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MONITORING AND MODELLING THE DYNAMIC FATE AND BEHAVIOUR OF PESTICIDES IN RIVER SYSTEMS AT CATCHMENT SCALE

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Dutch translation of the title:

Meten en modelleren van het dynamisch gedrag en voorkomen van pesticiden in riviersystemen op bekkenschaal.

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Summary

Pesticides are useful to society thanks to their ability to exterminate disease-causing organisms and control insects, weeds and other pests. At the same time, most pesticides may be harmful to humans, animals and the environment because of their ecotoxicity, their potential bio-accumulating properties or their hormone disrupting effects. In order to gain insight in the processes determining the fate of pesticides in river systems, monitoring and modelling are complementary tools.

From several studies it has become clear that pesticides in surface waters show a time-varying course which can not be monitored by grab sampling. Few monitoring studies performed in the past contained composite water samples instead of grab samples. As far as we know, no studies were performed on both the dynamics of pesticides in the water column and in the sediment. Therefore, it was decided to set up intensive monitoring campaigns taking into account both the water compartment and the sediment. Besides monitoring, models form useful tools for decision makers. For pesticides, there seems to be a lack of dynamic models taking into account point losses as entry route. Also models describing in-river processes based on closed mass balances usable at catchment scale are as far as we know not available. Moreover, few models are well validated with extensive monitoring data. The objective of this thesis was to fill these modelling gaps and to perform a validation by means of the collected monitoring data.

During spring 2004 and 2005, two continuous monitoring campaigns (sampling interval of 8 hours, for 3 months) were set up in river basins of varying sizes in Belgium. Both in the water column and in the sediment the following pesticides were investigated in detail: atrazine, carbendazim, chloridazon, diuron, isoproturon, lenacil and simazine. The water compartment showed hourly variations in pesticide peak concentrations, regularly exceeding the Flemish standards for basic water quality of surface waters (for instance 2 µg/l for atrazine and 1µg/l for simazine). The maximum measured concentrations were respectively 45, 0.25, 280, 40, 62, 3 and 18 µg/l. The concentration of pesticides in pore water, measured on a monthly basis, followed the trends of the water compartment remarkably well, but with concentrations that were 1 or 2 orders

of magnitude lower. A comparison between river basins of different scales demonstrates that a scaling effect exists: the highest concentrations occur in the smaller upstream areas, whereas the concentrations downstream are more diluted and dispersed. A risk assessment was performed based on the bulk water concentrations of diuron and isoproturon and their respective HC5-95% values. A HC5 represents a concentration that protects 95% of the species. A HC5-95% is the lower 95% confidence limit of the HC5 derived from the species sensitivity distribution that is based on no observed effect concentration (NOEC) data (SSD_{NOEC}). These HC5-95% values are rather rigorous thresholds. Longer periods of severe exceedance of the threshold occur in smaller catchments as compared to the bigger catchments where dilution and dispersion diminish the risk for local fauna and flora. Hence, an acute risk to pesticide exposure especially holds for upper catchments, that are, moreover, typically characterized by more sensitive ecosystems due to the absence or minimal impact of other pollution pressures from households and industries.

In order to model pesticide fate in river systems at catchment scale, 2 different models were used. The SWAT model was used for predicting pesticide fluxes towards the river whereas the RWQM1 model was extended in order to describe in-river processes for pesticides. The advantage of the RWQM1 model lies in the fact that it has closed elemental mass balances and that it explicitly considers microbial biomass as a state variable.

By means of an LH-OAT sensitivity analysis, the most influential parameters for hydrology and pesticide supply towards the river were determined for the Nil catchment. The LH-OAT method combines the One-factor-At-a-Time (OAT) sensitivity analysis and Latin Hypercube (LH) sampling by taking Latin Hypercube samples as initial points for the OAT-sensitivity analysis. It was shown that the curve number and some parameters related to groundwater were very influential. The importance of the groundwater related parameters could be attributed to the specific geology of the studied catchment. Besides a well calibrated hydrology, a correct estimation of the point losses is necessary for reliable pesticide predictions. To this end, the SWAT model was extended for direct losses, which were defined as the summation of drift losses and point losses occurring at the day of application. It was then found that the contribution of runoff events and point losses is much more important than the contribution attributable to drift. Besides, the SWAT source code was extended with processes occurring in a buffer strip.

Different management scenarios were simulated and compared to the initial situation. The results revealed that strip cropping seems to be more efficient than the implementation of cover crops, than buffer strips, than a 25% reduction of point losses and plough management, in that order. The study showed that modelling can be used to estimate the impacts of water quality management programs in river basins. Such an approach allows to rank different mitigation measures for pesticide fluxes towards surface waters.

The RWQM1 was extended and modified with processes determining the fate of non-volatile pesticides. The exchange of pesticides between the water column and the sediment is described by three transport processes: diffusion, sedimentation and resuspension. Burial of sediments is also included. The modified model was implemented in WEST (World Wide Engine for Simulation, Training and Automation, Hemmis NV, Kortrijk, Belgium) and used to predict the concentrations of diuron and chloridazon in the river Nil. Simulated pesticide concentrations were compared with measured values resulting from the intensive monitoring campaign performed during spring 2004. The comparison showed good agreement between model predictions and observed concentrations, even without calibration. The simulation results showed that pesticide concentrations in the bulk water were not sensitive to the selected biochemical model parameters along the 8-km long river stretch, but they were mainly determined by the imposed upstream concentrations. This is probably due to the short retention time in the considered stretch. The high concentrations in the bulk water were not observed in the sediment pore water due to a limited exchange between the water column and the sediment that is determined by diffusion and sorption. The concentrations on the sediment varied in time due to sorption, sedimentation and resuspension. Furthermore, the sensitivity of the model output to changes in the model parameters was tested. The concentrations in the pore water and on the sediment particles were highly sensitive to the diffusion and the sorption coefficient. Model users should determine these parameters with accuracy in order to reduce the degree of uncertainty in the results.

Some final conclusions and recommendations for further research are summarized at the end of the dissertation.