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Spatially distributed environmental fate modelling of terbuthylazine in a mesoscale agricultural catchment using passive sampler data

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Agricultural application of herbicides often leads to significant herbicide losses to receiving rivers. The impact of agricultural practices on water pollution can be assessed by process-based reactive transport modelling using catchment scale models. Prior to investigations of management practices, these models have to be calibrated using sampling data. However, most previous studies only used concentrations at the catchment outlet for model calibration and validation. Thus, even if the applied model is spatially distributed, predicted spatial differences of pesticide loss cannot be directly compared to observations.
In this study, we applied the spatially distributed reactive transport model Zin-AgriTra in the mesoscale (78 km^2) catchment of the Wark River in Luxembourg in order to simulate concentrations of terbuthylazine in river water. In contrast to former studies, we used six sampling points, equipped with passive samplers, for pesticide model validation. Three samplers were located in the main channel of the river and three in smaller tributaries. At each sampling point, event mean concentration of six events from May to July 2011 were calculated by subtraction of baseflow-mass from total collected mass assuming time-proportional uptake by passive samplers. Continuous discharge measurements and high-resolution autosampling during events allowed for accurate load calculations at the outlet. Detailed information about maize cultivation in the catchment and nation-wide terbuthylazine application statistics (341 g/ha in the 3rd week of May) were used for a definition of the pesticide input function of the model. The hydrological model was manually calibrated to fit baseflow and spring/summer events. Substance fluxes were calibrated using a Latin Hypercube of physico-chemical substance characteristics as provided by the literature: surface soil half-lives of 10-35 d, Freundlich KOC of 150-330 ml/g, Freundlich n of 0.9 – 1 and adsorption/desorption kinetics of 20 – 80 1/d.
Daily discharge simulations resulted in high Kling-Gupta efficiencies (KGE) for the calibration and the validation period (KGE > 0.70). Overall, terbuthylazine concentrations could be successfully reproduced with maximum KGE > 0.90 for all concentrations in the catchment and loads at the outlet. The generally lower concentrations in the tributaries that were measured by the passive samplers and the declining concentrations towards the outlet in the main channel could be reproduced by the model. The model simulated overland flow to be the major source of terbuthylazine in the main channel and soil water fluxes to be the most important pathways in the tributaries. Simulation results suggest that less than 0.01 % of applied terbuthylazine mass was exported to the river in the Wark catchment and less than 5 % of the exported mass was originating from the sampled tributaries.
In addition to calibration of substance characteristics, passive sampler data was helpful in model setup of application field connectivity. Since the spatial resolution of the model was 50m, input maps sometimes showed a field to be directly connected to a river, whereas it was in reality separated from it by a 30m wide field or forest strip. Such misconfigurations leading to high concentrations in tributaries could easily be identified by comparing model results to passive sampler data.
In conclusion, assigning different transport pathways of terbuthylazine to the rivers by model simulations was helped by using the additional spatial information on pesticide concentrations gained from passive samplers.