



Pesticide persistence and transport at the headwater catchment scale: towards coupling continuous and event-based models

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Predicting pesticide dissipation in distributed physically based models at hydrological catchment scale remains challenging, as pesticide degradation kinetics are usually fixed across space and time. In addition, field data distinguishing degradative from non-degradative pesticide dissipation processes for model calibration are scarce. Here control of degradation half-life (DT50) by topsoil water content and temperature was introduced in the pesticide degradation and transport component of a distributed model, and further tested in a 47-ha agricultural catchment. Controlled DT50 values improved predictions of S-metolachlor (SM) degradation across the catchment and the agricultural season, and decreased prediction uncertainties (i.e. 95% confidence intervals) of top soil pesticide leaching by a factor of 2. In contrast, constant DT50 values, independent of hydro-climatic conditions, increased prediction uncertainties. Compound-specific isotope analysis (CSIA) data constrained DT50 values and allowed to validate model predictions of SM degradation in soil and off-site export from the catchment. SM stable isotope data and concentrations reduced model equinality by teasing apart degradative and non-degradative SM dissipation processes. The range of DT50 values was reduced by a factor 2 when including SM stable isotope data into the calibration process. Pesticide CSIA data from topsoil collected weekly across the catchment helped to constrain SM degradation in the PiBEACH model. We anticipate our results as a preliminary step to develop daily long-term continuous models that include hydro-climatic control of pesticide degradation. More reliable predictions of pesticide degradation dynamics at catchment scale may eventually guide pesticide risk assessment and management practices.

Models capable of integrating both long-term, continuous and event-base hydrological scales should contribute to both the improvement of pesticide transfer risk science and the design of preventive and curative environmental land management strategies. Therefore, we addressed the need to integrate and link at different timescales relevant pesticide fate processes in headwater catchments in a modelling framework. The specific objectives were to: (i) couple a computationally efficient distributed model capable of simulating continuous processes (PiBEACH) with a distributed event-based model, the Limburg Soil Erosion Model (LISEM) capable of detailed representation of rapid pesticide export via runoff and erosion to evaluate improvements of pesticide transport prediction in headwater catchments by combining temporal scales (event and growing season), and (ii) to evaluate the use of CSIA to constrain and validate dominant water pathways useful in identifying prevailing zones of pesticide mobilization affecting stream water quality. To bridge the need for improved degradation constraints in pesticide fate models at multiple time-scales, this study makes use of a unique data set of catchment soil and outlet samples including concentrations and carbon isotope signatures (^{13}C) of SM, a widely used and well characterized pre-emergent herbicide. Finally, to ensure propagation of model parameter uncertainty, and thereby allowing the use of such a tool to associate risk assessment metrics to confidence intervals (CI) for management decision-making, the generalized likelihood uncertainty estimation (GLUE) technique using Monte-Carlo sampling was adopted.