High frequency monitoring of pesticides in runoff water to improve understanding of their transport and environmental impacts

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HIGHLIGHTS

- High frequency sampling enabled to estimate what the range of TU values is.
- The exported loads were homogeneously distributed throughout runoff events.
- The C-Q hysteresis patterns were highly dynamic and dependent on storm and chemical characteristics.
- Intense rainfall events induced stronger hysteresis patterns.

GRAPHICAL ABSTRACT
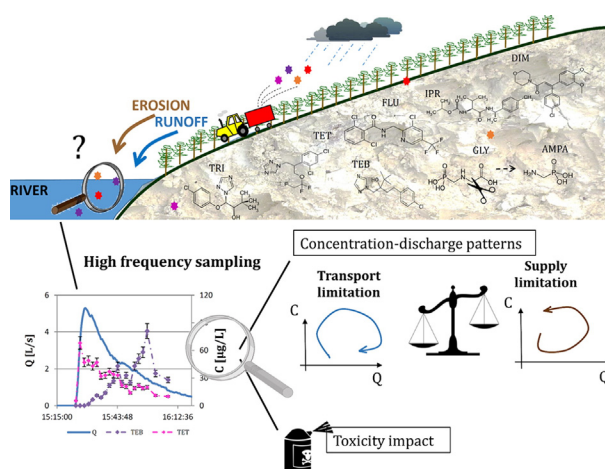
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ABSTRACT

Rainfall-induced peaks in pesticide concentrations can occur rapidly. Low frequency sampling may therefore largely underestimate maximum pesticide concentrations and fluxes. Detailed storm-based sampling of pesticide concentrations in runoff water to better predict pesticide sources, transport pathways and toxicity within the headwater catchments is lacking. High frequency monitoring (2 min) of seven pesticides (Dimetomorph, Fluopicolide, Glyphosate, Iprovalicarb, Tebuconazole, Tetraconazole and Triadimenol) and one degradation product (AMPA) were assessed for 20 runoff events from 2009 to 2012 at the outlet of a vineyard catchment in the Layon catchment in France. The maximum pesticide concentrations were 387 μg L^{-1}. Samples from all of the runoff events exceeded the legal limit of 0.1 μg L^{-1} for at least one pesticide (European directive 2013/39/EC). High resolution sampling used to detect the peak pesticide levels revealed that Toxic Units (TU) for algae, invertebrates and fish often exceeded the European Uniform principles (25%). The point and average (time or discharge-weighted) concentrations indicated up to a 30- or 4-fold underestimation of the TU obtained when measuring the maximum concentrations, respectively. This highlights the important role of sampling methods for assessing peak exposure. High resolution sampling combined with concentration-discharge hysteresis analyses revealed that clockwise responses

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were predominant (52%), indicating that Hortonian runoff is the prevailing surface runoff trigger mechanism in the study catchment. The hysteresis patterns for suspended solids and pesticides were highly dynamic and storm- and chemical-dependent. Intense rainfall events induced stronger C-Q hysteresis (magnitude). This study provides new insights into the complexity of pesticide dynamics in runoff water and highlights the ability of hysteresis analysis to improve understanding of pesticide supply and transport.

1. Introduction

Headwater streams significantly impact downstream water quality and contribute to the biodiversity of the overall stream network (Rasmussen et al., 2013; Salmon-Monviola et al., 2013). Headwaters in agricultural areas are subject to particularly high pesticide inputs as a result of their location near agricultural plots and their low discharge levels (Lorenz et al., 2016). However, headwaters are often not considered significant surface water bodies and are generally disregarded (e.g., by the European Water Framework Directive (WFD)) (Bundschuh et al., 2014). In headwater catchments, pesticide export dynamics is generally discontinuous and complex dependent upon rainfall occurrence and seasonal use (Stehle et al., 2012). Rainfall-induced peaks in pesticide concentrations can occur rapidly. However, even very short pulses (from a few minutes to several hours) of high pesticide concentrations may negatively impact aquatic organisms (Boxall et al., 2013; Cold and Forbes, 2004). Low frequency sampling largely underestimates pesticide concentrations and fluxes (Assoumani et al., 2013; Bieroza and Heathwaite, 2015), and fails to evaluate acute pesticide exposure (Lorenz et al., 2016; Stehle et al., 2012). The environmental effect of pesticides can be evaluated by observing the number of exceedances of the legal limit ($0.1\ \mu g\ L^{-1}$ for a single pesticide and $0.5\ \mu g\ L^{-1}$ for the sum of all pesticides in a given sample, European directive 2013/39/EC). Another option consists in comparing pesticide concentrations with results from ecotoxicological tests for key species (e.g., EC_{50}, LC_{50}, etc.) (Papadakis et al., 2015). Aquatic ecosystems are typically exposed to a mixture of pesticides, leading to possible combined action of co-occurring pesticides, potentiation or synergistic interactions that may result in higher toxicity than predicted (Abdo et al., 2015; Cedergreen, 2014). The combined toxicity of mixed pesticides is increasingly debated in the literature, stressing the need for a new assessment tool (Carvalho et al., 2014). The toxic unit (TU) is an easy and common tool that assumes a cumulative effect of pesticide toxicity. TU is the sum of the ratios between the concentrations of different pesticides and their respective toxicities for a given species (Allinson et al., 2015; Bundschuh et al., 2014). This indicator evaluates the toxicological impact of a given pesticide mixture. In the present study, TUs were estimated using point, average and maximum concentrations, as well as a discharge-weighted concentration of a runoff event, to assess the benefit of high frequency sampling in evaluating ecological risk.

High frequency sampling allows: (i) an assessment of much more reliable estimates of pesticide fluxes (Bieroza and Heathwaite, 2015), (ii) an estimation of the contribution of each hydrograph component (e.g., rising limb, falling limb, first flush, etc.) to pesticide transport (Granger et al., 2009) and (iii) an in-depth investigation of pesticide response patterns to rain events (Bende-Michl et al., 2013). Concentration-discharge (C-Q) patterns have already been largely documented for turbidity, temperature, suspended solids and nutrients such as nitrates and phosphorus. These patterns were applied to better predict and understand their sources and pathways within a catchment during rainfall events (Bende-Michl et al., 2013; Bieroza and Heathwaite, 2015; Donn et al., 2012; Dupas et al., 2015; Granger et al., 2009; Paul et al., 2015; Pietroń et al., 2015). A C-Q pattern may be hysteretic and follow either a clockwise or anti-clockwise hysteresis loop. A clockwise pattern may indicate transport limitations, while an anti-clockwise pattern may indicate supply limitations (Bieroza and Heathwaite, 2015). A clockwise pattern is generally observed when the solute peak occurs before the outflow peak. This is often related to a rapid flushing of solutes that are readily available due to their ability to dissolve, and the exhaustibility or the proximity of the solute source. Correspondingly, anticlockwise patterns can be the result of a delayed solute delivery due to the upstream source area or to its availability (sorption, complexation, etc.) (Pietroń et al., 2015; Zuecco et al., 2016). Studying hysteretic relationships for different events (Outram et al., 2016), different sites within a catchment (Paul et al., 2015) or different solutes (Bieroza and Heathwaite, 2015; Dupas et al., 2015) can thus reveal important information about the spatial origin of solutes and the underlying hydrological processes involved in solute transport (Fovet et al., 2015). However, little is known about the C-Q patterns of organic pesticides (Taghavi et al., 2011). Detailed storm-based sampling is thus required to better evaluate pesticide sources and transport in runoff water, as well as their ecological impact on aquatic ecosystems.

This study aims to explore the use of high frequency sampling to better understand the sources, transport pathways and ecological impacts of pesticides in runoff events. The objectives of this study were to evaluate the advantages of high frequency sampling in runoff water in the assessment of the ecotoxicological impacts of pesticides and to provide new insights into pesticide supply and transport pathways by evaluating first flush and concentration-discharge patterns. Runoff events from 2009 to 2012 were selected arbitrarily to cover the growing season and diverse rainfall and runoff occurrences during pesticide application periods. Due to the high cost of analyses and difficulties associated with the selected sampling procedure, only 20 runoff events were studied. The experimental setup was designed to obtain a wide range of runoff events and not to compare the yearly mass balance budget.

2. Material and methods

2.1. Description of the vineyard catchment

The 2.2-ha catchment is located in the commune of Rochefort sur Loire, (West of France, 47°19″19.47″N; 0°38″21.39″W) (Fig. 1). Its altitude ranges between 39.4 and 83.7 m along an ESE facing slope. Soils overlay an impermeable Armorican substratum (Namurian Shale, Sandstone and Psammites). The catchment boundary was determined using ArcGIS 10.1 (ESRI, Redlands, United States) and data derived from an electronic theodolite (1 pt. per 10 m²) and was validated by field observations. The outlet of the catchment is located 37 m from an influent of the Layon River that is itself 500 m downstream. The catchment is characterised by three different gradients: (i) The upper catchment has 0–5% slopes (51% of the total catchment area); (ii) The middle catchment has 5–15% slopes (40%); and (iii) The lower catchment has >15% slopes (9%), including agricultural terraces. Soil depths vary from 30 cm in the lower zone to 120 cm in the upper zone. Spatial variability of the soil was characterised using 50 surface soil samples (0–20 cm) taken from across the three areas. Soil characteristics for the catchment are as follows (mean ± SE): sand: $42.3 \pm 5.1\%$; silt: $36.1 \pm 3.0\%$; clay: $19.5 \pm 2.3\%$; OM: $2.1 \pm 0.4\%$; pH: 7.1 ± 0.4; CEC: 10.4 ± 0.8 meq $100\ g^{-1}$; CaCO3: 0.1%. The structural stability of the soils was measured by immersing soil aggregates in water followed by the separation of the soil fraction using mechanical sieving (Le Bissonnais et al., 2007). Fractions >250 μm were measured and constituted an index of soil stability. Grassed rows were comprised of $38 \pm 12\%$ stable aggregates while weeded rows were comprised of $18 \pm 6\%$