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Input dynamics of pesticide transformation products into surface water

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Some pesticide transformation products have been observed to occur in higher concentrations and more frequently than the parent active pesticide in surface water and groundwater. These products are often more mobile and sometimes more stable than the parent pesticide. If they also represent the major product into which the parent substance is transformed, these transformation products may dominate observed pesticide occurrences in surface water and groundwater. Their potential contribution to the overall risk to the aquatic environment caused by the use of the parent pesticide should therefore not be neglected in chemical risk and water quality assessments. The same is true for transformation products of other compound classes that might reach the soil environment, such as veterinary pharmaceuticals. However, the fate and input pathways of transformation products of soil-applied chemicals into surface water are not yet well understood, which largely prevents their appropriate inclusion into chemical risk and water quality assessments. Here, we studied whether prioritization methods based on available environmental fate data from pesticide registration dossiers in combination with basic fate models could help identify transformation products which can be found in relevant concentrations in surface and groundwater and which should therefore be included into monitoring programs.

A three-box steady state model containing air, soil, and surface water compartments was used to predict relative inputs of pesticide transformation products into surface waters based on their physico-chemical and environmental fate properties. The model predictions were compared to monitoring data from a small Swiss river located in an intensely agricultural catchment (90 km2) which was flow-proportionally sampled from May to October 2008 and screened for 74 pesticides as well as 50 corresponding transformation products. Sampling mainly occurred during high discharge, but additional samples during baseflow conditions were also taken. The analytical measurements included solid phase extraction, liquid chromatography and high resolution mass spectrometry (SPE-LC-HR-MS/MS). Quantification was achieved using reference standards and internal standards.

Besides the well-known transformation products of triazine and chloroacetanilide herbicides, transformation products of other compound classes such as azoxystrobin acid (from azoxystrobin, strobilurin fungicide), chloridazon-desphenyl and chloridazon-methyl-desphenyl (from chloridazon, pyridazinone herbicide), and metamitron-desamino (from metamitron, triazinone herbicide) were analyzed in surface water. For a selection of widely used pesticides in the catchment, modelled ratios of transformation product versus parent pesticide concentrations were compared to the measured concentration ratios in the river for the application period and for two 2-month periods following application. Concentration ratios agreed within a factor of 10 for all pairs of parent pesticides and transformation products, and for all seasons, with a single exception. The ratio of chloridazon-desphenyl to chloridazon was under-predicted by a factor of approximately 20. The data revealed that chloridazon-desphenyl was also found in elevated concentrations in all baseflow samples, indicating its presence in the groundwater component of the catchment. The same was true for other transformation products (e.g., metamitron-desamino, chloridazon-methly-desphenyl, metolachlor-ESA), but to a lesser degree. Based on baseflow separation of the hydrograph, the concentration ratio estimation model was supplemented with an additional baseflow component. The concentrations in the baseflow component were estimated with a simple leaching relationship that was compared against measured baseflow concentrations and groundwater findings in Switzerland. The final model yielded good agreement for all compounds and is therefore deemed suitable for prioritization of transformation products with a relevant exposure potential. It also clearly indicated the contribution of groundwater to the overall occurrence of pesticides and their transformation products in Swiss surface waters.