

## **High frequency monitoring of pesticides in runoff water from a vineyard: ecotoxicological and hysteresis pattern analysis**

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Rainfall-induced peaks in pesticide concentrations can occur rapidly; therefore, low frequency sampling may 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 head-water catchments is actually lacking. High frequency monitoring (2 min) of dissolved concentrations and loads for 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 pesticide concentrations reached 387  $\mu\text{g/L}$ . All of the runoff events exceeded the mandated acceptable concentrations of 0.1  $\mu\text{g/L}$  for each 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 instantaneous and average (time or discharge-weighted) concentrations indicated an up to 30- or 4-fold underestimation of the TU obtained when measuring the maximum concentrations, respectively, highlighting the important role of the sampling methods for assessing peak exposure. High resolution sampling combined with concentration-discharge hysteresis analyses revealed that clockwise responses 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 the understanding of pesticide supply and transport.