Geophysical Research Abstracts
Vol. 16, EGU2014-3900, 2014
EGU General Assembly 2014

Estimation of pesticide and transformation product export pathways in a headwater catchment

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Following their application, pesticide residues are exported towards rivers along several hydrological pathways in agricultural areas. The importance of each pathway is influenced by the substances' physico-chemical characteristics, mainly sorption and degradation. Incomplete mineralization results in the formation of transformation products (TPs) which have generally different environmental fate characteristics than their parent compounds (PCs). Therefore, the export pathways of pesticides and their transformation products towards rivers may also be different. In order to investigate this hypothesis, we extended a distributed process-based hydrological model (ZIN-AgriTra) by the environmental fate of pesticides and their TPs. The process-based nature of the model allowed for an analysis of PC and TP export pathways including overland flow, lateral preferential flow in soils and soil water flow to tile drains. The model was applied to a Swiss headwater catchment using three pesticides and their TPs as test substances. It was successfully calibrated to three sampling stations in the catchment. At the end of the simulated three-months period, most of the applied pesticides were either fully mineralized or incompletely transformed. Less than 2% of each pesticide was exported to the river as PC or TP. Although all three pesticides could be classified as slightly mobile they remained in the top soil layer during the whole period, whereas the more mobile TPs were additionally leached through the soil towards tile drains. Accordingly, PCs were exported largely by surface runoff, while a larger share of TPs was exported via tile drains. Additionally, the delayed formation and degradation of TPs led to an export under different hydrological conditions resulting in an increased subsurface export of TPs towards the end of the simulation period. A consequence of the different export pathways of PCs and TPs could be shown by an assessment of critical source areas (CSA) in the study catchment: CSA for PCs were restricted to small areas whereas CSA for TPs were more equally distributed in the catchment. Our study demonstrates that PCs and their TPs have generally different export pathways in catchments because of their different physico-chemical properties and the delayed formation of TPs. We suggest that these results should be considered in risk assessment of pesticide residues export to adjacent rivers and that catchment scale models should be extended to include both PCs and TPs.