

Increasing environmental awareness has generated concerns regarding the impact of pesticides on aquatic ecosystems. In a thorough investigation conducted by Palama et al. (2004) and Comoretto and Chiron, (2005) a high degree of concentration was detected in surface water in a number of countries. Protecting aquatic organisms and people's health against hazardous situation by the excessive use of pesticides have made it necessary for almost every country to reduce the presence of pesticides in surface water within concentration limits. For instance, the "Directive" concerning the quality of water intended for human consumption of European Union, foresees standards for pesticide residue in drinking water at 0.1 $\mu g.L^{-1}$ for each active substance and 0.5 $\mu g.L^{-1}$ for the sum of all pesticides (EEC, 1991). Higher rates of water contamination during storm events has been demonstrated by several investigators (Wu et al., 1983; Roth et al., 1992; Bach et al., 2001; Taghavi et al., 2010). But, little is known about the mechanisms of pesticide transfers from soils to stream waters, and about the parameters which are controlling these transfers. It is therefore essential to examine and to verify the interaction of pesticides with their controlling factors such as total suspended matters (TSM), particulate (POC) and dissolved DOC) organic carbon in order to assess the impact of storm events on water quality and aquatic ecosystems.

The main objectives of this study are:

- to determine the pesticide concentrations and their temporal variations, particularly during stormflow events in an agricultural catchment, the Save river basin draining the Gascogne region in South West of France.
- to assess the relationships between pesticide concentrations or their main controlling factors (TSM, DOC and POC contents) and the river discharge.
- to evaluate the role of the main controlling factors on pesticide transfers.
- to determine the contribution of storm flow period to pesticide river fluxes using storm hydrograph separation.

MATERIALS AND METHODS

Watershed description

The Save river, located in the “Coteaux de Gascogne” region (South West of France), drains an agricultural catchment with an area of 1110 km^2 (Figure 1) at Larra station. The upstream part of the catchment is a hilly agricultural area mainly covered by forest and pasture (56%) while the lower part is flat and devoted to intensive agricultural activities (44%), mostly wheat, corn and sunflower which make the use of pesticides indispensable. Non-calcic silty soils, locally named “boulbènes”, represent less than 10% of the soils in this area. Calcic soils are dominated by clay content ranging from 40% to 50%, while non-calcic soils are silty (50-60%). The geological substratum is a Miocene molassic deposit resulting from the erosion of the Pyrénées Mountains. This molassic substratum is impermeable due to its widely extended clay content that induce discharge of river by surface and subsurface runoffs. The climate is characterized as Atlantic - oceanic because the influence of the Atlantic ocean plays an important role in regulating temperature variations and therefore determining climate conditions. The average annual precipitation is about 700 to 900 mm, mostly in the form of rain, which is the main hydrological source of supply for surface and subsurface runoffs in this area with the highest rate of discharge in February to June while the water flows are lower from July to September.

Sample collection

Water sampling started in March 2008 and continued until March 2009. The main sampling months were February to June, with daily sampling during storm events. Out of the raining period, water samples were collected manually each week.

Each sample has been collected in the same big bottle and then it was splited into three sub-samples. Two sub-samples are put in glass bottles of 2.5 L (for pesticide and TSM analyses) and one in a glass bottle of 500 mL (for DOC and POC analyses). The first one is used for pesticide analyses in unfiltered water, dichloramethane (DCM) was added in the field (1:40V/V) to inhibit microbial degradation of the pesticides (Kreuger, 1998; Devault et al., 2007) and also used for extraction in the laboratory. The second one was filtered on 0.45 µm cellulose ester Millipore filters for pesticide analyses in the filtrate after DCM extraction and for TSM measurements in the filters. The third one is filtered at 0.7 µm on Whatman GFF membrane for DOC (on the filtrate) and POC (on the filter) analyses. Concerning the result obtained and shown in this paper we only concentrated on unfiltered water for pesticide concentration.

The glass bottles used were carefully cleaned in the laboratory then in the field they were rinsed three times to ensure representative of the samples. Sampling was done in an area where water is steady and continues flowing in an immersion condition. The glass bottles with Teflon-lined lids were finally transported in ice-boxes and stored under refrigeration until analyzed.

Measurements of TSM, DOC and POC

To measure total suspended matter (TSM), water samples were filtered by applying vacuum on a cellulose ester filter (Millipore, 0.45µm) (Namiesnik et al., 1997). The sediment retained on the filter paper was dried for 24 h at 60 °C to ensure accurate sediment weight. The filter papers were then-weighted before and after filtration to determine TSM concentration.

To analyze dissolved (DOC) and particulate (POC) organic carbon, the samples were filtered on pre-combusted (by combusting it at 550°C for 2 hours), Whatman GF/F with 0.7 µm porosity. DOC measurement was carried out with an analyzer of total organic carbon (Shimadzu TOC-Analyser 5500). Before analyzing DOC and in order to remove inorganic carbon, the samples were acidified by HCL (pH< 2). POC is measured by determining the mass lost upon combustion of a sample by using CHN analyzer (NA 2100).

Pesticides analyses

Twelve molecules of pesticides (herbicides and fungicides, see table 1) were investigated in this study based on historical data of the French Water Agency Adour-Garonne and also by the study performed by Institutional networks (GRAMIP for example). And the selections of five families of pesticides were then further based on the study and on the availability of data of a 4-year lasting study by Devault et al. 2007.

Pesticide analyses are performed by solvents of analytical grade (pestipure by SDS, Solvent Documents Syntheses, Peypin, France). Anhydrous sodium sulphate from SDS was used for drying the organic phases. Pesticide mix 44 prepared by Dr Ehrenstorfer (purchased from Cluzeau Information Laboratory (CIL), Sainte Foy-la-Grande, France) was used as reference material.

To extract water samples, the liquid/liquid extraction technique, the most common method, was applied (Tan, 1992), by using a shake flask (3-4 with Teflon key) as a means and dichloromethane as a solvent for phase exchange. The total water ratio was noted as 1:6, V/V. Once the extraction performed, dichloromethane was dried on 50 g anhydrous sodium sulphate, and the remaining organic phase is evaporated under vacuum and the dry residue was recuperated with 2ml of hexane.

The pesticide molecules (herbicides, fungicides) have been analysed by multi-residue technique on filtered and unfiltered waters (Devault et al., 2007 and Taghavi et al., 2010). Gas chromatography coupled to mass spectrometry were used for separation and detection of different components. GC separation was done on a column of Zebra ZB-5MS 30m 0.25 mm i.d., 0.25 mm film from Phenomenex (Torrance CA) with Thermo Fishers Scientific (Whatman, MA). Trace GC 2000 is coupled to a DSQ II mass detector. Extraction recoveries were done on spiked water samples with mixes of the different molecules analysed in this study by using Pesticide- Mix44 reference material and other different molecules separately (prepared by Dr Ehrenstorfer), although complete analytical methodology is described in Taghavi et al. (2010). The limits of detection based on a signal to noise ratio of 3 vary from 0.001 to 0.003 $\mu g.L^{-1}$ according to the molecules.

Flux calculation

The flux is defined as the mass of the compound transported in the river at each sampling point during a specified time period. The fluxes of pesticide, TSM and DOC are calculated for each sampling interval (i to i+1) as the product of discharge weighted concentration C ($C_{i \text{ to } i+1} = (C_iQ_i+C_{i+1}Q_{i+1})/(Q_i+Q_{i+1})$) and river discharge (Q) during the time interval i to i+1. The storm event fluxes and the annual fluxes are calculated by summing the fluxes of the different intervals (i to n). Hourly mean discharge values were available for all sampling points for the entire investigation periods from CACG (Compagnie d’Aménagement des Coteaux de Gascogne) in charge of the Larra gauging station. This method is common in the literature to estimate the flux of the organic carbon, the total suspended matter and the pesticide (Hope et al., 1997; Worrall and Burt, 2005; Clark, et al., 2007).

Statistical analysis

The SPSS 11 software (SPSS Inc., Chicago, IL, USA) was used to carry out the statistical analysis of the data set. The significance of correlations was tested by using Pearson or Spearman tests.

RESULTS

Watershed hydrology

All of the runoff events were monitored and analyzed during a year ending in March 2009. The discharges measured for each storm event were plotted hourly on an x-axis as an hourly discharge hydrograph. The discharge measured in a stream is combination of these three main flow components: surface runoff, subsurface runoff and groundwater flow (Figure 2).
Hydrograph separation method proposed by Probst (1985) and based on Maillet's equation ($Q_t=Q_0e^{-\alpha t}$) with some modification was applied for separating the stormy periods. To check the relationship between pesticide concentration and their controlling factors with discharge of water we have turned our attention particularly on storm of April 2008 since this period is coinciding with the pesticide application period and, moreover, our sampling points are nearly covered all of the storm phases (rising and falling).

Concentration of pesticides in river water

Pesticides were detected in almost every stream water sample collected at the out-let of Save watershed. The overall frequency levels at which pesticides were identified during a year long observation is statistically summarized in Table 1.
The highest rate of concentration 1.97 (µg.L^{-1}) was recorded for chlortoluron and the lowest rate was detected at 0.02 µg.L^{-1} for fenpropimorph.
The highest and lowest concentration was calculated to 0.391 and 0.004 µg.L^{-1}, respectively for chlortoluron and fenpropimorph.

Pesticide, TSM and DOC riverine fluxes

During entire investigation period, 41 out of 65 water samples were taken during storm periods in order to determine the total pesticides, TSM and DOC fluxes. The hydrograph separation method was used to distinguish the contribution of storm period (mainly supplied by surface and subsurface runoffs) from that of baseflow (mainly supplied by groundwater flows). Our findings revealed over 59% of studied molecules were transported during the storm periods and the percentages of pesticides in base flow remains several times less than those in storm flow despite the relatively important water contribution of baseflow (36.1%) to the annual river discharge. In the present study, 63.9 % of the water volume discharged annually by the Save river, nearly 71% of DOC river fluxes and 94% of TSM exported by the river were transported during the flood events. Concerning pesticide river fluxes (Table 2), 59% to 90% are exported during the storm flow periods according to the molecules.

Concentration-discharge relationships: hysteresis patterns

Hysteresis is a circular pattern relationship between dissolved or particulate concentration and river discharge which can be observed during a storm event. The results presented in this part are concerning three selected molecules of pesticides with varying degrees of solubility. Solubility (S_w in mg.L^{-1}) and different K_{ow} (octanol-water partitioning coefficient) values are used as indicators for estimating bioaccumulation in animals and plants and in predicting the toxic effects of substances (Veith et al., 1979; Briggs et al., 1982; Calamari and Vighi, 1990). The later values for three molecules under our investigation are: aclonifen, a low soluble molecule (K_{ow} = 4.37, S_w = 1.4), linuron as a moderately soluble molecule (K_{ow} = 3 and S_w= 63.5) and metolachlor representative of a high soluble molecule (K_{ow} = 2.9, S_w = 488).

C-Q relationships present generally hysteresis patterns, showing that the concentration is different between the rising and the falling period of the hydrograph for the same river discharge. Two cases can be observed according to the transfer dynamic of the molecule from the soils to the river waters:

- clockwise hysteresis is produced when concentration is higher during the rising limb than during the falling limb of the hydrograph. This is the case for aclonifen and linuron molecules.
- anticlockwise hysteresis appeared when higher concentration is noticeable during the falling limb of the hydrograph, i.e. during the recession period, as it is the case for metolachlor.

These results indicate that transport of metolachlor (soluble molecule) is primarily controlled by subsurface water flow of which its contribution is at the highest during the falling limb of the flood hydrograph. DOC also shows the anticlockwise hysteresis that explains the highest concentration of DOC occurs in falling stage of storm period which coincides with the time of draining of different hydrological reservoirs, particularly to the soil leaching. On the contrary, clockwise hysteresis shows that the surface runoff, whose contribution is maximum during the rising limb of the flood, is controlling the transfer of aclonifen (low soluble molecule) and linuron (moderate soluble molecule) that are strongly associated with TSM and POC which present the same hysteresis patterns than these molecules. Different patterns of hysteresis observed in our study are depicted in Figure 3.

TSM, POC and DOC as vectors of pesticides' transport

Properties of pesticides play a major role in influencing their concentration in runoff. Pesticide can be adsorbed onto eroded particles and transported into the river water by the total suspended matters (TSM). They can also be complexed by dissolved organic carbon (DOC) which is regarded as the main sorbent for hydrophilic pesticides in soil/water. Our results revealed that low to moderately soluble molecules such as aclonifen and linuron are exported in association with TSM and POC, since there is a significant interaction between concentration of aclonifen and the concentration of TSM and POC (Figure 4). Metolachlor as a molecule with high degree of solubility shows a good relationship with DOC which highlights the important role of DOC as a vector in transporting of hydrophilic pesticides such as metolachlor (Figure 4).

DISCUSSION

This careful survey of pesticide concentrations, particularly during storm flow events, showed that pesticides are mainly exported during these hydrologic periods. These periods are very short temporal events but very intense in the Gascogne region (South West of France) which is intensively cultivated (mainly corn, wheat and sunflower). Our findings revealed that more than 59% of pesticides are transported during storm events into river systems. Results obtained by previous studies indicate that pesticide transport and losses are related to some phenomenons which generally appear close to the application periods (Brown et al., 1995; Lennartz et al 1997). Moreover, the characteristic of rainfall, runoff volume, and storm events, have a great impact on pesticide transport and losses (Muller et al., 2003). The role of stormy period is highlighted in transport of TSM and DOC, the findings is in accordance with the results' survey of Clark et al. (2007), Zhang et al. (2009) and Ollivier et al. (2010). Cyclical trajectory relationship (hysteresis) has been already reported between river discharge and solute concentration during storm events (Jardine et al., 1990; Hill, 1993). However, none of these studies have shown the hysteresis phenomenon for pesticide molecules, and pesticide transport was rarely observed from this particular angle. The hysteresis patterns allow us to assess the potential contribution of different stream flow components in pesticide exportation and their controlling factor displacement. Clockwise hysteresis shows the important role of surface runoff and mechanical erosion in transport of particulate elements such as aclonifen as low soluble molecule and linuron, a molecule with moderate solubility, both of them were transferred from the soils to the river waters by surface runoff. Moreover, TSM and POC also show the similar pathway of transport. Previous studies have shown the important role of surface water in transporting of low soluble elements such as phosphorus and total suspended matter (Probst, 1985; Probst and Bazerbachi, 1986). Anticlockwise hysteresis highlighted the role of subsurface water in transporting of metolachlor and DOC. Findings of Probst (1985), Kattan et al. (1986) and Wagner et al., (2008), have revealed the role of subsurface water in transporting of other soluble elements, such as nitrate. This result confirms the pre-eminent role of subsurface flow in metolachlor and DOC displacement, and both of them are transported with each other by complexation processes. And TSM, POC play an important role in transporting of aclonifen and linuron by adsorption processes onto organic or inorganic particulate fractions. This conclusion is strongly supported by the very good relationship between metolachor and DOC, and also between aclonifen or linuron and TSM or POC. The study conducted by Taghavi et al. (2010) in small agricultural catchment, Montoussé at Auradé (320 ha), highlights also the role of TSM for aclonifen transport, whereas linuron shows a good relationship with DOC. We could therefore conclude that for moderately soluble molecules such as linuron the partitioning between dissolved and particulate phases depends on relative concentration of dissolved and particulate fractions which both play an important role in linuron transport. Overall, our results revealed high concentration of pesticides is a serious external threat to water contamination and aquatic organism health, especially during storm periods when we have a large quantity of TSM, POC and DOC.

In 1984, Schubel and Carter pointed out pesticide associated with suspended particles may have different environmental effects in aquatic ecosystems than dissolved pesticide since suspended particles are a primary source of nutrition for filter feeding organisms such as clams. But, both dissolved and particulate fractions are considered as potentially harmful elements to aquatic organisms. That is in agreement with the findings of Frankart et al. (2002).

A closer look at the data in this paper indicates that:

- 59% to 90% of pesticide, 94% of TSM and 70% of DOC are transported during flood periods, representing a potential vector for the transport of pesticides adsorbed onto these fractions and a potential contamination risk for the aquatic ecosystems,
- the concentration-discharge relationships exhibit hysteresis phenomenon with different concentration during the falling and the rising limbs of the hydrograph, showing that the potential contamination risk for the ecosystems is different according to the hydrologic phases of the storm flow period and according to the physico-chemical characteristics of the molecules.

Higher contamination risks for the aquatic ecosystems can be observed:

- for low soluble molecules such as aclonifen during the rising water period due to the maximum contribution of mechanical erosion and surface runoff,
- for soluble molecules such as metolachlor during the recession period (falling water period) due to the maximum contribution of soil leaching and subsurface flows.

This study is centred on putting forward the essential parameters for accurate theoretical model of pesticide's transport into aquatic ecosystems. Understanding the role and influence of TSM, POC and DOC parameters are, therefore needed in introducing such a model.

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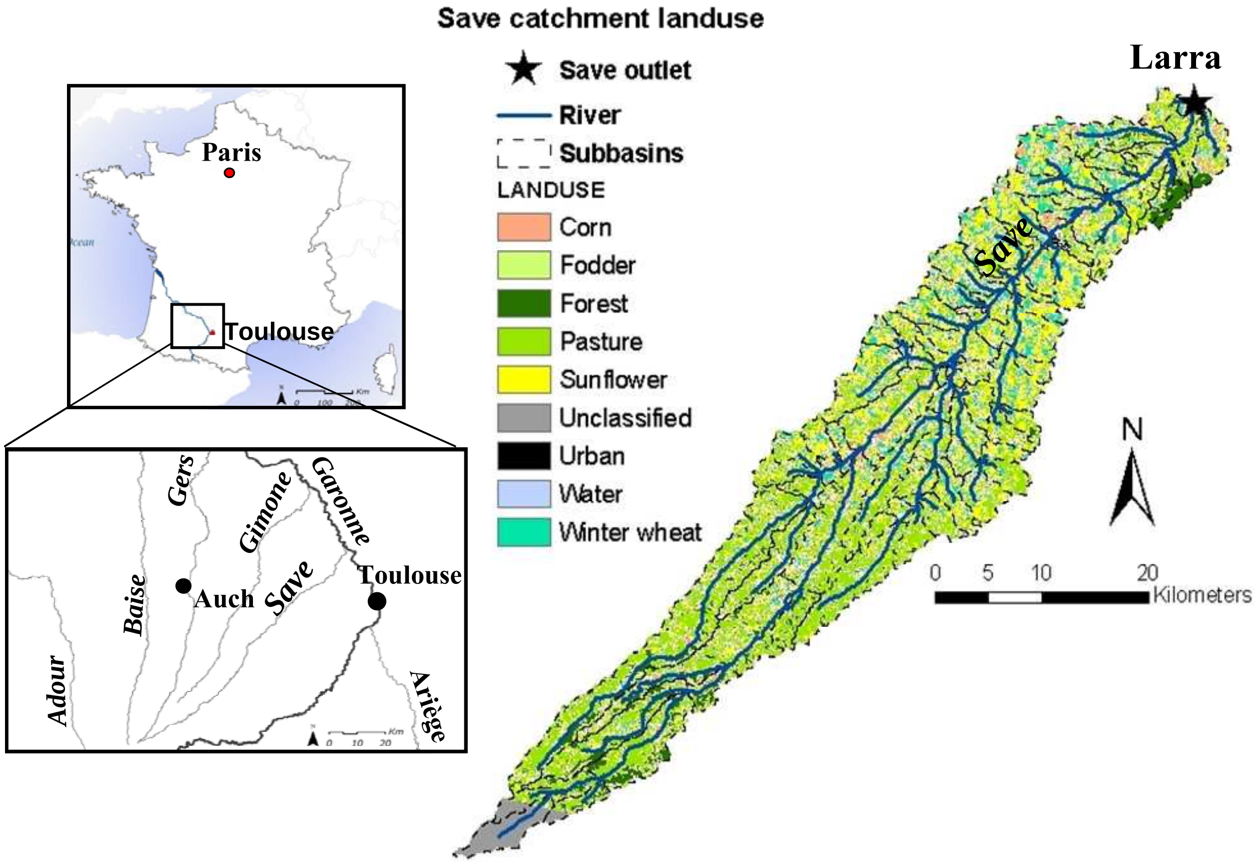
Figure 1



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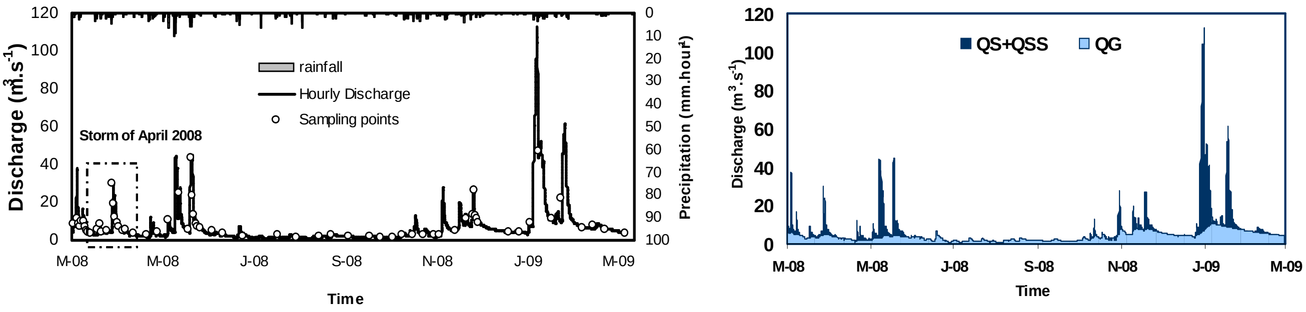

Figure 3

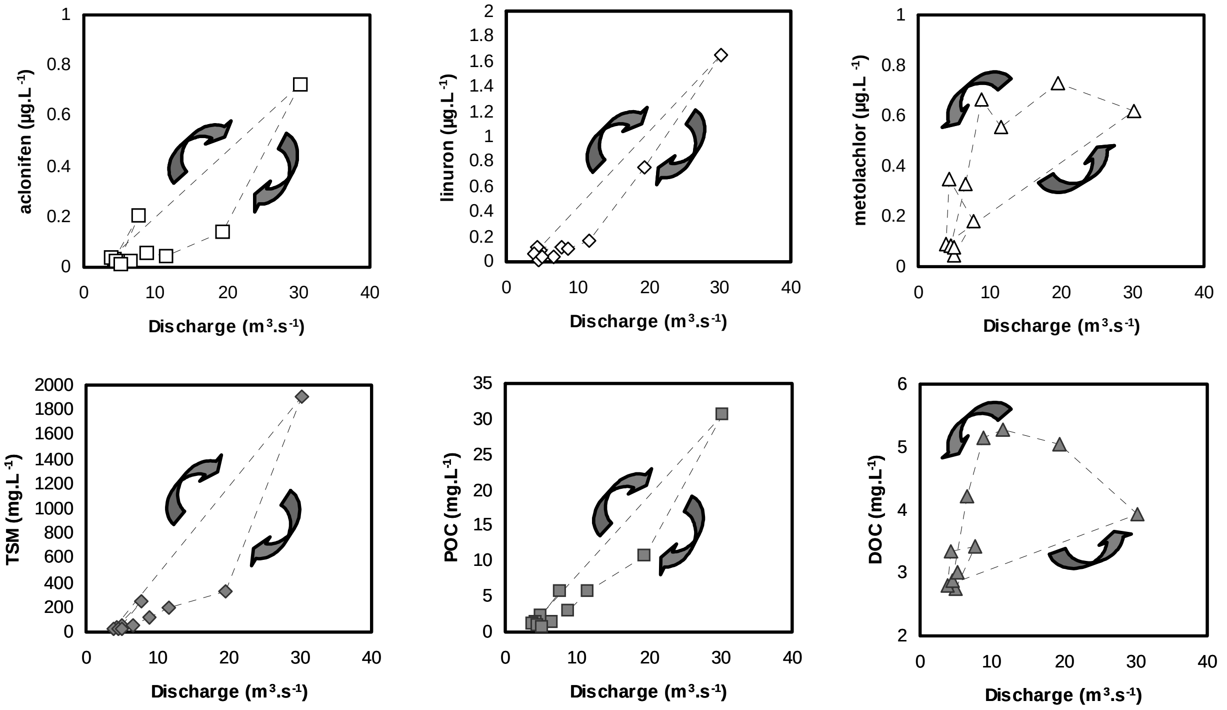

Figure 4

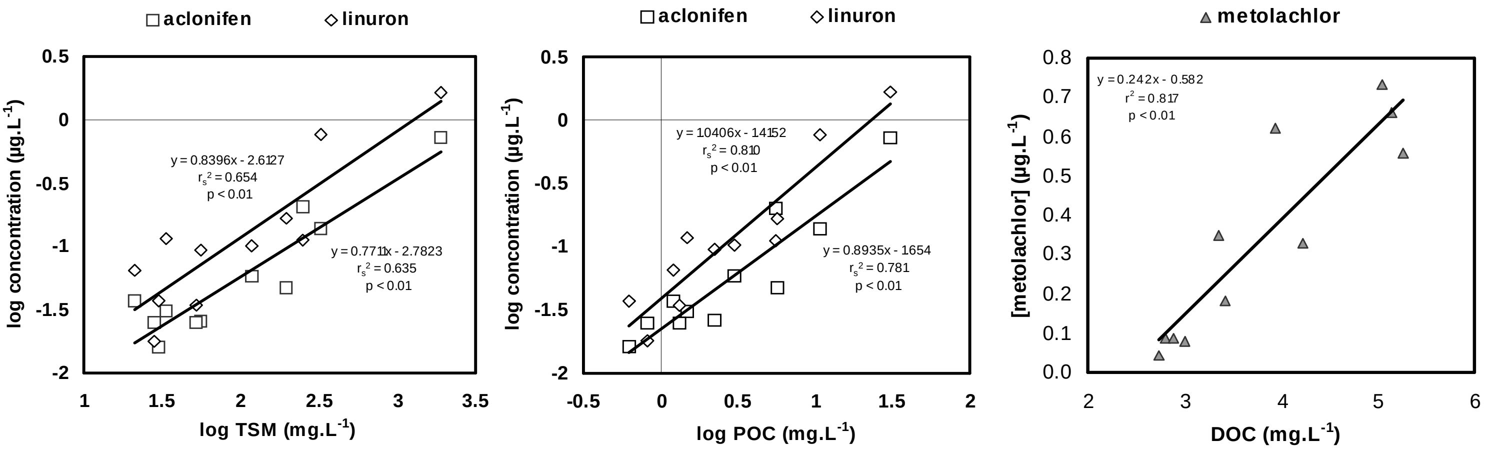

Table 1

Molecules	Type	Number of detection during whole period (n=65)	% DF during whole period	Number of detection during stormy periods (n=41)	% DF during storm events	Average C (µg.L^{-1})	**Maximum C (µg.L^{-1})**
chlortoluron	Herbicide	64	98	40	98	0.391	**1.97**
isoproturon	Herbicide	62	95	40	98	0.144	**1.16**
linuron	Herbicide	58	89	37	90	0.270	**1.65**
metolachlor	Herbicide	64	98	40	98	0.197	**0.95**
alachlor	Herbicide	46	71	28	68	0.007	**0.05**
aclonifen	Herbicide	60	92	39	95	0.144	**1.34**
trifluralin	Herbicide	54	83	34	83	0.076	**0.51**
fenpropimorph	fungicide	53	82	36	88	0.004	**0.02**
fluzilazol	fungicide	65	100	41	100	0.010	**0.07**
cyproconazol	fungicide	50	77	29	71	0.020	**0.12**
tebuconazol	fungicide	63	97	40	98	0.255	**0.778**
epoxiconazol	**fungicide**	**65**	**100**	**41**	**100**	**0.165**	**0.11**

DF: Detection Frequency
C: Concentration

Table 2

Period	Duration (Day)	Chl %	Iso %	Lin %	Met %	Ala %	Acl %	Tri %	Fen %	Flu %	Cyp %	Teb %	Epo %	TSM %	DOC %	**Volume of water %**
Storm flow	142	73.4	59.2	86.2	88.6	76.6	90.1	74	72.8	67.6	86	80.2	77	94.2	71	**63.9**
Baseflow	**223**	**26.6**	**40.8**	**13.8**	**11.4**	**23.4**	**9.9**	**26**	**27.2**	**32.4**	**14**	**19.8**	**23**	**5.8**	**29**	**36.1**

Here are the abbreviated symbols of the 12 molecules under observation: trifluralin (Tri), aclonifen (Acl), fenpropimorph (Fen), tebuconazol (Teb), fluzilazol (Flu), epoxiconazol (Epo), alachlor (Ala), linuron (Lin), cyproconazol (Cyp), metolachlor (Met), Isoproturon (iso), Chlortoluron (c

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Pesticide transfers in a small agricultural catchment (Aurade, south west of France) during flood flows: partitioning into dissolved and particulate fractions

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Abstract - Pesticide transfer dynamic is studied during 2 flood events in a small experimental catchment close to Toulouse (South West of France). 16 to 25 pesticide molecules (herbicides, fungicides) have been analysed by multi-residue technique on filtered and unfiltered waters and on bottom sediments. The results show very high pesticide concentrations in the different fractions compared to low flow periods and to the data collected by the French institutional networks in charge of the pesticide river water pollution survey. Several molecules present concentration higher than 0.1 µg/L and even higher than 1 µg/L in the unfiltered waters. In the suspended matters and in the bottom sediments, the concentrations vary respectively between 0.1-30 µg/g and 0.01-1 µg/g according to the molecules. All the molecule concentrations increase during the flood flows and present positive relationship with the stream discharge, but hysteresis between rising and falling periods can be observed for some molecules. Pesticide concentrations in unfiltered waters are generally controlled by dissolved organic carbon (DOC) content and total suspended matter (TSM) concentration. Partitioning between dissolved and particulate (K_d) fractions is also controlled by DOC, and TSM. A good negative relationship can be established between log K_d and log K_{ow} for 6 molecules.

Keywords fungicide, herbicide, stream waters, suspended matter, bottom sediments, dissolved organic carbon

Introduction

Pesticides are mainly exported during flood flows which are very short temporal events but very intense in the Gascogne region (South West of France) which is intensively cultivated (mainly corn, wheat and sunflower). A few data are available on pesticide concentrations in the rivers of this region. The data that are only available are collected by the French institutional networks (GRAMIP and French Water Agency Adour-Garonne) in charge of the pesticide river water pollution survey and they concern mainly the unfiltered waters, but these data never concern the flood periods. Moreover only a few studies have been devoted all around the world to pesticide transfer dynamic on catchment during flood events (Borah et al., 2003; Smalling et al., 2007). The main objective of this study is first to determine the concentration levels of pesticides in the different fractions during the flood events, their spatial variations among the whole catchment (10 stations) and their temporal variations at the outlet. It is also to determine their relationships with the stream discharge variations and to assess the role of the main controlling factors (pH, conductivity, DOC, TSM) on their variations and on the partition coefficient (K_d) of the different pesticide concentrations between the dissolved and the particulate fractions. Finally, it is to check if there is a relationship between the Kd estimated from field measurements and the octanol-water partition coefficient (K_{ow}) given in the literature for the different molecules.

Material and methods

This investigation is performed in the Gascogne region (South West of France) on the experimental catchment of Auradé (35 km West of Toulouse) which is drained by the Montoussé creek (fig.1). Its drainage area covers 320 ha, the soils are mainly carbonated and the main culture is wheat and sunflower in rotation. This experimental catchment is studied ever since 2004 by our EcoLab group, but previous pesticide data are available from GRAMIP since 1991.

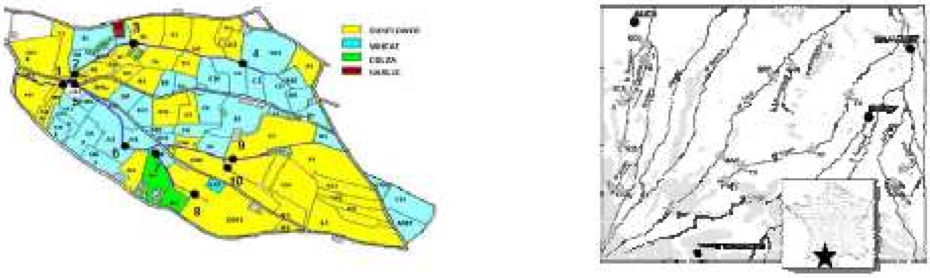


Figure 1- Location map of the Montoussé Catchment (right, black star) and of the different sampling stations (1 to 10) within the catchment (left) from the outlet to the upstream part of the catchment.

Two storm events (March 2006 and May 2008) have been sampled in this catchment. During the first one (Marchand, 2006), one sample (water, suspended matters (SM) and bottom sediments (BS)) per station has been collected at the peak discharge on 10 stations (fig. 1) spatially distributed in the whole catchment according to soil occupation. During the second one (Taghavi, in preparation) 12 samples (unfiltered and filtered waters) have been collected during the whole period of the event at the outlet of the catchment. The bottom sediments have been sieved at 2 mm (coarse fractions) and 63 µm (fine fractions) and pesticides have been extracted with hexane and acetone by using a Dionex ASE200. Filtered (at 0.45 µm) and unfiltered (with addition of dichloromethane) waters were collected in glass bottles and stored in dark conditions. The extraction was made with a shake flask using dichloromethane p.a.. The samples have been analyzed on a Thermo-Finnigan TraceDSQ GC-MS by using a multi-residue technique developed by our research group (Devault et al., 2007). Finally, 16 to 25 molecules (herbicides, fungicides) have been analysed by this technique on filtered and unfiltered waters and on bottom sediments. The detection limit is 0.01 µg/L in water and 0.001 µg/g for BS and SM, except for metobromuron and metazachlor (0.01-0.005 µg/g). The mean recovery for a spiked reference material (IRMM-443 Eurosoil 4) is 95.4±6.5%.

Results and discussion

Spatial variations of the concentrations in the different fractions

The results obtained during the flood of March 2006 show the spatial distribution of the different molecules in the different fractions (unfiltered water, suspended matter (SM) and bottom sediments (BS)). The pesticide concentrations are very high in the different fractions compared to low flow periods and to the data collected by the French institutional networks in charge of the pesticide river water pollution survey. Several molecules present concentration higher than 0.1 µg/L (aclonifen, atrazine desethyl, tebuconazole) and even higher than 1 µg/L (metobromuron, isoproturon, chlorotoluron, pendimethalin, terbuthylazine) in the unfiltered waters (fig.2). The concentrations are generally higher at the outlet, but few variations can be observed on the other stations.

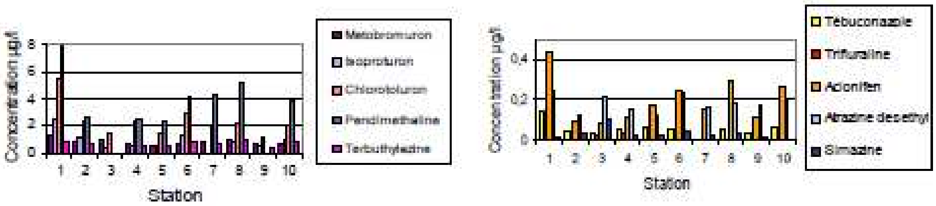


Figure 2- Spatial variations of pesticide concentrations in the unfiltered waters at the outlet of the Montoussé catchment during the peak discharge of March 2006 event. The station numbers correspond to those of the map (fig.1).

In the suspended matters (fig.3 left) and in the bottom sediments (fig.3 right), the concentrations vary respectively between 0.1-30 µg/g (highest values for pendimethalin>metobromuron) and 0.01-1 µg/g (highest values for chlorotoluron>epoxiconazole>tebuconazole>DEA>terbuthylazine>hexazinone) according to the molecules.

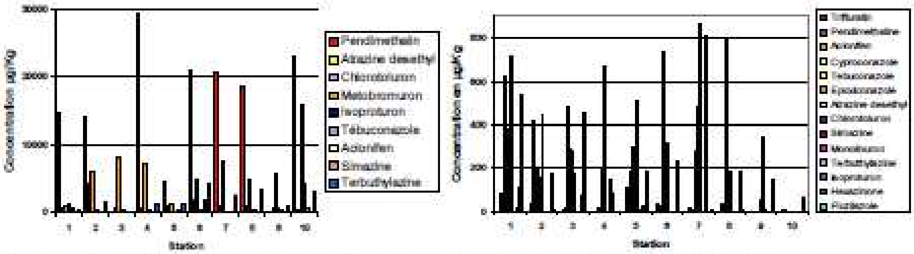


Figure 3- Spatial variations of pesticide concentrations in SM (left, >0.45 µm) and BS (right, <63 µm) at the outlet of the Montoussé catchment during the peak discharge of March 2006 event. The station numbers correspond to those of the map (fig.1).

It appears clearly that there are 2 orders of magnitude between pesticide contents in SM and BS. Moreover the highest concentration values do not concern the same molecules in SM and BS. Concerning SM, the spatial variations of pesticide contents are very low. On the contrary for BS the concentrations generally increase from upstream to downstream (except station 7 due to Colza).

Temporal variations of pesticide concentrations in the unfiltered waters at the outlet

DOC, TSM and all pesticide concentrations increase during the flood with increasing discharge (fig. 4 and 5). Nevertheless, there is a lag between the peak discharge and the maximum concentration of DOC, TSM and pesticide contents. It can be observed in figure 4 that TSM concentrations reach the maximum before the DOC content but decrease more rapidly than the DOC which remains relatively high during the recession period. Linuron and aclonifen concentrations follow respectively the same pattern than TSM and DOC.

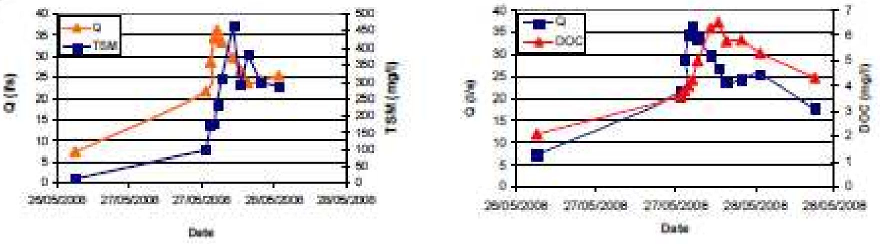


Figure 4- Temporal variations of stream discharge compared to TSM (left) and DOC (right) concentration fluctuations during May 2008 flood event at the outlet of the Montoussé catchment.

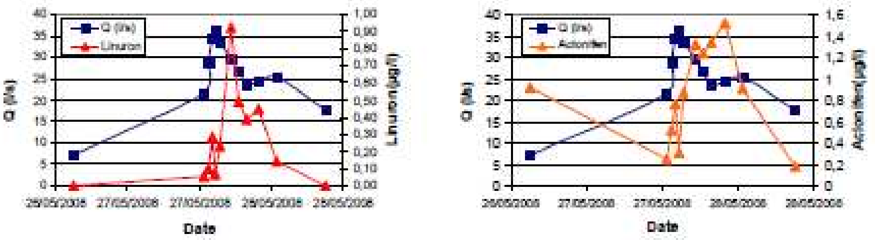


Figure 5- Temporal variations of stream discharge compared to linuron (left) and aclonifen (right) concentration variations during May 2008 flood event at the outlet of the Montoussé catchment.

Consequently, as seen in figure 6, the concentrations are higher during the falling discharge than during the rising period, showing an hysteresis between the two hydrological periods. That means that DOC and most of the pesticides are mainly exported by the subsurface runoff (as already shown by Probst (1985) for nitrates in the Garonne basin) which reaches its maximum after the stream discharge peak rather than by the surface runoff which generally reaches its peak before or during the maximum stream discharge.

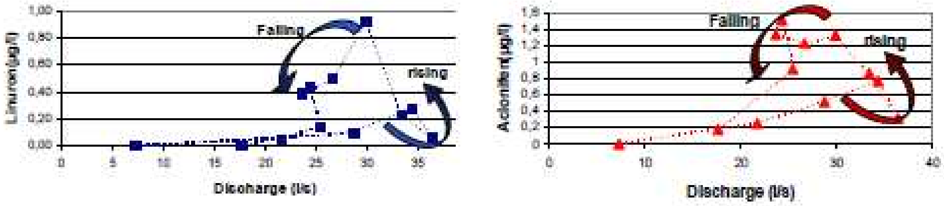


Figure 6- Relationships between linuron (left), aclonifen (right) concentrations and stream discharge during May 2008 flood event at the outlet of the Montoussé catchment.

Controlling factors and partitioning between dissolved and particulate fractions

DOC and TSM are two parameters very well known to controlling pesticide concentrations (Gao et al. 1998; Worral et al. 1999). According to the molecule, particularly to their solubility and partition coefficients (K_{ow} (octanol/water) and K_{oc} (organic carbon/water)), very significant relationships can be observed between TSM concentration or DOC content and pesticide concentration, like for linuron or aclonifen respectively. Some other molecules like pendimethalin, metolachlor and epoxiconazole are significantly correlated both with DOC and TSM.

For the flood event of March 2006, one has calculated for each molecule the partition coefficient (K_d) between dissolved and particulate fractions. There are good negative relationships between K_d and TSM concentrations for tebuconazole, metobromuron, pendimethalin, terbuthylazine and chlorotoluron (fig. 7 left) showing that the adsorption of these molecules onto particulate phases increases with increasing TSM concentrations. On the contrary, for tebuconazole, DEA, pendimethalin, terbuthylazine and chlorotoluron, K_d values increase with increasing DOC contents, showing that these molecules are highly complexed by the DOC.

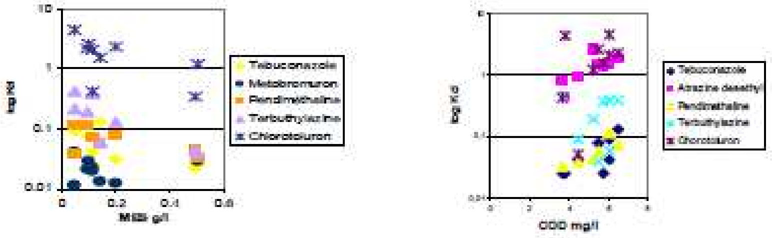


Figure 7- Relationships between log K_d and TSM concentrations (left), and DOC contents (right) during March 2006 flood event at the outlet of the Montoussé catchment.

Other physico-chemical parameters like pH and conductivity seem to have no influence in that case on the K_d values probably because pH (7.9-8.3) and conductivity (500-800 µS/cm) are relatively high and low variable in such a carbonated environment. Finally, as seen in figure 8, there is a good relationship between the K_d one could calculate from field measurements and the K_{ow} values published in the literature for the different pesticide molecules, except for metobromuron for which the K_d is very low in such a catchment.

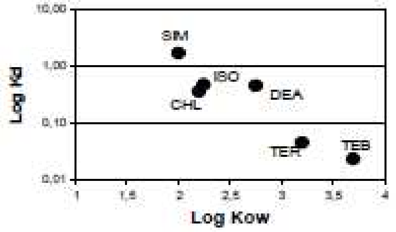
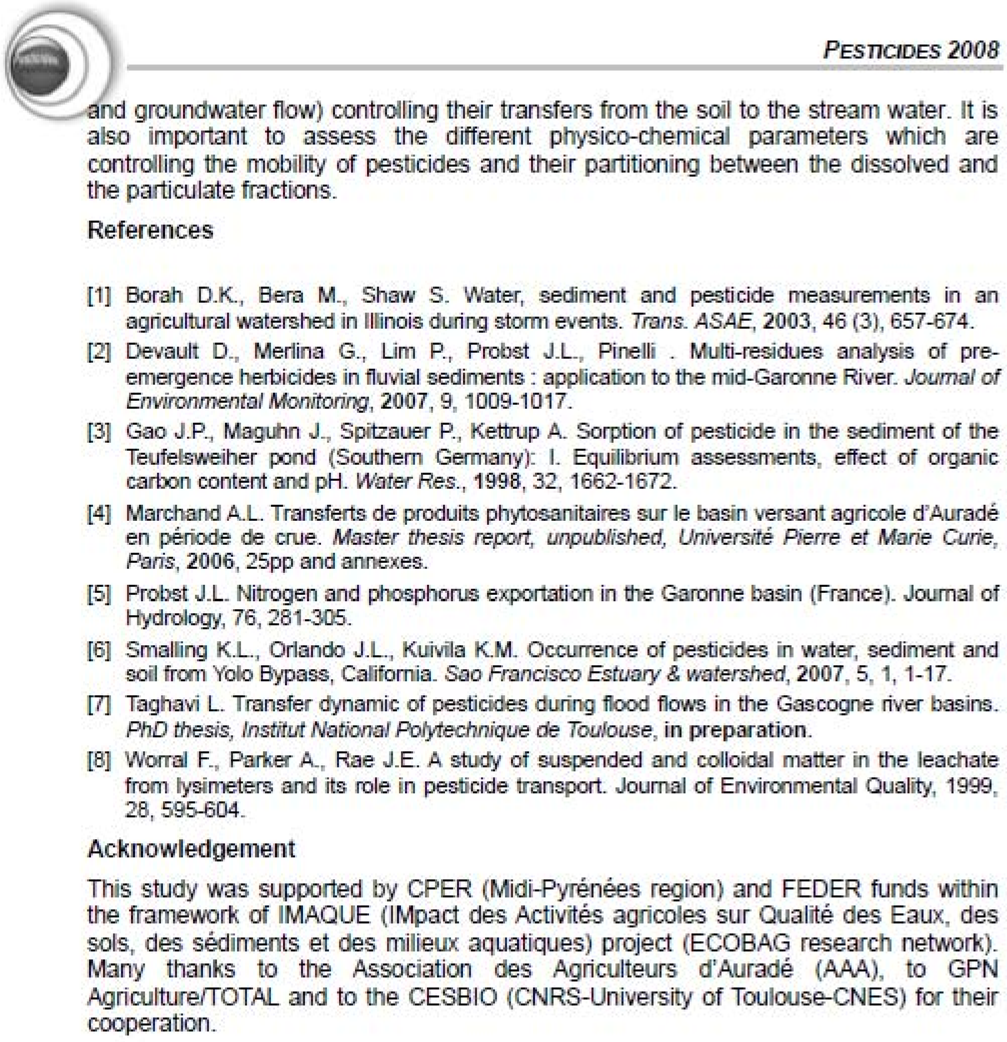


Figure 8- Relationships between log K_d and log K_{ow} during March 2006 flood event at the outlet of the Montoussé catchment. SIM: simazine, CHL: chlorotoluron, ISO: isoproturon, DEA: desethyl atrazine, TER: terbuthylazine, TEB: tebuconazole.

Conclusions

This study shows that the flood flows can be taken into account in the transfer of pesticides because all the molecules measured during these events present high to very high concentrations in the different fractions, leading to very high fluxes exported at the outlet of the catchment. The contribution of these periods to the annual exportation by the stream is very important. These hydrological periods are also very important to better understand the transfer dynamic of these molecules and particularly, to determine the main hydrological processes (runoff, subsurface runoff



and groundwater flow) controlling their transfers from the soil to the stream water. It is also important to assess the different physico-chemical parameters which are controlling the mobility of pesticides and their partitioning between the dissolved and the particulate fractions.

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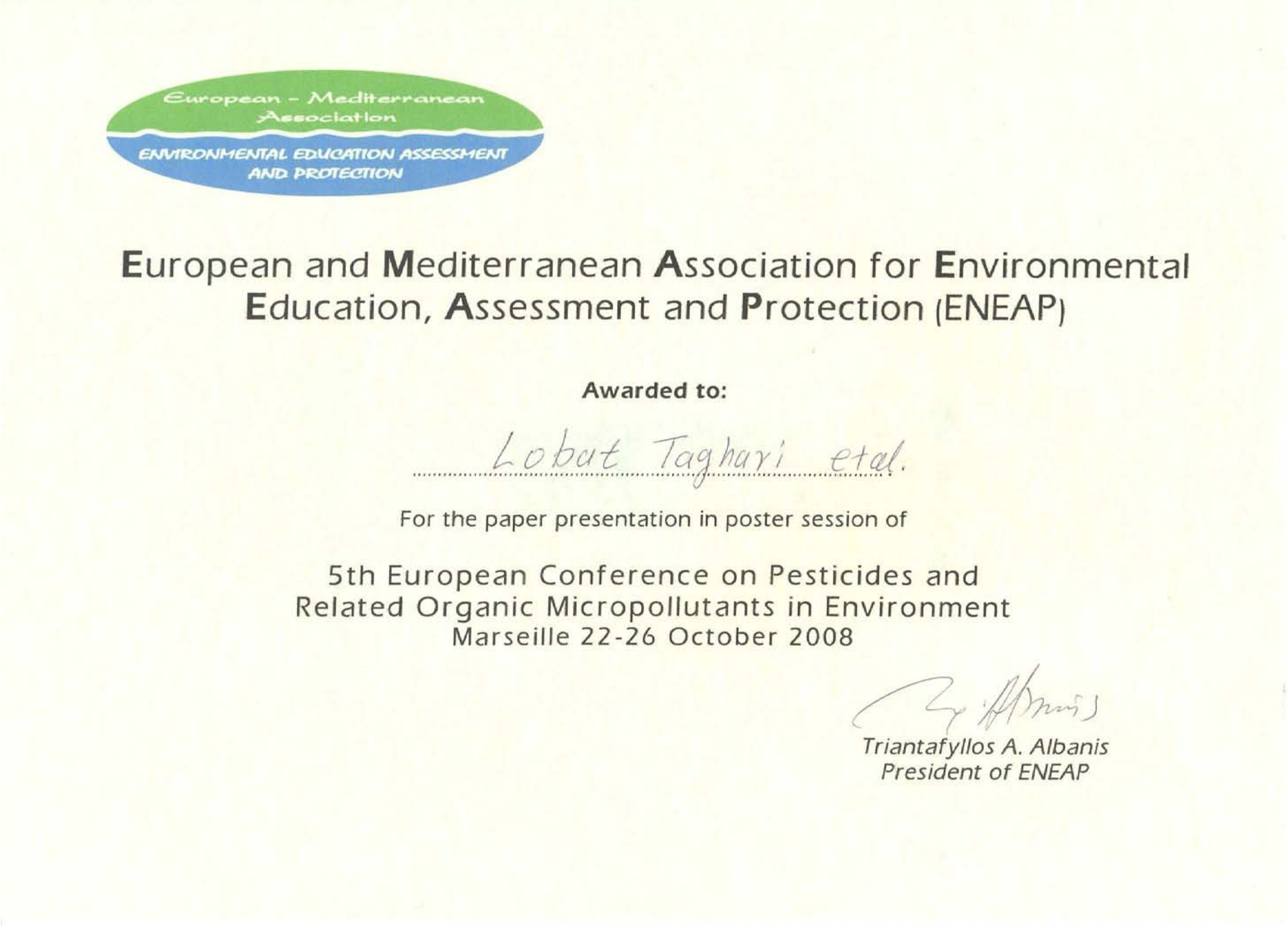

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Annexe V (d)- Taghavi et al. 2010. Proceedings 6th European Conference on Pesticides and Related Organic Micropollutants and 12th symposium on chemistry and fate in the Environment, Matera, Italy. (oral presentation)

Contribution of the different stream flow components to the transfer of pesticides in an agricultural watershed (Save, south west of France)

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Abstract

The dynamic of pesticide transfer was observed during the water-year 2008-2009 in an agricultural watershed in the vicinity of Toulouse (South west of France). During the whole period of study, we focussed on storm events. Some fourteen molecules of pesticide (herbicide, fungicide) substances were analysed by multi-residue technique, both in filtered and unfiltered waters. The analyses revealed high pesticide concentrations during storms in comparison to low flow periods and to the data collected by the French institutional networks in charge of pesticide river water pollution survey. Concentrations of a number of molecules registered figures higher than 0.1 $\mu g.L^{-1}$ and even higher than 1 $\mu g.L^{-1}$ in unfiltered water. Moreover, a hysteresis pattern could be observed only for some molecules between rising and falling periods of stream discharge. The important role of dissolved organic carbon (DOC) and total suspended matter (TSM) in the pesticide transport was clearly established. We proceeded with hydrograph separation of the main stormflow components so that the main pesticide routing could be traced for its soil-river transfers. We also came to the conclusion that there is a positive relationship between riverine TSM, DOC and pesticide, concentrations and the discharges of surface or subsurface runoffs according to pesticide properties. Pesticide flux calculation shows between 60 to 90% of the molecule transport takes place during storm periods.

Keyword: pesticide, hydrograph separation, surface runoff, subsurface runoff, hysteresis, total suspended matter, dissolved organic carbon, flux.

Introduction

During the past decades, pesticide contamination in fresh water, has emerged as an important environmental problem and poses a serious threat to aquatic ecosystems, drinking water resources and non-target species [1-2]. Highest concentrations of pesticides in agricultural streams are measured during flood period, when surface and subsurface runoffs become a major mechanism for pesticide transfers from soils to river waters. Higher water contamination during this event has been demonstrated by several authors [3-4-5-6]. The main objective of this study is to determine the concentration level of pesticides in different fractions (dissolved and particulate) and to evaluate their relationships with the different flow components of stream discharge (surface and subsurface runoffs, groundwater) and with the controlling factors such as total suspended matter (TSM), particulate and dissolved organic carbon (POC , DOC). Finally, it is also to determine the contribution of storm periods to the total pesticide fluxes exported by the river at the outlet of the watershed during the study period.

Material and Methods

The Save river located in the "Coteaux de Gascogne" region, drains an agricultural catchment with an area of 1110 km^2. Sampling was conducted at Larra station (01° 14 '40 ''E-43°43 '4'' N), ahead of the confluence of the Save river with the Garonne river. The upstream part of the catchment is a hilly agricultural area mainly covered with pasture and forest (56%), while the lower part is flat and devoted to intensive agricultural activities (44%), mostly wheat, corn and sunflower which make the use of pesticides indispensable. Water sampling in our research started in March 2008 and continued until March 2009. The main sampling months were January to June. During storm periods water sampling were collected daily, whereas out of the rainy season, sampling was done manually each week. In total 65 water samples were collected for analyses on unfiltered and filtered waters. Each water sample was filtered at 0.45µm with Millipore membrane by applying vacuum. The extraction was made with a shake flask using dichloromethane. The samples have been analysed on a Thermo-Finnigan Trace DSQ GC-MS by using multi-residue technique developed by our research group [7]. Finally, 14 molecules (herbicides, fungicides) have been analysed by this technique on unfiltered and filtered waters. The detection limit is 1-3 ng.L^{-1} depending on the molecules and the mean recovery for spiked reference material is 95±6.5%. Graphical method was used to separate stream flow components on the hydrograph [8]. In fact since Maillet (1905) [9], the exponential function $Q_t=Q_0e^{(-at)}$ has been widely used to describe the recession of each stream flow, and to distinguish the contribution of each flow component.

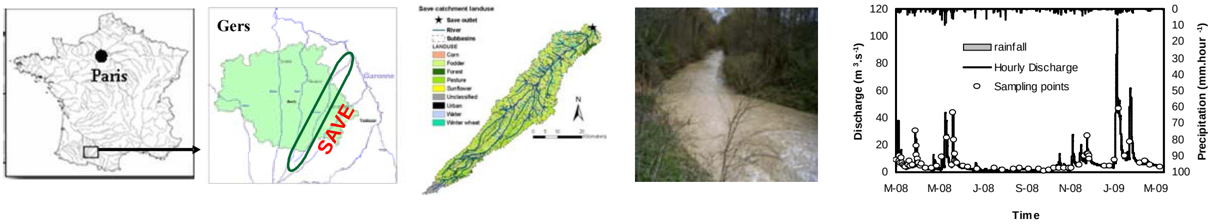

Figure 1- Location map of the Save watershed with star symbol representing outlet of this watershed, and sampling points on discharge hydrograph during the study period 2008-2009.

Results and discussion

6.2 Temporal variation of pesticides

The occurrence of pesticides in water is controlled by myriad factors, including their physicochemical properties, amount and rate of use, amount and intensity of rainfall or irrigation [10]. In this paper we focused our study on aclonifen and metolachlor, as a representative of low and high soluble pesticide molecules with solubility ranging from 1.4 to 488 mg.L^{-1}. As depicted in figure 2, concentrations of aclonifen and metolachlor reached the highest level in April and June, considered as an application period of pesticide. Metolachlor concentration reaches 1 µg.L^{-1} at most and there are few differences between filtered and unfiltered waters. Whereas, the maximum concentration of aclonifen is about 1.4µg.L^{-1} and the difference between unfiltered and filtered water is quite significant. This phenomenon shows an important role of TSM in transport of this molecule. Hydrograph separation was carried out in order to better understand the mechanism of transport of these elements throughout the storm events. In this paper, we focussed on the storm of April 2008, since this period coincides with the time of pesticide application and, moreover, our sampling points nearly covered all of the hydrograph phases (rising and falling limb).

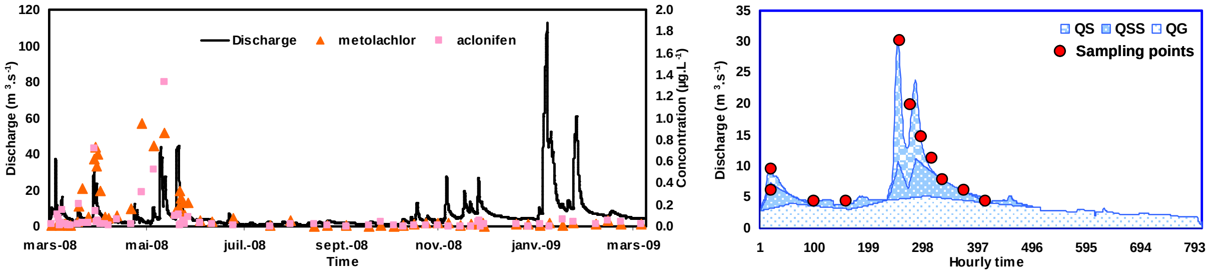

Figure 2- Temporal variations of aclonifen and metolachlor concentrations in unfiltered water (left) during the study period and separation of streamflow components during the April 2008 storm (right): QS (surface runoff), QSS (subsurface runoff) and QG (groundwater). Red circles: sampling periods.

6.3 Discharge – concentration relationships: hysteresis patterns

A biogeochemical interaction in river systems when the discharge is increasing has attracted the attention of a good number of researchers. Cyclic trajectory relationships have been reported between solute concentration and discharge during storm period [11-12]. However, none of these studies have analysed the hysteresis phenomenon on pesticide's concentration, and pesticide transport was rarely observed from this point of view. In fact understanding how discharge is affecting pesticide concentration behaviour help us to follow up the process of their transport. Interpretation of hysteresis phenomenon during a single storm episode is important to understand the origin and the pathway of each pesticide transfer. During April 2008 storm, the interactions of discharge with pesticide concentrations in unfiltered and filtered waters, present two types of hysteresis: clockwise or anticlockwise patterns like for aclonifen or metolachlor respectively. Similar hysteresis patterns were recorded for TSM,and POC (clockwise) and DOC (anticlockwise). And as a matter of fact, the rising limb of the hydrograph coincides with soil saturation and surface runoff. The falling limb corresponds to the draining of different hydrological reservoirs, particularly to the soil leaching [13].

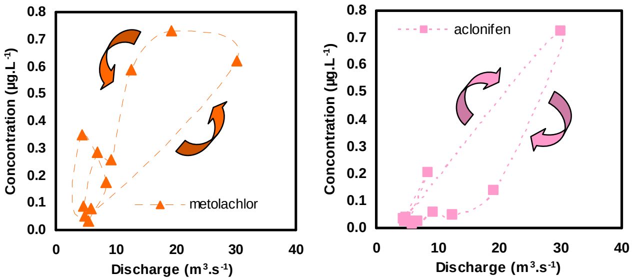

Figure 3- Relationship between aclonifen (right) and metolachlor (left) concentration and stream discharge for the Save river (April 2008 storm event): clockwise or anticlockwise hysteresis patterns.

6.4 Hydrological pathway of pesticide transfer

Hydrograph separation allowed quantifying the contribution of each stream flow component. Then, in order to have a better understanding about the principal pathway for pesticide transfer, we determined the relationship between the discharge of each storm flow component and the riverine pesticide concentration. The latter results show that aclonifen and metolachlor are both of superficial origin but, aclonifen concentration is mainly related to the proportion of surface runoff while metolachlor content is associated to subsurface runoff, (figure 4). There are also good relationships between TSM (r_s^2=0.734, $p < 0.01$) or POC (r_s^2= 0.894, $p < 0.01$) and the contribution (%) of surface runoff to the total discharge, and between DOC (r^2=0.582, $p < 0.01$) and subsurface flow. Probst (1985) and Probst and Bazerbachi, (1986) came to the conclusion that for TSM and the elements of lower degree of solubility, such as phosphorus, the pathway of exportation is surface runoff and mechanical erosion processes, while elements with higher degree of solubility like nitrate for example, the main exportation route is paved by subsurface runoff and soil leaching processes [13-14].

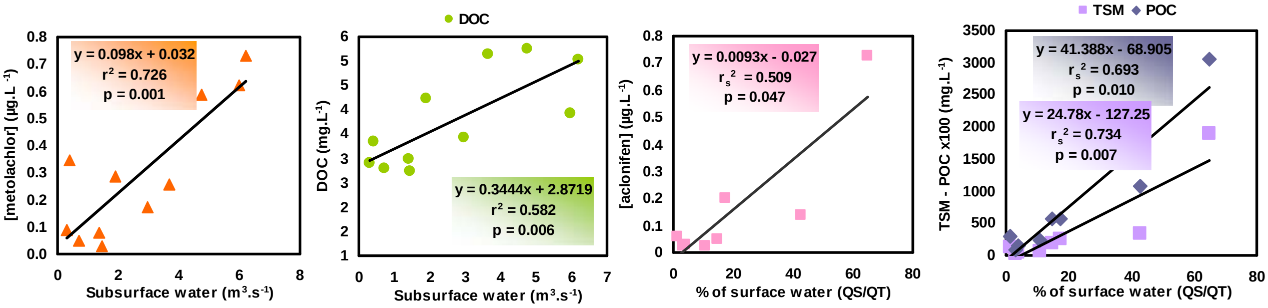

Figure 4- Relationships between metolachlor and DOC concentration with subsurface runoff discharge (left), and between aclonifen , TSM and POC concentration with surface runoff contribution (%) to the total river discharge (right).

6.5 Role of controlling factors (TSM, POC and DOC)

When pesticide is introduced into the environment, a large proportion of the pesticide gets transported to various environmental compartments. Pesticide behaviour and their partitioning between dissolved and particulate fractions depends not only on their physical-chemical properties but also on their degree of adsorption onto particulate phases (TSM) and on their complexation by dissolved phases such as DOC [6-15]

The results obtained in this study exhibit good log-log relationships between the aclonifen concentration and TSM or POC, while metolachlor as soluble molecule shows a good linear relationship with DOC (figure 5). These results confirm previous studies showing the important role of particulate and dissolved phases in the transport of pesticide molecules such as aclonifen, linuron and atrazine [6-16].

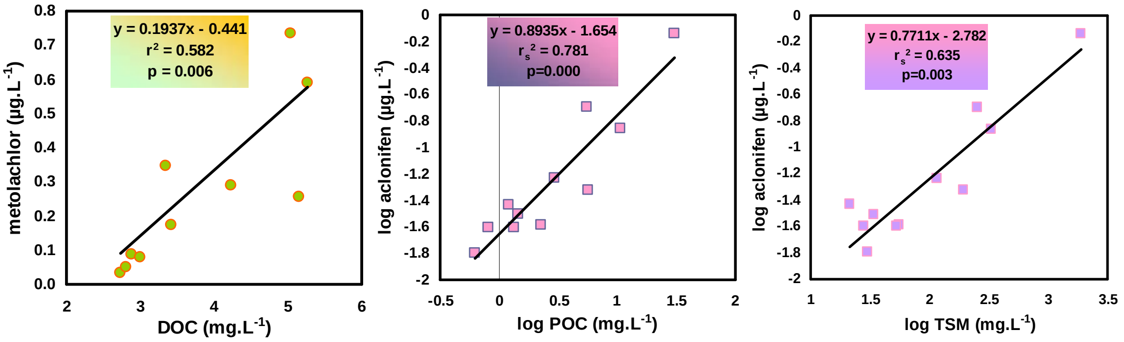

Figure 5- Relationships between metolachlor concentration and DOC content (left) and between, aclonifen concentration and POC (center) or TSM (right) for the Save river at Larra during the storm of April 2008.

6.6 Calculation of pesticide flux

The fluxes of pesticide, TSM and DOC are calculated for each sampling interval (i to i+1) as the product of discharge weighted concentration C (Ci to i+1= $(C_iQ_i+C_{i+1}Q_{i+1})/(Q_i+Q_{i+1})$) and river discharge (Q) between i and i+1. The storm event fluxes and the annual fluxes are calculated by summing the fluxes of the different intervals (i to n)... The results obtained shows the importance of storm events in the transport of pesticide, since 60 to 90% of pesticide fluxes, according to the molecules, and more than 70% of TSM and DOC are exported during these periods. Low soluble molecules ($S_w < 40$ mg.L^{-1}) such as epoxiconazole, tebuconazole, fenpropimorph, trifluralin, and aclonifen, are mainly exported in the particulate fractions (more than 50%) while soluble molecules such as metolachlor and alachlor are mainly exported in the dissolved fractions.

Conclusions

This case study contains a detailed account of pesticide transfer by flood flows during a year-length observations. All the molecules measured during these episodes present high to very high concentrations in the different fractions leading to very high fluxes at the outlet of the watershed. A hydrograph separation of stormflow components shows the important role of the surface runoff in transferring low soluble molecules, POC and TSM, while molecules with higher degree of solubility and DOC are transferred by subsurface runoff. Our findings reveal also over 60% flux of pesticide is attributed to storm waters and total load of DOC and TSM reaches 70% during storm events.

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Annexe V (e)- Taghavi et al. 2010. Proceedings 6th European Conference on Pesticides and Related Organic Micropollutants and 12th symposium on chemistry and fate in the Environment, Matera, Italy. (poster)

Pesticide transfer dynamic in an agricultural watershed (Save-South west of France): contribution of the flood flows to the total fluxes.

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Abstract- The fluxes of pesticide are calculated during the water year 2008-2009 in the Save watershed close to Toulouse (South West of France). Hydrograph separation technique was used to evaluate the contribution of storm and baseflow in transporting of 12 molecules of pesticides. Transport of over 60 % of pesticide during storm episodes indicates the importance of this period in pesticide displacement. The analyses of pesticides both in filtered and unfiltered water enabled us to estimate the contribution of particulate and dissolved phases. Moreover, the pesticide flux values allow calculating average partition coefficients k_d between dissolved and particulate phases which present good relationship with Kow values (octanol-water) extracted from literature. The percentage of each pesticide transported as particulate forms is well correlated to K_{ow} and to the solubility Sw of each molecule.

Keywords: Flux- separation of hydrograph- pesticide- dissolved and particulate fractions- partition coefficients K_{ow} and K_d, solubility S_w.

1 Introduction

Increasing environmental awareness has generated concerns regarding the impact of pesticides on aquatic ecosystem especially during storm period by runoff. The previous studies pointed out runoff as a key process of pesticide contamination of surface water in agricultural area [1]. The objective of this study is to estimate the contribution of runoff during storm period in pesticide's transport. Subsequently, it is to determine the contribution of pesticides' fluxes in particulate or dissolved phases and finally, to establish a relationship between the proportion of pesticide in particulate phase with the value of K_{ow} and solubility that is listed in literature.

2 Material and Methods

The Save river, located in the Coteaux de Gascogne region (South West of France), drains an agricultural watershed of 1110 Km^2 , mainly devoted to intensive agricultural activities (wheat, corn and sunflower). The monitoring period extends from March 2008 to March 2009 at the outlet (Larra station) of Save watershed. Throughout this period 41 samples, out of total of 65, were collected during flood periods. Daily Sampling was done during storm events and out of the flooding period, water samples were collected manually each week. The samples have been analysed on a Thermo-Finnigan Trace DSQ GC-MS by using multi-residue technique [2,3]. Graphical method was used to separate streamflow components [4].

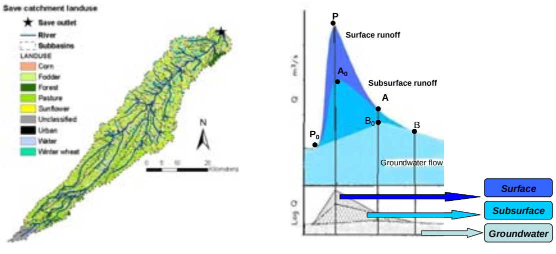

Figure 1- Location map of the Save watershed with star symbol representing outlet of this watershed (left), and separation hydrograph technique (right) based on Maillet's equation ($Q_t=Q_0e^{-at}$) for recession period.

3 Result and Discussion

3.1 Flux calculation

The fluxes of pesticide, TSM and DOC are calculated following the method proposed by [5]. For each sampling interval (i to i+1), the flux is the product of discharge weighted concentration C (Ci to i+1= (CiQi+Ci+1Qi+1)/(Qi+Qi+1)) and river discharge (Q) between i and i+1. The storm event fluxes and the annual fluxes are calculated by summing the fluxes of the different intervals (i to n).

3.2 Contribution of storm periods

The contribution of storm events is estimated by hydrograph separation technique during the whole study period. The results show the important role of storm episodes in transporting of pesticides when 63% volume of water is displaced in these periods. More than 60% of pesticide's displacement, according to the molecules, occurs during storm events. Pesticide concentration in particulate fractions during all of the storm events was estimated as concentration difference between unfiltered and filtered waters. Three pesticide molecules with different degree of solubility have been selected to show their distribution between dissolved and particulate transport during the whole study period: aclonifen (low solubility, S_w=1.4), linuron (moderate solubility, S_w=63.5) and metolachlor (high solubility, S_w=488). The results show that for aclonifen the contribution of dissolved phase is almost negligible, and if we analyse this type of molecules only in filtered water, the riverine aclonifen fluxes are largely underestimated, confirming the suspended sediment serves as a transport vector for adsorbed contaminants such as hydrophobic pesticides [3,6]. Transport of molecules with moderate solubility is well distributed between particulate and dissolved phases according to the nature and the quantity controlling factors such as TSM, POC and DOC. Finally, molecules with high solubility are mainly transported by the dissolved fractions.

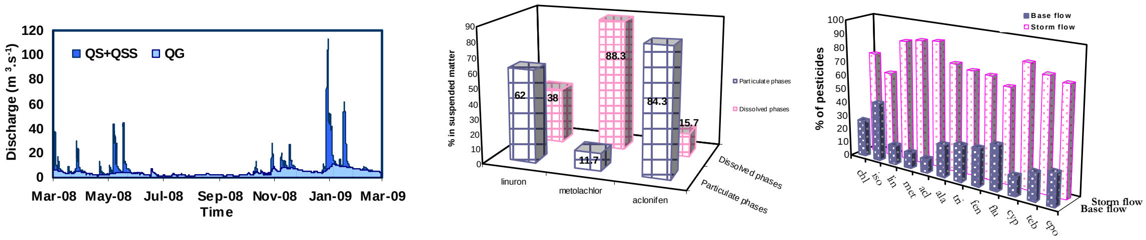

Figure 2–Separation of storm (Q_S and Q_{SS}) and base (Q_G) flows during monitoring period (left), contributions of particulate and dissolved phases to the transports of linuron, metolachlor and aclonifen (centre), and contributions of storm events and baseflow periods to the riverine transport of pesticides (right)[1].

3.3 Relationship between K_d and K_{ow} and role of K_{ow} and S_w on the particulate transports

Pesticide partitioning into dissolved and particulate fractions depends on the pesticide's properties and characteristics of the fractions. In Save watershed, K_d values (K_d (g.L^{-1}) = $C_{dissolved}$ (µg.L^{-1})/$C_{particulate}$ (µg.g^{-1}) [3]) are calculated for all of the storm events from flux values, and K_{ow} values is taken from the pesticide manual [7]. The relationship between log K_{ow} and log K_d (fig. 3 left) shows that when K_{ow} increases, the contribution of particulate phases will increase, and pesticide molecules have more affinity to be adsorbed onto suspended matters. Significant relationships can also be observed between the % of pesticide in particulate fractions and K_{ow} (centre) or solubility, S_w (right). All these models enabled us to estimate the proportion of pesticide in particulate fractions in the Save and alike watershed with a similar physico-chemical characteristic such as pH (8.2 ± 0.2), EC (482 ± 190 µS.cm^{-1}), TSM (349 ± 621mg.L^{-1}), DOC (4.2 ± 1.3mg.L^{-1}), with an annual flux of TSM and DOC 83281and 821 tonnes.

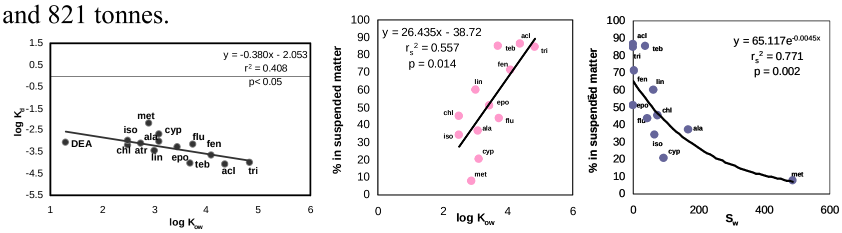

Figure 3- Relationships between log K_d and log K_{ow} (based on flux calculation) (left), the % of pesticides in particulate fractions and K_{ow} (centre) or solubility, S_w (right) values during storm periods at the outlet of Save watershed.

4 Conclusion

High degree of concentration and fluxes of the molecules studied highlight the major role in pesticide's displacement by flooding events. An important amount of pesticide load is missed when only filtered water is analyzed particularly for low soluble molecules. Transfer functions could be established between K_{ow} and S_w extracted from literature and the partitioning of pesticides between dissolved and particulate fractions measured in the Save river. These equations are useful for pesticide riverine transport modelling.

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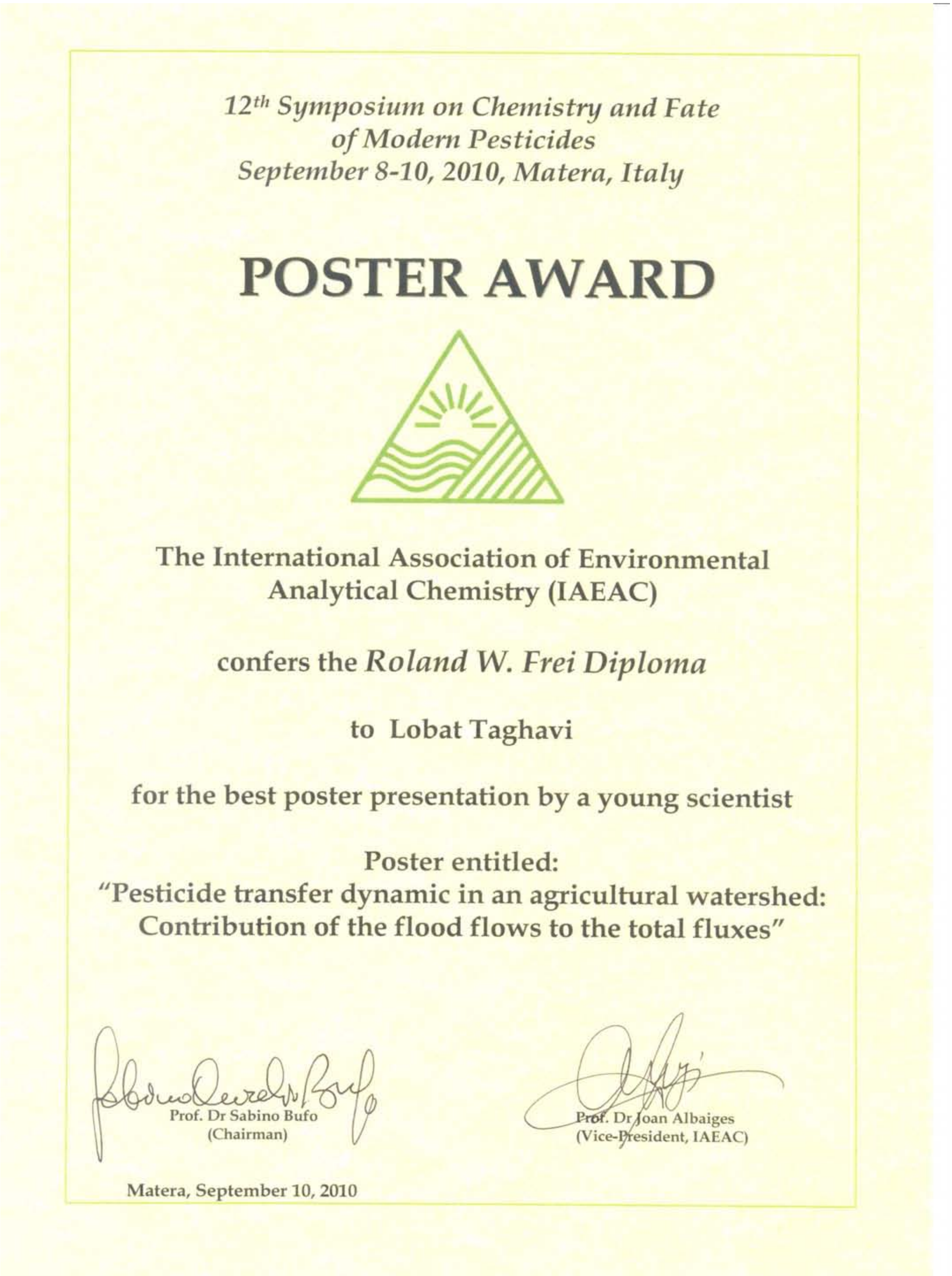
[1] **Here are the abbreviated symbols of the 14 molecules under observation: Trifluralin (tri), aclonifen (acl), fonpropimorph (fen), tebuconazole (teb), fluzilazol (flu), epoxiconazole (epo), alachlor (ala), linuron (lin), cyproconazole (cyp), atrazine (atr), metolachlor (met), isoproturon (iso), chlrotoluron (chl), desethyl atrazine (DEA).**



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POSTER AWARD

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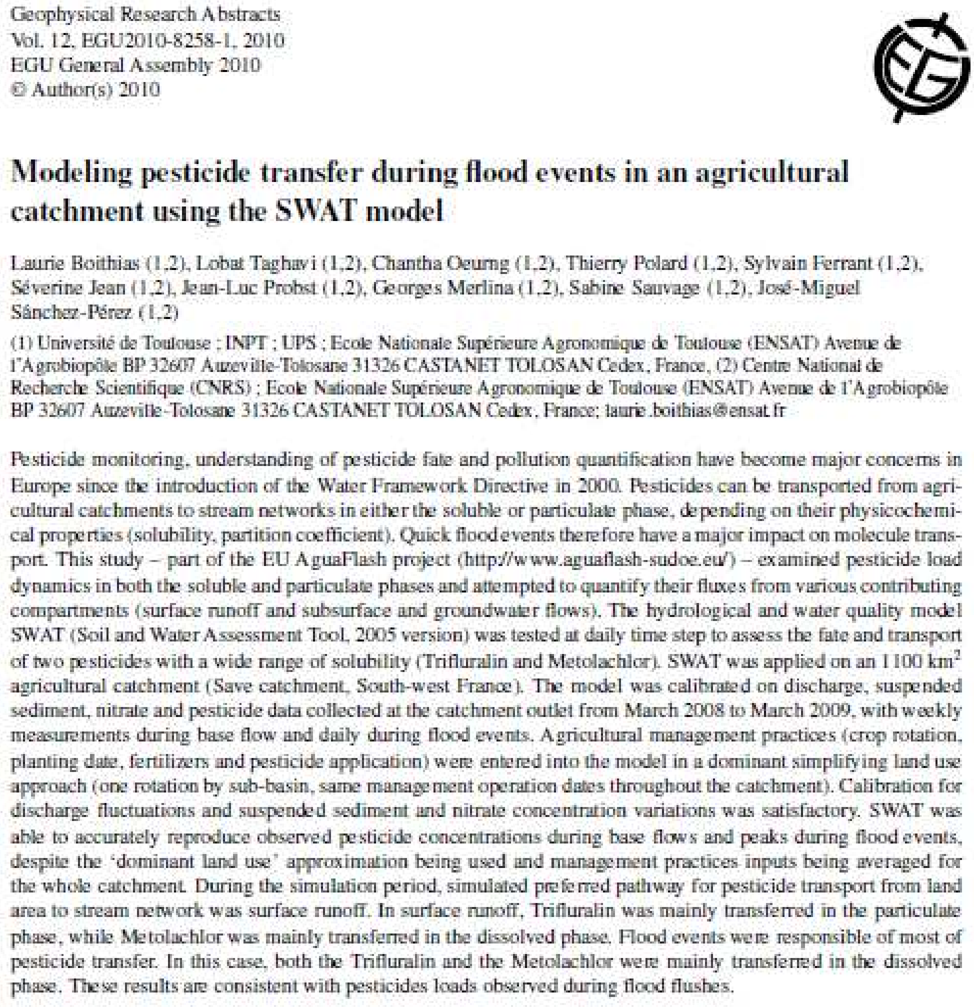
Poster entitled:
"Pesticide transfer dynamic in an agricultural watershed:
Contribution of the flood flows to the total fluxes"

Prof. Dr Sabino Bufo
(Chairman)

Prof. Dr Joan Albaiges
(Vice-President, IAEAC)

Matera, September 10, 2010

Annexe V (f)- Boithias et al. 2010. Proceedings European Geosciences Union (EGU), Vienne, Autrich. (poster)



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Modeling pesticide transfer during flood events in an agricultural catchment using the SWAT model

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Pesticide monitoring, understanding of pesticide fate and pollution quantification have become major concerns in Europe since the introduction of the Water Framework Directive in 2000. Pesticides can be transported from agricultural catchments to stream networks in either the soluble or particulate phase, depending on their physicochemical properties (solubility, partition coefficient). Quick flood events therefore have a major impact on molecule transport. This study – part of the EU AguaFlash project (http://www.aguaflash-sudoe.eu/) – examined pesticide load dynamics in both the soluble and particulate phases and attempted to quantify their fluxes from various contributing compartments (surface runoff and subsurface and groundwater flows). The hydrological and water quality model SWAT (Soil and Water Assessment Tool, 2005 version) was tested at daily time step to assess the fate and transport of two pesticides with a wide range of solubility (Trifluralin and Metolachlor). SWAT was applied on an 1100 km^2 agricultural catchment (Save catchment, South-west France). The model was calibrated on discharge, suspended sediment, nitrate and pesticide data collected at the catchment outlet from March 2008 to March 2009, with weekly measurements during base flow and daily during flood events. Agricultural management practices (crop rotation, planting date, fertilizers and pesticide application) were entered into the model in a dominant simplifying land use approach (one rotation by sub-basin, same management operation dates throughout the catchment). Calibration for discharge fluctuations and suspended sediment and nitrate concentration variations was satisfactory. SWAT was able to accurately reproduce observed pesticide concentrations during base flows and peaks during flood events, despite the 'dominant land use' approximation being used and management practices inputs being averaged for the whole catchment. During the simulation period, simulated preferred pathway for pesticide transport from land area to stream network was surface runoff. In surface runoff, Trifluralin was mainly transferred in the particulate phase, while Metolachlor was mainly transferred in the dissolved phase. Flood events were responsible of most of pesticide transfer. In this case, both the Trifluralin and the Metolachlor were mainly transferred in the dissolved phase. These results are consistent with pesticides loads observed during flood flushes.

Annexe V (g)- Taghavi et al. 2010. Proceeding 39th French National Conference on Pesticides (Toulouse, France). (oral presentation)

XXXIXème congrès du Groupe Français des Pesticides - 13-15 mai 2009, Toulouse

Dynamique de transfert des pesticides en périodes de crue sur le bassin versant de la Save (Sud-Ouest de la France)

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Résumé

L'objectif de cette étude est de déterminer le rôle des périodes de crue dans l'exportation des pesticides sur un bassin versant agricole de taille moyenne grâce à un suivi à pas de temps réduit des variations de débits et de concentrations des pesticides dans les fractions dissoute et particulaire. Les résultats montrent que les molécules présentent des teneurs supérieures à celles observées par les réseaux institutionnels. Ces teneurs sont en général corrélées positivement aux débits. Certaines molécules montrent des concentrations supérieures à 0,1 µg.L^{-1}, voire même à 1 µg.L^{-1} pour aclonifen, isopruturon, linuron, métolachlore. Les relations débit-concentration mettent en évidence des hystérésis (teneurs différentes entre la montée et la descente de crue) dextres ou senestres suivant les molécules, dues à des contributions variables des différents écoulements (ruissellements de surface et hypodermique, écoulement de nappe) à l'exportation totale des pesticides par la rivière. Les teneurs en pesticides sont également corrélées aux MES ou au COD suivant les caractéristiques des molécules.

Mots-clés : herbicides, fongicides, crue, COD, MES, hystérésis

1. Introduction

La contamination des rivières par les pesticides est un problème environnemental majeur. Le transfert des pesticides des sols vers les eaux de surface se produit principalement pendant les périodes de crue. En Gascogne, ces périodes sont en général de courte durée mais relativement intenses. Il est important de connaître les variations de concentration en pesticides pendant ces périodes d'une part, pour mieux comprendre les mécanismes de transfert sols-eaux des pesticides et d'autre part, pour obtenir une meilleure estimation des flux exportés à l'exutoire du bassin versant. Les résultats présentés ici concernent 2 épisodes de crue parmi les 4 qui ont été échantillonnés en 2008 (1 crue complexe en avril avec Q_{max} = 30 m^3.s^{-1} et une succession de crue en mai-juin avec Q_{max} = 45 m^3.s^{-1}) sur le bassin versant de la Save, affluent rive gauche de la Garonne, à la station de Larra (débit moyen interannuel de 6,3 m^3.s^{-1}). Les principaux objectifs de cette étude sont de déterminer les variations des concentrations en pesticides dans les différentes fractions (dissoute et particulaire) et de déterminer les relations entre ces variations et les fluctuations de débit. Il s'agit aussi d'évaluer le rôle des principaux facteurs de contrôle, Matières En Suspension (MES) et Carbone Organique Dissous (COD), sur ces variations.

2. Matériel et méthode

Cette étude est réalisée en Gascogne (Sud-Ouest de la France), sur le bassin versant de la Save (1150 km^2), un des principaux affluents rive gauche de la Garonne. Ce bassin versant est principalement dédié aux activités agricoles, avec plus de 75 % de terres arables. Dans cette région, les principales

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cultures (maïs, blé et tournesol) nécessitent l'utilisation de grandes quantités d'herbicides de pré-émergence.

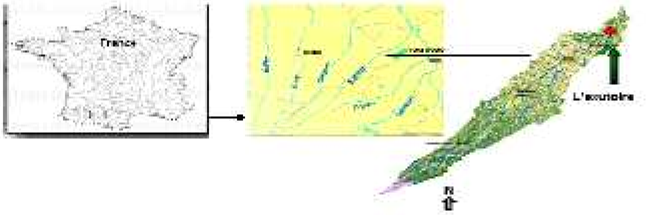

Figure 1. Situation du bassin versant de la Save en Gascogne

Les analyses de pesticides ont porté sur les eaux brutes (non filtrées) et sur les eaux filtrées (filtration sur membrane Millipore de porosité 0,45µm). Les échantillons ont été recueillis dans des bouteilles en verre, transportés au laboratoire rapidement et préservés en chambre froide. Les échantillons d'eau brute ont été conservés par ajout sur le terrain de dichlorométhane. L'extraction a été réalisée dans un ballon à l'aide de dichlorométhane. Une vingtaine de molécules (herbicides et fongicides) ont été analysées sur les échantillons d'eau filtrée et non filtrée par GC-MS (Thermo Finnigan Trace DSQ) en utilisant une technique multi-résidus (Devault et al. 2007). La limite de détection est de 0,01 $\mu g/L^{-1}$.

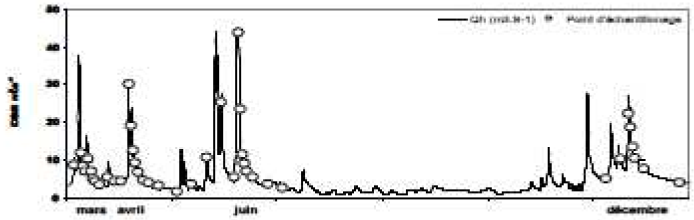

Figure 2. Variations des débits horaires de la Save à Larra au cours de la période d'étude (mars à décembre 2008)

3. Résultats et discussion

3.1 Évolution des concentrations durant les crues d'avril et de juin

Les résultats obtenus au cours des épisodes de crue d'avril et juin 2008 montrent que certaines molécules ont des concentrations supérieures à $0.1\mu g.L^{-1}$ voire même à $1\ \mu g.L^{-1}$ pour aclonifen, isoproturon, linuron, métolachlore. Pour illustrer les variations des teneurs en pesticides, nous avons choisi de présenter ici sur la figure 3, à titre d'exemple, les variations de concentrations dans l'eau brute et l'eau filtrée pour une molécule très soluble, le métolachlore (S = 488 $mg.L^{-1}$ et Kow = 2,9) et pour une molécule peu soluble, l'aclonifen (S = 1,4 $mg.L^{-1}$ et Kow = 4,37). Les concentrations augmentent lors des forts débits comme l'ont déjà observé Phillips et Bode (2004).

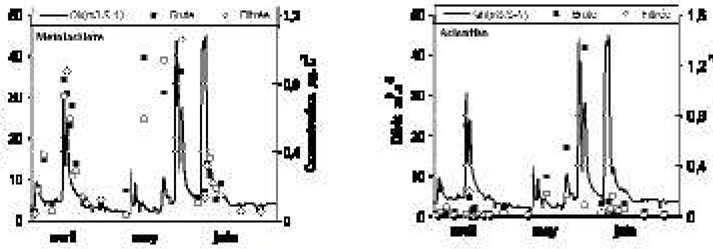

Figure 3. Variations des débits et des teneurs en métolachlore (à gauche) et Aclonifen (à droite) dans l'eau brute (carré noir) et l'eau filtrée (rond blanc) au cours des crues d'avril et de juin 2008 sur la Save à Larra

La différence de concentration entre l'eau brute et l'eau filtrée permet d'estimer la teneur des différentes molécules dans les MES. Cette différence est faible pour les molécules solubles comme le métolachlore et élevée pour les molécules peu solubles comme l'aclonifen. Ainsi, le pourcentage moyen de chaque molécule (métolachlore et aclonifen) dans la fraction particulaire (MES) par rapport à la concentration totale mesurée dans l'eau brute (fractions dissoute et particulaire) varie de 19 % (métolachlore) à 64 % (aclonifen) pour la crue d'avril, et de 16 % (métolachlore) à 47 % (aclonifen) pour la crue de juin.

3.2 Relations débit-concentration

Comme on peut le voir sur les relations entre les concentrations et les débits (figure 4), les teneurs sont plus élevées en descente qu'en montée de crue pour le métolachlore (hystérésis senestre) alors que c'est le contraire (hystérésis dextre) pour l'aclonifen. L'hystérésis senestre observée pour le métolachlore est comparable à celle que l'on peut observer sur les bassins versants agricoles pour les nitrates (Probst, 1985), montrant que les transferts de métolachlore (molécule soluble) sont principalement contrôlés par les écoulements hypodermiques dont la contribution est maximale en descente de crue (ressuyage des sols). A l'inverse, l'hystérésis dextre montre que c'est le ruissellement de surface (dont la contribution est maximale en montée de crue) qui contrôle les transferts d'aclonifen (molécule peu soluble) qui est fortement associé aux MES.

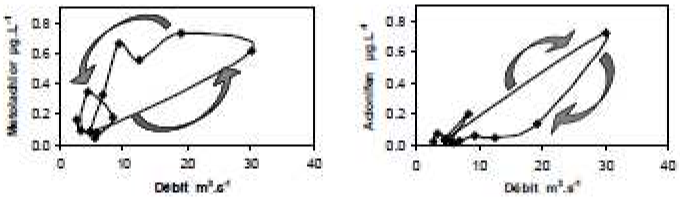

Figure 4. Relations entre les concentrations en métolachlore (à gauche) ou aclonifen (à droite) et les débits au cours de la crue d'avril 2008 sur la Save à Larra. Phénomènes hystérésis entre montée et descente de crue

3.3 Rôle des facteurs de contrôle (COD, MES)

Le transfert des pesticides et leur transport dans les eaux sont également contrôlés par les MES et le COD auxquels ils sont associés par des phénomènes d'adsorption et de complexation (Tanimoto et Hoshika 1997; Gao et al. 1998; Worral et al. 1999 ; Wu et al. 2004 Taghavi et al. 2008 et 2009).

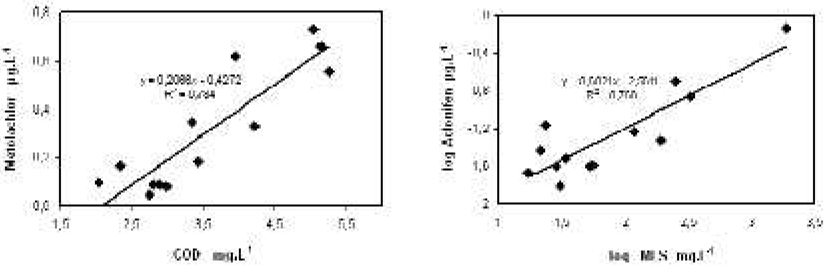

Figure 5. Relations entre les teneurs en métolachlore et en COD (à gauche) et entre les teneurs en aclonifen et MES (à droite) au cours de la crue d'avril 2008 sur la Save à Larra

En fonction des caractéristiques physico-chimiques des molécules (solubilité et coefficients de partage octanol/eau (Kow) et carbone organique/eau (Koc)), on peut observer des relations significatives entre les teneurs en pesticides et les teneurs en MES ou COD. Ainsi pour la crue d'avril 2008 (figure 5), le métolachlore (très soluble) est corrélé positivement aux teneurs en COD ($R^2 = 0{,}784$, $p < 0{,}05$) alors que l'aclonifen (peu soluble) présente une corrélation positive avec les teneurs en MES ($R^2 = 0{,}760$ $p < 0{,}05$).

4. Conclusion

Cette étude montre l'importance d'un suivi à pas de temps réduit de l'évolution des teneurs en pesticides dans les différentes fractions (dissoute et particulaire) au cours des périodes de crue pour une meilleure compréhension des processus de transferts des pesticides des sols vers les eaux de surface. Ces suivis permettent d'évaluer le rôle des différents processus (ruissellement de surface/érosion mécanique des sols et ruissellement hypodermique/lessivage des sols) dans l'exportation totale des pesticides par les cours d'eau. Ces suivis permettront aussi d'estimer avec précision les flux des différentes molécules exportés à l'exutoire du bassin versant de la Save comme nous avons pu le faire pour celui d'Auradé (cf Taghavi et al. 2009). Les principaux résultats obtenus dans cette étude sont les suivants :

- augmentation des teneurs de toutes les molécules au cours de la crue
- relations positives entre teneurs et débits, mettant en évidence des phénomènes d'hystérésis dextre (molécules peu solubles) ou senestre (molécules solubles)
- contribution élevée des fractions particulaires pour les molécules peu solubles, montrant que le dosage de ces molécules uniquement dans l'eau filtrée sous-estime largement les teneurs totales
- contrôle des teneurs des molécules solubles par COD et des molécules peu solubles par MES

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Annexe V (h)- Taghavi et al. 2010. Proceeding 40th French National Conference on Pesticides (Toulouse, France). (oral presentation)

Dynamique de transfert des pesticides en périodes de crue sur le bassin versant de la Save (Sud-Ouest de la France) : approche par découpage des hydrogrammes de crue

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Résumé

Cette étude a pour but de déterminer le rôle des périodes de crue dans l'exportation des pesticides sur un bassin versant agricole. A cet effet, un suivi à pas de temps réduit des variations de débits et de concentrations sur les phases dissoute et particulaire a été mis en place. Les résultats montrent que les différentes molécules pesticides présentent des teneurs supérieures à celles observées par les réseaux institutionnels. Ces teneurs sont corrélées positivement aux débits. Des concentrations supérieures à 0,1 µg.L^{-1} sont à noter pour certaines molécules. La trifluraline, l'aclonifène et le linuron ont même des concentrations supérieures à 1 µg.L^{-1}. Des hystérésis (teneurs différentes entre montée et descente de crue pour un même débit), dextres ou senestres selon les molécules, ont été mises en évidence entre le débit et les concentrations. Ces hystérésis sont le résultat d'une contribution variable des différents écoulements (ruissellements de surface et hypodermique, écoulement de nappe) à l'exportation totale des pesticides par la rivière. Pour mieux évaluer la contribution des eaux provenant du ruissellement de surface, de l'écoulement hypodermique et de l'écoulement de nappe, nous avons séparé ces 3 composantes par découpage des hydrogrammes de crue, basé sur la loi de Maillet ($Q_t=Q_0e^{-\alpha t}$). On a pu ainsi mettre en évidence l'existence d'une relation positive entre la concentration en pesticides et le débit de l'écoulement responsable du transfert. Les teneurs en pesticides sont également corrélées aux MES, COP au COD suivant les caractéristiques des molécules. Le suivi précis de tous les épisodes de crue permet d'estimer à 60%-90% suivant les molécules la contribution de ces périodes au flux total annuel de pesticides exportés par la rivière, montrant ainsi le rôle prépondérant de ces périodes dans le transfert des pesticides.

Mots-clés : Herbicide, Crue, Découpage d' hydrogramme, MES, COP, COD, Flux

1. Introduction

La dégradation de la qualité des eaux de surface et de nappe est actuellement une des conséquences de l'agriculture intensive. La présence de produits phytosanitaires est fréquemment détectée dans les écosystèmes aquatiques (MEDD, 2003). La connaissance scientifique sur le transfert des pesticides est insuffisante, en particulier durant les périodes de crue. Il est donc important de connaître avec précision les variations des teneurs en pesticides pendant ces périodes, d'une part pour mieux comprendre leurs mécanismes de transfert sols-eaux et d'autre part, pour obtenir une meilleure estimation des flux exportés à l'exutoire du bassin versant. Les résultats présentés ici concernent 4 crues moyennes d'un débit maximal entre 20 et 45 m^3.s^{-1}, et une crue exceptionnelle (Janvier 2009), avec un débit maximal d'environ 120 m^3.s^{-1}, échantillonnées sur le bassin versant de la Save, affluent rive gauche de la Garonne, à la station de Larra (débit moyen interannuel de 6.3 m^3.s^{-1}). Les principaux objectifs de cette étude sont de déterminer la variation des concentrations en pesticides avec les fluctuations de débit, d'estimer la contribution des composantes de l'hydrogramme de crue à l'exportation des pesticides, d'appréhender le rôle des facteurs de contrôle comme les Matières En Suspension (MES), le Carbone Organique Particulaire (COP) et le Carbone Organique Dissous (COD) sur les teneurs en pesticides, et enfin, d'évaluer avec précision les flux de pesticides exportés durant ces périodes.

2. Matériel et méthodes

Cette étude est réalisée en Gascogne (Sud-Ouest de la France), sur le bassin versant de la Save (1110 km^2), un des principaux affluents rive gauche de la Garonne. Ce bassin versant est dédié aux activités agricoles, principalement à la culture maïs-blé-tournesol qui nécessite l'utilisation de grandes quantités d'herbicides de pré-émergence.

Les analyses ont porté sur les eaux brutes (non filtrées) et sur les eaux filtrées (filtration à 0,45µm). De mars 2008 à mars 2009, 65 échantillons ont été prélevés, dont 41 en périodes de crue, et analysés. Les échantillons ont été recueillis dans des bouteilles en verre, transportés au laboratoire rapidement et préservés en chambre froide. Les eaux brutes ont été conservées par ajout sur le terrain de dichlorométhane. L'extraction a été réalisée en fiole à décanter à l'aide de dichlorométhane. Quatorze molécules (herbicides et fongicides) ont été analysées sur les eaux brute et filtrée par GC-MS (Thermo Finnigan Trace DSQ) en mode multi-résidus (Devault et al. 2007). La limite de détection est 1 à 3 (ng.L^{-1}). Le découpage des hydrogrammes de crue a été effectué sur la base de la loi de Maillet (1905), cette loi exponentielle $Q_t=Q_0e^{(-at)}$ a été largement utilisée pour décrire la récession de chaque écoulement, et séparer la contribution de chaque composante de la crue.

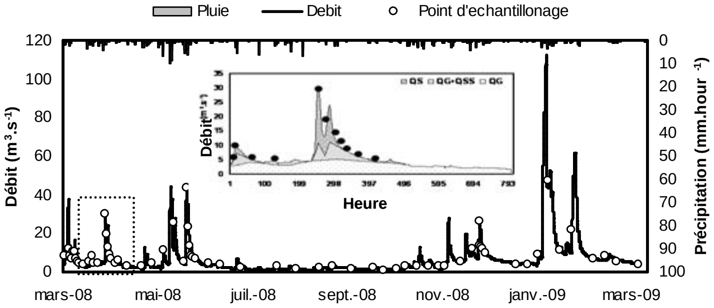

Figure 1. Variations des débits de la Save à Larra au cours de la période mars 2008-mars 2009.

3. Résultats et discussion

3.1 Evolution de la concentration durant la période d'étude

Les résultats obtenus au cours de l'année d'étude (2008-2009) montrent que certaines molécules atteignent des concentrations supérieures à 0.1µg.L^{-1} pour le métolachlore voire même à 1 µg.L^{-1} pour le linuron et l'aclonifène.

La figure 3 présente les variations de concentrations dans l'eau brute pour une molécule très soluble, le métolachlore (S_w = 488 mg.L^{-1} et K_{ow} = 2,9), une molécule avec un degré de solubilité modéré, le linuron (S_w= 63.8 mg.L^{-1} et K_{ow} = 3), et une molécule peu soluble, l'aclonifène (S_w = 1,4 mg.L^{-1} et K_{ow} = 4,37). On peut noter une augmentation des concentrations lors des forts débits et durant les périodes de crue, comme l'ont déjà observé Wu et al. (1983), Phillips et Bode (2004) et Taghavi et al. (2010).

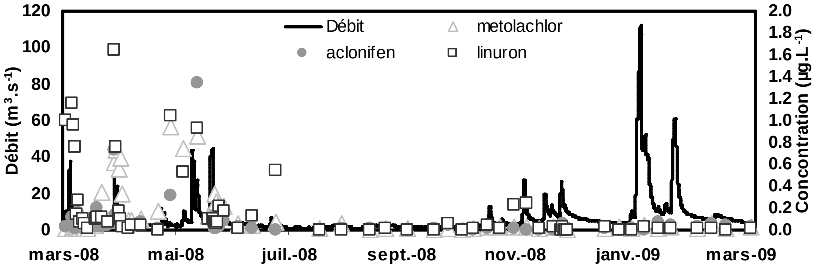

Figure 2. Variations des débits et des teneurs en métolachlore, linuron et aclonifène dans l'eau brute au cours de la période 2008-2009 sur la Save à Larra

3.2 Relations débit (Q)-concentration(C)

Les relations C-Q (fig. 4) montrent que la teneur est plus élevée en descente qu'en montée de crue pour le métolachlore (hystérésis senestre) alors que c'est le contraire (hystérésis dextre) pour l'aclonifène et le linuron. L'hystérésis senestre mise en évidence pour le métolachlore est comparable à celle que l'on peut observer sur les bassins versants agricoles pour les nitrates (Probst, 1985 ; Kattan et al. 1986), montrant ainsi que les transferts de métolachlore (molécule soluble) sont principalement contrôlés par les écoulements hypodermiques dont la contribution est maximale en descente de crue (ressuyage des sols). A l'inverse, l'hystérésis dextre montre que c'est le ruissellement de surface (dont la contribution est maximale en montée de crue) qui contrôle les transferts d'aclonifène (molécule peu soluble) et de linuron (solubilité modérée) qui sont fortement associé aux MES. Les facteurs (MES, COD et COP) contrôle les teneurs de ces pesticides présentent les mêmes hystérésis : dextres pour MES et COP et senestre pour COD.

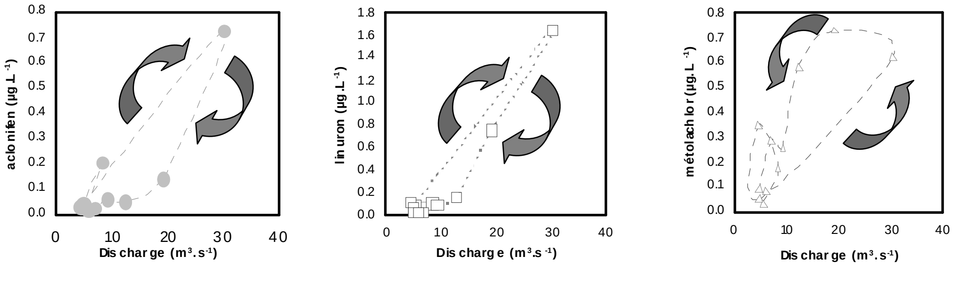

Figure 3. Relations entre les teneurs en aclonifène (à gauche), linuron (centre) et métolachlore (à droite) et le débit au cours de la crue d'avril 2008 sur la Save à Larra. Hystérésis entre montée et descente de crue.

3.3 Relations concentration - débit des différentes composantes de l'écoulement fluvial

En associant les teneurs des différents pesticides aux débits des différents écoulements (superficiel, hypodermique, nappe) plutôt qu'au débit total de la rivière, on peut mettre en évidence l'origine des molécules et leur mode de transfert. Ainsi, il existe une bonne relation entre les teneurs en aclonifène (peu soluble) et linuron (moyennement soluble) et le débit du ruissellement superficiel. Ce genre de relation a déjà été montrée pour les MES par Probst et Bazerbachi (1986). Pour une molécule soluble comme le métolachlore, il existe une bonne relation avec le débit de l'écoulement hypodermique. Ce phénomène a été déjà montré dans le cas d'éléments solubles comme les nitrates par Probst (1985), Kattan et al. (1986) et Wanger et al. (2008). Ces résultats mettent en évidence les voies préférentielles d'exportation de ces pesticides vers la rivière : la première associée à l'érosion mécanique et au ruissellement de surface sur les sols et la deuxième au lessivage des sols et au drainage hypodermique.

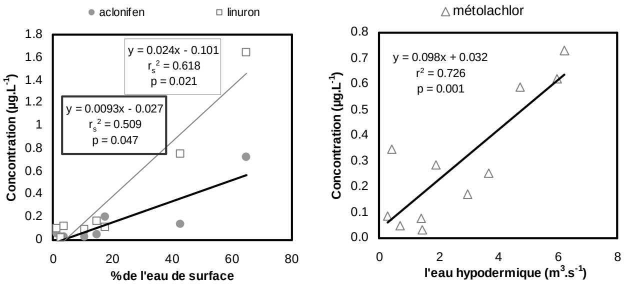

Figure 4. Relations entre les concentrations en pesticides et le débit des différents écoulements : ruissellement de surface-aclonifène et linuron (à droite) et écoulement hypodermique-métolachlore (à gauche).

3.4 Rôle des facteurs de contrôle (MES, COP et COD)

Le transfert des pesticides et leur transport dans les eaux sont également contrôlés par les MES, le COP et le COD auxquels ils sont associés par des phénomènes d'adsorption et de complexion (Worral et al. 1999 ; Wu et al. 2004 ; Taghavi et al. 2010).

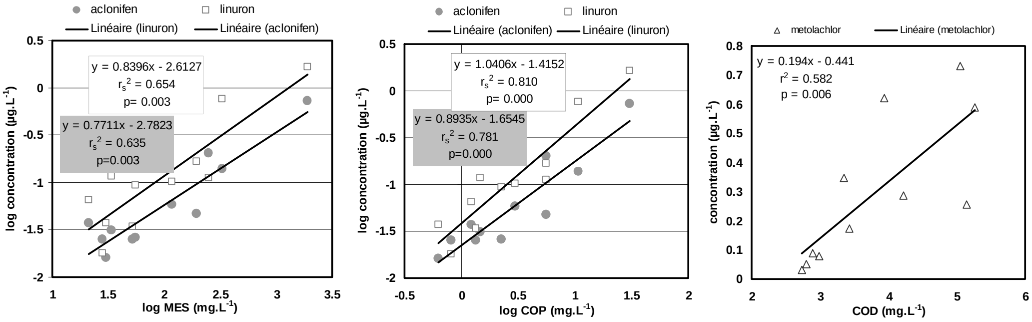

Figure 5. Relations entre les teneurs en pesticides et les facteurs de contrôle : métolachlore-COD (à droite), aclonifène et linuron-MES (à gauche) et COP (au centre) au cours de la crue d'avril 2008 sur la Save à Larra

Ces relations montrent que les molécules peu ou moyennement solubles comme l'aclonifène ou le linuron sont associées aux phases particulaires, alors que les molécules solubles comme le métolachlore sont complexés par le COD.

3.5 Flux de pesticides

Le découpage de l'hydrogramme annuel nous a permis d'estimer la contribution respective des périodes de crue et des étiages au flux total annuel de pesticides (eau brute). Cette contribution est évaluée à 60-90% pour les périodes de crue, suivant les molécules (respectivement 90, 86 et 89 % pour l'aclonifène, le linuron et le métolachlore). Pour les MES et COD, les crues exportent respectivement 94% et 71 % du flux total annuel alors que le volume d'eau exporté durant ces périodes représente 63% du volume total annuel d'eau. La distribution des pesticides entre les phases dissoute et particulaire varie suivant les molécules : l'aclonifène (molécule peu soluble) est principalement (84%) exporté en phase particulaire montrant qu'une mesure de cette molécule uniquement dans les eaux filtrées sous estimerait largement le flux total. En revanche, le métolachlore (molécule très soluble) est exporté principalement (88%) sous forme dissoute. Le linuron (solubilité moyenne) est exporté à 62% par les phases particulaires et à 38% sous forme dissoute. La distribution de ces molécules entre les différentes phases va dépendre également de l'abondance relative des MES, du COP et du COD.

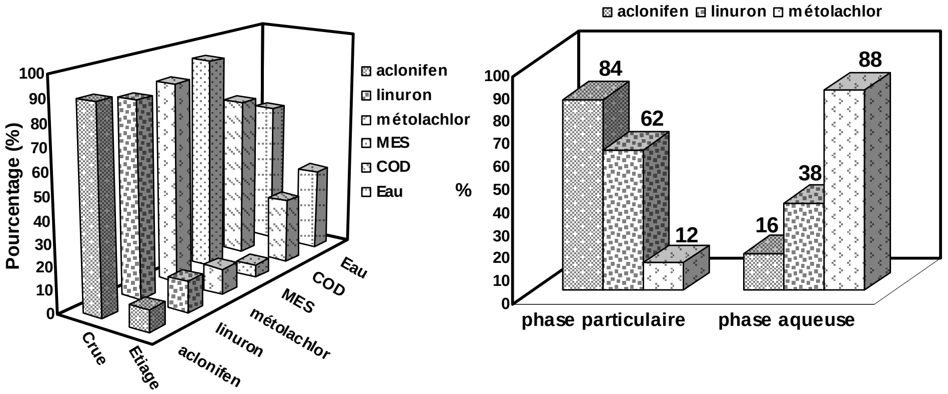

Figure 6. Contribution (%) des périodes de crue et d'étiage à l'exportation des pesticides, des MES, du COP, du COD et du volume d'eau (à gauche) et distribution (%) des pesticides entre les phases particulaire et dissoutes (à gauche)

4. Conclusion

Un suivi précis en périodes de crue de l'évolution des teneurs en pesticides dans les différentes fractions (dissoute et particulaire) permet de mieux comprendre des processus de transferts des molécules des sols vers les eaux de surface. Ce suivi permet notamment d'évaluer le rôle des différents processus (ruissellement de surface/érosion mécanique des sols et écoulement hypodermique/lessivage des sols) dans l'exportation totale des pesticides par les cours d'eau. Il permet aussi d'estimer avec précision les flux durant ces épisodes. Les principaux résultats obtenus sont les suivants :

- augmentation des teneurs en pesticides avec le débit au cours de la crue.
- relations C-Q mettant en évidence des phénomènes d'hystérésis dextre (molécules peu solubles) ou senestre (molécules solubles).
- rôle important du ruissellement de surface dans l'exportation des molécules peu ou moyennement solubles ainsi que des MES et du COP.
- rôle important de l'écoulement hypodermique dans l'exportation des pesticides solubles et du COD.
- contrôle des teneurs en pesticides solubles par le COD et des molécules peu solubles par les MES.
- molécules peu solubles principalement exportées par les phases particulaires et molécules solubles par les phases dissoutes.

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