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## **Pesticide transfer dynamics and fluxes in the stream of a small vineyard watershed - Assessing the effect of sampling strategy on fluxes estimation**

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**Abstract.** This study reports on the occurrence and behaviour of eight pesticides and metabolites in a small stream draining a vineyard watershed in the Beaujolais area (France). Punctual and automatic sampling strategies were achieved along the river during one hydrological year in order to assess the spatial and temporal variability of pesticide concentrations and loads in the river. Flood events were also monitored in order to evaluate the role of hydrological conditions on pesticide mobilisation. Results show the strong temporal and spatial variability of pesticide concentrations in the river in relation with the periods of pesticide application. A large mobilisation of pesticides was observed during floods (representing more than 80% of the total pesticide load in August 2007); these results highlight the major role of floods in the transport of pesticides. The evaluation of pesticide loads using different sampling strategies (i.e., weekly and monthly punctual; automatic sampling for floods and for weekly composite sampling) and methods of calculation, showed that punctual sampling largely underestimates pesticides fluxes transiting through the river whereas the weekly composite sampling appears as more representative.

**Key Words.** Agricultural watershed, Diuron, Flood, Sampling strategy, Pesticides fluxes, Surface water, Vineyard

### **Introduction**

The intensive use of pesticides for crop protection against diseases led to the widespread presence of these compounds in all the compartments of the environment (soil, water, air). These environmental problems are particularly highlighted in vineyards, where pesticides play a major role in grape production. Large-scale studies, that monitored pesticides losses to surface waters, show that the transfert of pesticides is largely influenced by the intrinsic properties of the compounds but also by the weather conditions, the soil types and land use (Kreuger, 1998). Several authors emphasize the significance of rainfall-induced surface runoff as a major source of pesticides in streams (Richards and Baker, 1993; Kuivila and Foe, 1995; Ng and Clegg, 1997; Kreuger, 1998; Capel et al., 2001; Bach et al., 2001; Schulz, 2001a; Schulz, 2001b, Holvoet et al., 2007).

The aim of the present study is on the one hand, to better estimate the spatial and temporal variability of pesticide concentrations in a small stream draining an agricultural watershed and on the other hand, to assess the role of floods on the mobilisation of pesticides and total fluxes in surface water. Moreover, the effect of the sampling strategy on the evaluation of pesticides loads was estimated using various methods.

### **Materials and method**

#### *Study area*

The investigation site is the Morcille catchment's, located about 70 km north of the city of Lyon in France (Figure 1). Its small size (8 km<sup>2</sup>) allows to define a study area where transfers are more easily comprehensible. The head of the basin is essentially covered by forest, whereas downstream, it is mainly dedicated to vineyard. On the whole, the vine covers about 70% of the catchment total area. No industrial activities are present on the site. The hydrology of the Morcille river varies considerably over a year, with water flow ranging from 0.005 to more than 0.5 m<sup>3</sup>/s. It is characterized by significant hydrological events (strong and fast floods, especially in spring and summer). In this area, climatic, geological, topographical and agricultural conditions concur to create very dynamic hydrological conditions and a high erosion rate.

#### Water sampling and analysis

A punctual monitoring survey was performed from March 2007 to March 2008, in order to achieve a better understanding of surface water exposure levels to pesticide during a whole hydrological year. The spatial variability was approached owing to the choice of three sampling sites along the Morcille river from upstream (1), intermediate (2) to downstream (3) (Figure 1). In addition, water samples were also collected during storm events at the intermediate site (site 2) during spring and summer 2007. Sampling was performed using two refrigerated automated samplers. Additionally, a weekly composite sampling was performed in July and August 2007 with a refrigerated automated sampler.

Eight pesticides and metabolites were chosen for monitoring from different families of herbicides and fungicides currently used for vineyard treatments: azoxystrobin, carbendazim, dimetomorph, procymidone, tebuconazol, diuron and two of its metabolites: 3-(3,4-dichlorophenyl)-1-methyl urea (DCPMU), 3,4-dichloroaniline (DCA). They were

analysed by ESI-LC-MSMS (LC 1100 Agilent, API 4000 Applied Biosystems) after sample filtration and extraction by SPE technique.

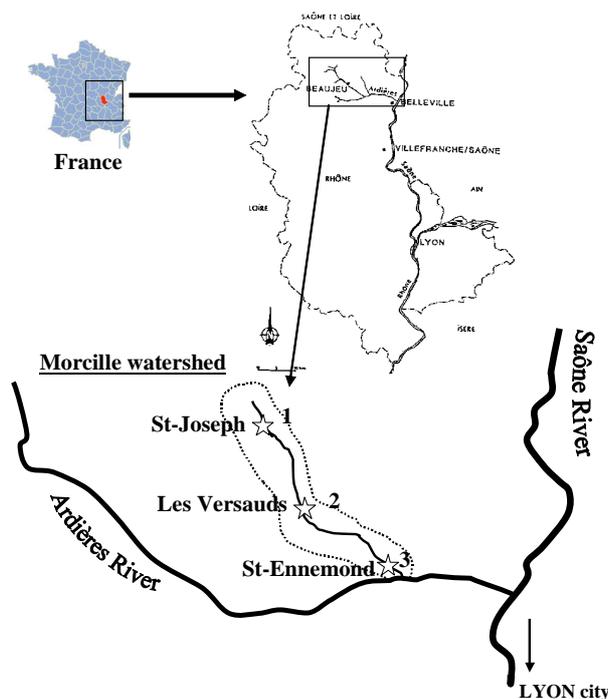


Figure 1. Location of the Morcille watershed and the sampling sites along the stream.

## Results and discussion

### *Punctual monitoring of pesticide concentrations along the Morcille River*

The presence of pesticides was highlighted throughout the investigation period with a large seasonal variation, in relation with the pesticides application calendar (Figure 2). Indeed, total dissolved pesticide concentrations ranged from below detection quantification to 16.4 µg/L. The maximum total pesticide concentrations are observed in June and July, which corresponds to the increase of storms occurrence, as well as to fungicides treatments. Pesticide concentrations declined in August but remained above quantification level throughout the year. Concentrations were 0.3 µg/L, in March 2007 and 2008, corresponding to a residual background linked to previous vineyard treatments. Water contamination by pesticides largely overstepped the application period, as shown by the high concentrations measured in October (up to 7.8 µg/L at site 2). The weekly loads of the studied pesticides, calculated with punctual weekly concentrations, ranged from 0 to 337 g over the study period, which led to an annual load of pesticides of 1525 g. Pesticides fluxes transiting during June and July represent more than 70 % of the annual load. On a spatial point of view, a large increase of pesticide concentration was observed from upstream to downstream, which is coherent with the increasing vineyard surface proportion downstream.

### *Storm events monitoring during spring and summer 2007*

A large mobilisation of pesticides in the river was observed during the floods, with concentrations rising rapidly and usually peaking almost at the same time as water discharge. With the exception of 2 extreme values, maximum concentrations during floods were between 7.3 and 21.1 µg/L, with an average value of  $12.7 \pm 4.3$  µg/L. Depending on the flood, pesticide maximum concentrations varied within only a factor of 3, whereas maximum water discharge varied by a factor of up to 30. In fact, pesticide maximum concentration was not a simple function of water discharge; it is likely that other processes interfere, such as pesticide availability in the soil, dilution and dominant hydrological processes (such as surface runoff or subsurface flow), which induce various residence times. During floods, the total dissolved pesticides fluxes ranged from 1.0 to 60 g.

### *Effect of sampling strategy on the estimation of pesticides fluxes in the river*

In order to assess the effect of the sampling strategy on fluxes estimations, different methods were applied on the data collected in August 2007. Monthly fluxes were estimated using weekly, bimonthly and monthly simulated punctual monitoring by choosing either the first, second, third or fourth weekly sample as a reference for the calculation (Figure 3). In addition, pesticides monthly fluxes were calculated with the weekly average composite samples results. Lastly, pesticide monthly loads were estimated in base flow and storm flow using punctual monitoring achieved during base flow conditions and automatic sampling achieved during floods, respectively. According to the method used, monthly loads ranged from 18.6 to 130.5 g. The highest estimation corresponds to the weekly composite sampling, which we considered as the most accurate value. Monthly loads, estimated from punctual surveys (weekly, bimonthly, monthly) vary between 16.9 and 40.7 g, largely below the "most realistic" flux value (i.e., 130.5 g). In fact, in August 2007, around 83% of the total pesticides fluxes were transported during floods, which, in total lasted for less than 5 days.

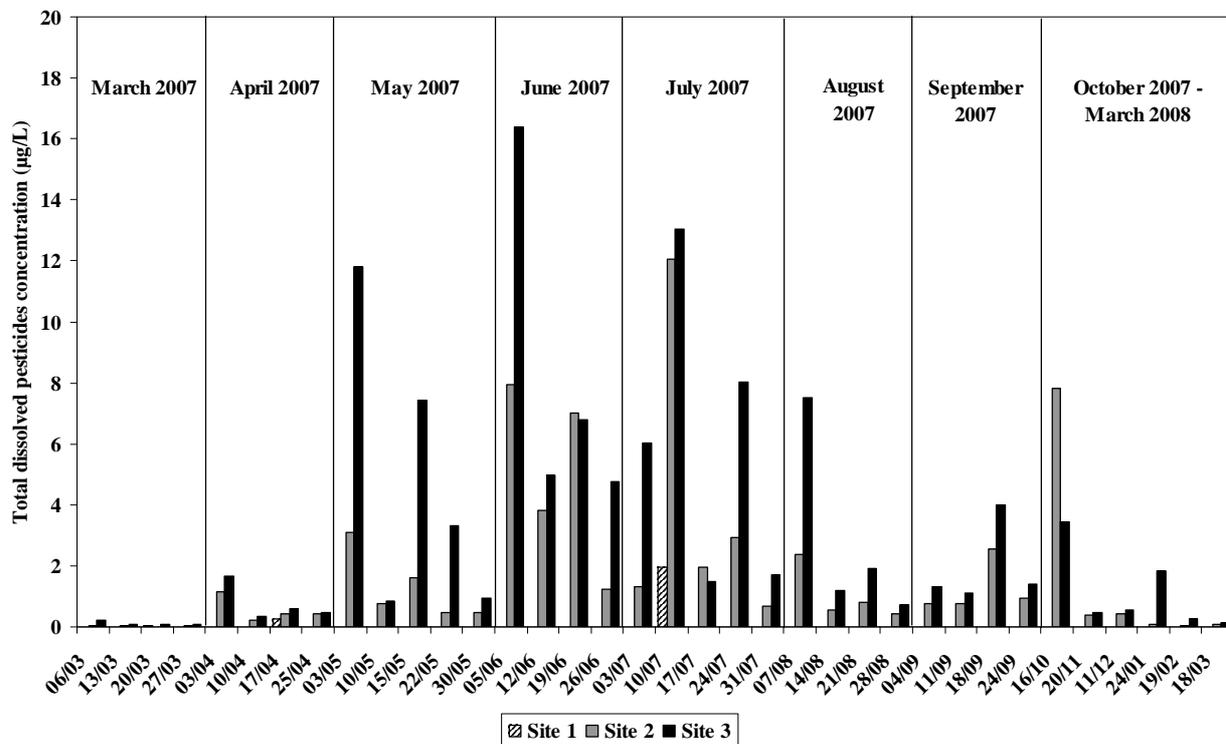


Figure 2. Total dissolved pesticide concentrations (µg/L) along the Morcille stream from March 2007 to March 2008.

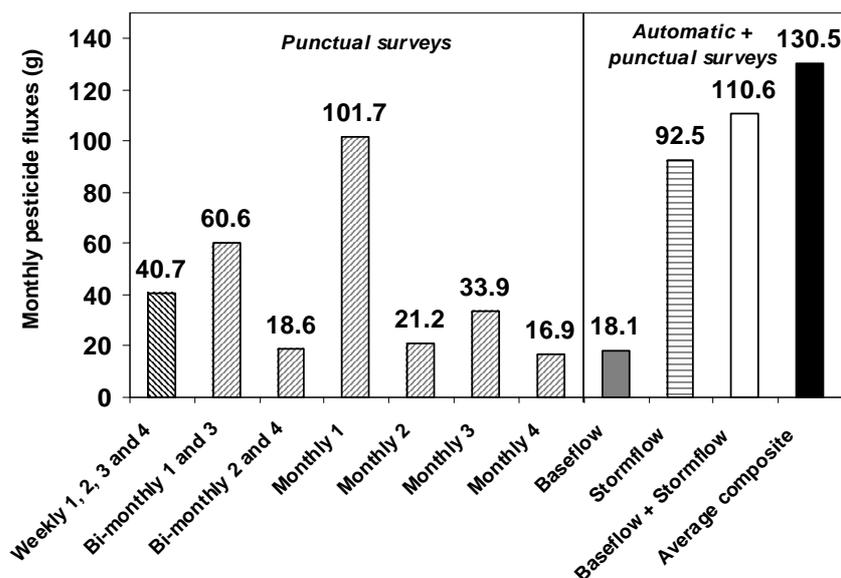


Figure 3. Monthly pesticides fluxes (g) at site 2, estimated using several methods and monitoring data in August 2007.

### Conclusion

The occurrence of pesticides is closely related to the application calendar and the hydrological conditions. Pesticides concentrations were higher during the application season, with maximum concentrations occurring during June and July. Some pesticides were quantified in surface water for several months after application, and throughout the year for diuron, indicating their potential to persist in soils and shallow groundwater. Along the river, we observed a large increase of pesticide concentrations from upstream to downstream, which could be related to the increasing vineyards surface downstream. Our study of pesticides behaviour during floods show the major role of hydrological conditions in the transport of pesticides. In August 2007, floods contributed to more than 80% of the total load of pesticides transiting through the stream. These results provide further evidence that floods are the dominant pathways for the transport of pesticides in the Morcille stream.

A major conclusion of this study is that punctual monitoring of surface water is not adapted for an accurate evaluation of the contaminant exposure level. This is especially the case in dynamic hydrosystems such as the Morcille stream, where such sampling methods largely underestimate the variability of pesticide concentrations and

pesticides fluxes. These observations have critical consequences for the monitoring requirements of pesticides, in particular for the implementation of the Water Framework Directive.

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