MONITORING AND MODELLING PESTICIDE DYNAMICS IN SURFACE WATER

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Abstract. Pesticides occur frequently in surface water. We used a combination of monitoring and modelling to assess the fate of pesticides at the catchment-scale. We continuously (sampling interval of eight hours) monitored eight pesticides (atrazine, carbendazim, chloridazon, diuron, isoproturon, lenacil and simazine) in surface water of two Belgian catchments. The surface water showed hourly variations in pesticide concentrations, temporarily exceeding ecotoxicological thresholds. We used the SWAT model to predict hydrology and pesticide fluxes from agricultural land to the river at the catchment scale. In addition, we used an extended version of the RWQM1 model to calculate in-river transformation of pesticides. The models adequately reconstructed the highly dynamic behaviour of the pesticides in the river. The simulations further demonstrated the importance of point sources due to poor agricultural practices and the effectiveness of measures to reduce pesticide inputs into surface water.

Keywords: catchment; modeling; monitoring; pesticides; RWQM1; surface water; SWAT

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1. Introduction

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, pesticides may be harmful to humans, animals and the environment because of their ecotoxicity, their potential bio-accumulating properties or their anticipated hormone disrupting effects. To gain insight in the processes determining the fate of pesticides in river systems, monitoring and modelling are necessary tools.

Pesticides enter river systems via diffuse sources. As diffuse input pathways run-off, drainflow, drift, atmospheric deposition and groundwater flow can be distinguished. Based on modeling, Bach et al. (2001) showed that surface runoff is expected to be a major source of diffuse pesticide input in Germany. Non-point source input via preferential flow in soil is important in tile-drained structured soils (Leu et al., 2004) and spray-drift is rather specific for orchard regions (Bach et al., 2001). From field measurements, Kreuger (1998) found that inputs by drift or direct spraying were less important.

Pesticides can enter river systems as point sources, i.e., at punctual locations along the river. Examples of point sources of pesticides are sewage treatment plants, sewer overflows and direct inputs due to bad management practices of farmers. The contribution of point sources to pesticide pollution in river systems was demonstrated to be very important in several catchments in Europe. In different catchments in Germany (Neumann et al., 2002) with varying catchment sizes between 7 and 1940 km^2, in Switzerland (Gerecke et al., 2002; Leu et al., 2004), in Sweden (Kreuger, 1998), in the UK (Mason, 2003) and in Belgium (Beernaerts et al., 2005), it was shown that the load of pesticides in rivers could be attributed for 30 up to 90% to point sources.

In view of the risk assessment of pesticides under the EU Plant Protection Products Directive (91/414/EEC) and in view of the river basin management plans in the EU Water Framework Directive (2000/60/EC), a clear need exists to realistically predict surface water concentrations of pesticides. To this purpose, both monitoring and modelling pesticide fate at the appropriate temporal and spatial scales is necessary. In the next paragraphs, we will demonstrate this with a few cases of pesticide pollution in Belgian rivers.

2. Pesticide Monitoring

To date, very few studies looked at the short-term dynamics of pesticides in river water (Kreuger, 1998; Neumann et al., 2002; Leu et al., 2004; Beernaerts et al., 2005). Besides the temporal variation of pesticide concentrations in river systems, there is also spatial variation. Upstream river stretches in agricultural areas are more likely to be exposed to higher pesticide concentrations (Leu et al., 2004; Konstantinou et al., 2006).

2.1. MONITORING DESIGN

We focused on 6 herbicides and 1 fungicide, that are (or were, in the near past) found in high concentrations in Belgian surface waters (Beernaerts et al., 2005; Flemish Environment Agency, 2007). Two typical rural catchments in Belgium, mainly receiving water from agricultural fields, were sampled. Major crops grown were corn, sugar beat, winter wheat and orchards.

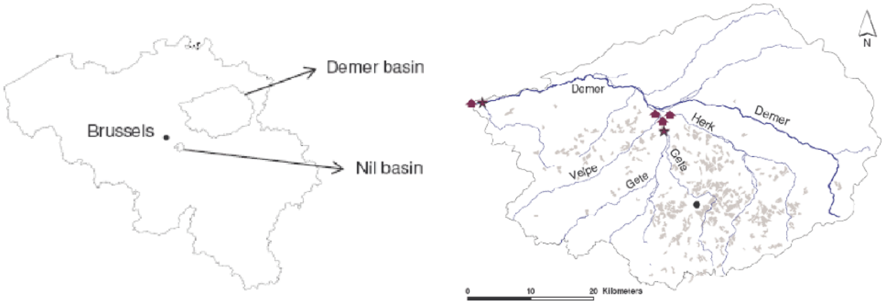

Figure 1. Geographical location of the sampling stations

In the 32 km^2 Nil basin (Figure 1a), an intensive monitoring campaign was conducted between March 15th and June 15th 2004. Two refrigerated sampling stations took 50 ml river water samples every 15 minutes and collected the water in a composite sample every 8 hours along the river: one upstream and one at the outlet of the catchment. During rainfall events, the frequency was increased and each composite sample then represented 6 hours. In the 2100 km^2 Demer basin, a similar campaign was set up in 2005 from May 15th till July 1st. On four locations in the Demer basin (Figure 1b), sampling stations were placed. The pesticides were analyzed using LC-MS/MS after extraction over an on-line SPE (solid phase extraction) unit and after detection in multiple reaction monitoring mode (MRM) using positive ion electrospray.

Daily rainfall data for the meteorological stations in Chastre-Blanmont and Sint-Truiden were obtained from the Royal Meteorological Institute (RMI) and hourly discharge data were made available by DGRNE (Direction Génerale des Ressources Naturelle et de l’Environnement) for the Nil and by the HIC (Hydrological Information Centre) for the Demer.

2.2. MONITORING RESULTS

The measured pesticide concentrations for the Nil (small scale, tens of km^2) and Demer (larger scale, hundreds to thousands of km^2) catchment are represented in Figure 2.

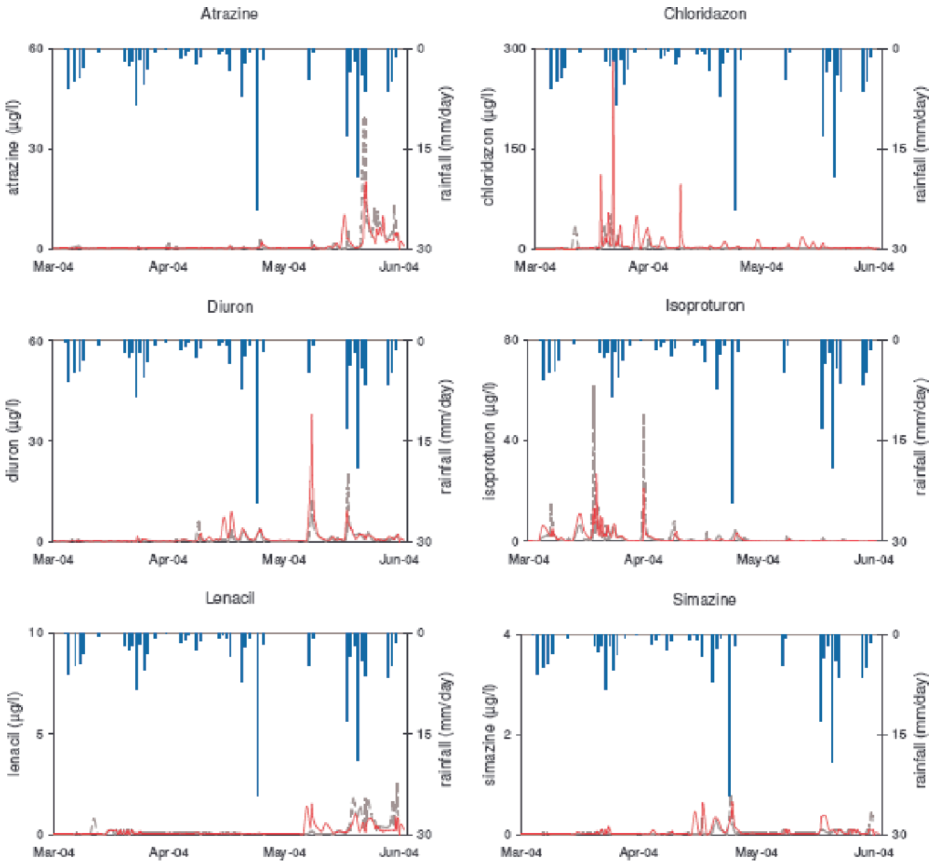

Figure 2. Subdaily pesticide concentrations in (a) the Nil, a small-scale catchment (tens of km^2) and (b) the Demer, a larger-scale catchment (thousands of km^2). In the Demer, the solid line represents the concentrations at the outlet, whereas the broken lines refer to pesticide concentrations in the upstream tributaries

The results show extremely dynamic pesticide concentrations in surface water. The concentration fluctuations are the largest in the small-scale catchment. High pesticide concentrations could be found in the river after application and rainfall, and are mainly attributed to runoff. Even larger peaks were observed in the absence of rain immediately after application. We attribute these peaks to direct input of pesticides to the water system due to the clean-up of spray equipment, leaking tools, processing of spray waste, and application on paved surfaces. In Figure 2 such an event can be seen for chloridazon around the 15th of April: there is a period without rain, but still high chloridazon concentrations were observed. It can be shown that 30 to 95% of the total annual pesticide load passing in the small catchment could be attributed to point sources.

Similar to small-scale catchments, the pesticide concentrations show a highly variable course in the larger-scale catchments. Nevertheless, the maximum concentrations for all observed pesticides at all monitoring stations in the larger-scale catchment are lower than those measured in the small-scale catchment, except for simazine. The importance of point sources can be assessed for pesticides that were applied during the monitoring campaign, i.e., atrazine, carbendazim, diuron, lenacil and simazine. High concentration peaks originating from point sources are clearly visible for atrazine around mid June. The results also clearly show an effect of dilution along the larger-scale catchment: the concentration peaks are higher and more narrow in the upstream tributaries as compared to those seen downstream, which are more suppressed and spread out due to dilution and dispersion.

In summary, high-frequent monitoring reveals that pesticide concentrations in surface water show an extremely dynamic behaviour, which can be explained to a certain extent by rainfall/runoff characteristics of the catchment, but to a large extent also by point sources. This causes pesticide concentrations in surface water in the application period to follow a random pattern. This random behaviour determines the design of monitoring programmes of pesticides in surface water. Given the large variability in pesticide concentrations during application, a sufficient number of samples needs to be taken in order to estimate the true water quality status with an acceptable certainty. For example, atrazine showed a coefficient of variation of 92% based on the high-frequent monitoring in the Demer catchment in June 2005. A total number of 34 samples needs to be taken to state with a confidence of 95% that the true mean water quality for that period lies between 346 and 620 µg/L, or an accuracy of 28% (relative to the mean). The selection of the desired level of accuracy depends on the measurement accuracy. If one wants 20% accuracy, a number of 67 samples would be needed. When there is no clear trend in the concentrations, time-series of pesticide concentrations during application over multiple years may be used to determine the true water quality.

3. Pesticide Modelling at the Catchment Scale

A whole range of models exist that predict pesticide concentrations in river systems. They range from rather simple screening tools to complex catchment or watershed models. Watershed models are useful for analyzing long-term effects of hydrological changes and water management practices, e.g., AnnAGNPS (Bingner and Theurer, 2001), HSPF (Donigian et al., 1993) and the Soil and Water Assessment Tool SWAT (Arnold and Fohrer, 2005). SWAT is a model for continuous simulations in predominantly agricultural watersheds and HSPF is suited for mixed agricultural and urban watersheds. MIKE SHE (Refsgaard and Storm, 1995) is both a single-event and long-term continuous simulation model. MIKE SHE is suitable for small areas or watersheds for studies of hydrology and non-point-source pollution (Borah and Bera, 2003). The new generation of models includes fully-coupled watershed models. Three fully-coupled numerical models are currently available, namely InHM (Loague et al., 2004), MOD-HMS (Panday and Huyakorn, 2004), and HydroGeoSphere (Sudicky et al., 2005). The main distinguishing feature of these models is that they fully couple the surface and subsurface hydrologic domains by simultaneously solving one system of non-linear discrete equations describing flow and transport in both flow regimes.

3.1. MODELLING SETUP

We selected the SWAT model to calculate pesticide fluxes from agricultural land to the river in the small Nil catchment. SWAT simulates pesticide movement into the stream network via surface runoff (in solution and sorbed to sediment transported by the runoff), and via percolation in the soil profile and transport through the aquifer. The movement of the pesticide is controlled by its solubility, degradation half-life, and soil organic carbon adsorption coefficient. Pesticides on plant foliage and in the soil degrade exponentially according to the appropriate half-life. Pesticide transport by water and sediment is calculated for each runoff event and pesticide leaching is estimated for each soil layer when percolation occurs.

We used an extended version of the RWQM No. 1 model (Reichert et al., 2001) as implemented in the WEST modeling and simulation software (MOSTforWATER NV, Kortrijk, Belgium) to model in-river transformation processes from one location in the river to a downstream location. The advantage of using RWQM No. 1 instead of SWAT for modelling pesticide processes in the river lies in the fact that it has closed elemental mass balances and that it explicitly considers microbial biomass as a state variable. A better accounting of biological activities will also affect the way the environmental conditions in the river change (e.g., pH, dissolved oxygen concentration) which may influence the fate of the pesticide in the water column. Another advantage of RWQM No. 1 lies in its capability to study the fate and behaviour of different pesticides at the same time while the SWAT model can only route one pesticide at a time. With the RWQM1 model very small time steps can be used (e.g., minutes) compared to the SWAT model which uses daily or hourly (ESWAT) time steps. For modeling sedimentation and resuspension processes, and follow the fast pesticide concentration dynamics, this an important advantage.

3.2. MODELLING RESULTS

3.2.1. Pesticide Fluxes to the River

The first step in watershed modelling of chemicals is to get hydrology well simulated. Figure 3 shows the calibrated model results for discharge at the outlet of the small Nil catchment. The model is specifically calibrated for the spring period, since most herbicides were applied and monitored during that period. Generally, a good fit is obtained between observed and modelled discharge. The most sensitive parameter in the model was the curve number, an empirical parameter that accounts for rainfall/runoff properties of the landscape. Since the Nil catchment shows a distinct topography and is not tile-drained, hydrology is dominated by surface runoff properties.

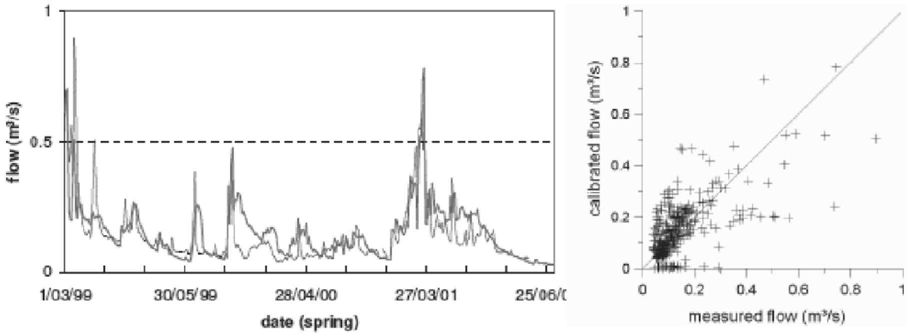

Figure 3. Calibrated model predictions for discharge in the spring period in the small catchment

To account for point sources of pesticides to surface water, adaptations to the original SWAT model were needed. To check model performance, the SWAT model results were compared to the results of the intensive monitoring campaign performed during the years 1998–2002. The results are shown in Figure 4. Calibration was performed for 1998, while 1999 up to 2002 were used to validate model predictions. A relatively good approximation of the pesticide concentrations, e.g., the lower concentrations in 2001, and representation of the concentration pattern was obtained with the model.

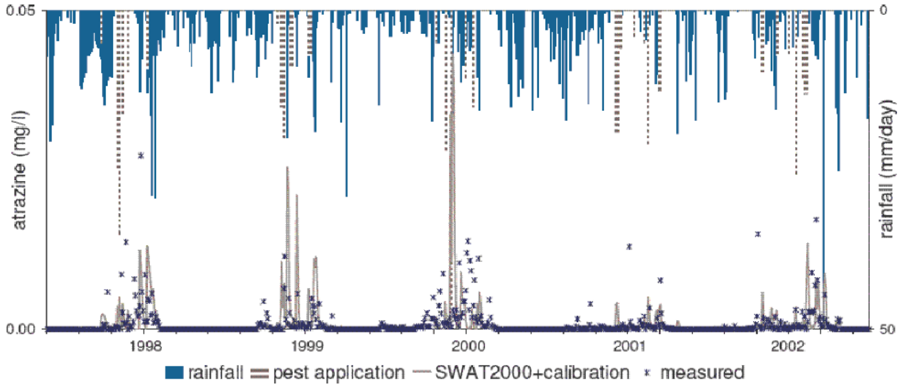

Figure 4. Measured and predicted atrazine concentrations at the catchment outlet after calibration (spring periods of 1998–2002)

The validated SWAT model was subsequently used to quantify the loads resulting from run-off, atmospheric drift, and point sources. The results show that the total atrazine load to the river represents 1.5–2.2% of the amount applied in the catchment (2001 showed 0.3% lost). This is in good agreement with the measured quantities. The model further shows that 9–38% can be attributed to point sources, which underestimates the estimated real load (assumed in dry periods) of 39–54%. This is due to the sensitivity of the model to hydrology: overpredictions of flow lead to underpredictions of pesticide concentrations. A negligible load can be attributed to drift. The validated SWAT model was further used to quantify the effect of agricultural measures on pesticide fluxes to the river, such as residue management, sowing cover crops, buffer strips, strip cropping or contour farming. Preliminary calculations show that strip cropping is more efficient in reducing pesticide loads than buffer strips or residue management. Since the soil processes in SWAT are described empirically, the results are qualitative and can be used for ranking measures, not for quantifying them.

3.2.2. Pesticide Transformation in the River

Predictions of pesticide concentrations at the outlet of the Nil catchment were made using the extended RWQM No.1 model. The measured concentrations in the upper reaches of the river were taken as upper boundary condition for the model. The results are shown in Figure 5.

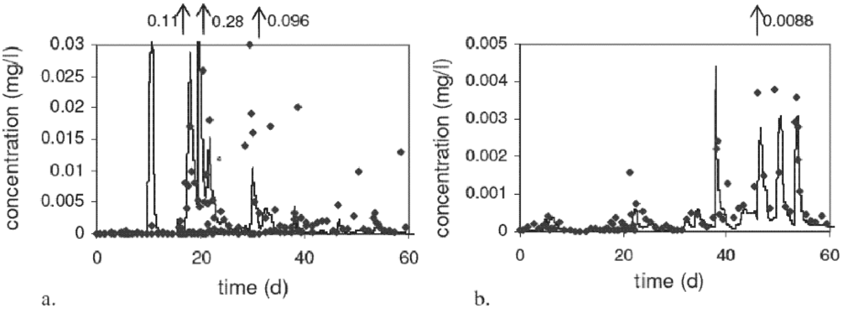

Figure 5. Predicted surface water concentrations of (a) chloridazon and (b) diuron at the outlet of the Nil catchment based on measured concentrations 8 km upstream

The model predicts the concentrations at the outlet extremely well without extensive calibration. In this case, the outlet concentrations are determined to a large extent by the measured concentrations upstream, rather than additional processes or fluxes along the 7-km-river stretch. River processes will become much more important in larger catchments where rural subcatchments deliver pesticides that are further diluted and degraded in the river downstream.

4. Conclusions

Pesticides occur in surface waters in a highly dynamic pattern, resulting from the distinct pesticide applications during the season and from rainfall events. Monitoring programmes of pesticides and other priority chemicals should take this dynamic behaviour into account. Pesticides end up in the rivers due to diffuse sources but to a large extent also due to point sources. This causes pesticides to occur randomly in rivers during the period of application. Given the large temporal variability, a sufficient number of samples needs to be taken to adequately represent water quality.

Catchment models such as SWAT are able to reproduce the dynamics of pesticides in the river. SWAT showed the importance of runoff and point sources and the relative unimportance of drift in a small Belgian catchment. The model also allowed to rank various management options to reduce pesticide loads. Modelling the river system using RWQM1 further showed that in-river processes are relatively unimportant in small catchments.

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