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Assessment of model uncertainty during the river export modelling of pesticides and transformation products

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The modelling of organic pollutants in the environment is burdened by a load of uncertainties. Not only parameter values are uncertain but often also the mass and timing of pesticide application. By introducing transformation products (TPs) into modelling, further uncertainty coming from the dependence of these substances on their parent compounds and the introduction of new model parameters are likely.
The purpose of this study was the investigation of the behaviour of a parsimonious catchment scale model for the assessment of river concentrations of the insecticide Chlorpyrifos (CP) and two of its TPs, Chlorpyrifos Oxon (CPO) and 3,5,6-trichloro-2-pyridinol (TCP) under the influence of uncertain input parameter values. Especially parameter uncertainty and pesticide application uncertainty were investigated by Global Sensitivity Analysis (GSA) and the Generalized Likelihood Uncertainty Estimation (GLUE) method, based on Monte-Carlo sampling. GSA revealed that half-lives and sorption parameters as well as half-lives and transformation parameters were correlated to each other. This means, that the concepts of modelling sorption and degradation/transformation were correlated. Thus, it may be difficult in modelling studies to optimize parameter values for these modules. Furthermore, we could show that erroneous pesticide application mass and timing were compensated during Monte-Carlo sampling by changing the half-life of CP. However, the introduction of TCP into the calculation of the objective function was able to enhance identifiability of pesticide application mass.
The GLUE analysis showed that CP and TCP were modelled successfully, but CPO modelling failed with high uncertainty and insensitive parameters. We assumed a structural error of the model which was especially important for CPO assessment. This shows that there is the possibility that a chemical and some of its TPs can be modelled successfully by a specific model structure, but for other TPs, the model structure may not be suitable.
Concluding, this study confirmed that the introduction of TPs into pesticide fate and export modelling from hydrological catchments amplifies parameter uncertainty and model structure uncertainty.