The dynamic water–sediment system: results from an intensive pesticide monitoring campaign

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Abstract To gain insight into the dynamics of pesticides in the different compartments of a river system, an intensive monitoring campaign was set up. An extensive dataset is useful when planning to model the fate of pesticides in river systems. In this study we focus on the Nil, a small, hilly basin situated in the central part of Belgium. Two automatic samplers were placed in the river basin, i.e., one at the mouth and one upstream, taking composite samples of water and suspended solids. Undisturbed sediment samples were taken by means of a macro-core and immediately frozen with CO_2-ice. The samples were sliced and analysed for pesticides in pore water and on sediment. The results of the study revealed the dynamics of the different compartments of a river system. The water compartment showed hourly variations in pesticide peak concentrations, regularly exceeding the standards. The amount of pesticides transported by suspended solids increased after a rainfall event. The concentration of pesticides in pore water, measured on a monthly basis, followed the trends of the water compartment remarkably well, but in a significantly lower concentration. These observations may be explained by combined diffusion, biodegradation and chemical reactions occurring in the water column and the sediment. Further insight into the importance of each of these processes can be gained by dynamic modelling, an approach that is currently being followed.

Keywords Monitoring campaign; pesticides; risk assessment; river water quality

Introduction

Pesticides are useful to society because of their ability to destroy disease-causing organisms and control insects, weeds and other pests. At the same time, most pesticides may be harmful to humans, animals and environment because of their ecotoxicity, their potential bio-accumulating properties and their hormone disrupting effects. Therefore, risk assessments are performed. By comparing environmental concentrations with predicted no observed effect concentrations (PNECs), the risk related to the release of a certain compound can be determined. In cases where there are only few data available concerning pesticide concentrations in river systems, one has to make assumptions and insert assessment factors. Also, worst case scenarios are commonly used. A realistic risk assessment needs more detailed data. Such data can originate from an intensive monitoring campaign or from a dynamic model for pesticides in river systems (Verdonck *et al.*, 2002; Deksissa *et al.*, 2004).

In order to develop a dynamic model predicting the fate of pesticides in river systems, more insight into the dynamics of pesticides in the different compartments of a river system is required. From the literature, it seems that various pesticides can be detected in high concentrations (μg/l) in the water column of surface waters in many countries all over the world (Palma *et al.*, 2004; Comoretto and Chiron, 2005). It was also found that pesticide peaks passing through the river show a highly dynamic course (Beernaerts *et al.*, 2002). This irregular course can be attributed to a supply through direct losses (e.g. through

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the clean-up of spray equipment, leaking tools, processing of spray waste and this on paved surfaces) and losses through run-off, leaching to groundwater and atmospheric drift. Different studies showed the importance of direct losses to the total amount of pesticides detected in a river (Albanis *et al.*, 1998; Neumann *et al.*, 2002; Holvoet *et al.*, 2005).

The purpose of this study was to set up an intensive monitoring campaign which results in: (i) representative data that can be used in a realistic risk assessment; (ii) knowledge about the dynamics of the different compartments of a water system; and (iii) data that can be used for the development and calibration of a dynamic model for pesticides in surface waters.

Methods

Study area

In this study we focus on the Nil, a small, hilly basin situated in the central part of Belgium. It drains an area of 32 km^2, is 14 km long and has a retention time of about 1 day. The average elevation measures 151 m a.s.l., with the highest top reaching 167 m a.s.l. and the watershed outlet lying at 110 m a.s.l. The area consists predominantly of loamy soils, 7% of the area is inhabited and the main crops grown are winter wheat (22% of the catchment area), corn (15%) and sugar beet (10%). 18% of the catchment consists of pasture (Figure 1).

The Nil catchment was selected because it is a well documented basin, studied in detail in terms of pesticide application (Beernaerts *et al.*, 2002). Table 1 represents the main crops grown in the catchment and the periods in which the appropriate pesticides are applied.

Monitoring campaign

An intensive monitoring campaign was run during spring 2004, i.e., the application period of herbicides. The campaign started 15 March and ended 15 July. To this end, two automatic samplers were placed in the river basin, i.e. one at the mouth and one upstream (Figure 1). Every 15 minutes, 50 ml of river water was taken by each sampler and collected in one glass bowl during 8 hours. This resulted in a composite sample every 8 hours. During rainfall events, the frequency was increased and each composite sample represented 6 hours of passing water. The automatic samplers were dark inside and were kept at a temperature of 4°C. Every 3 days, the samples were collected. They were then

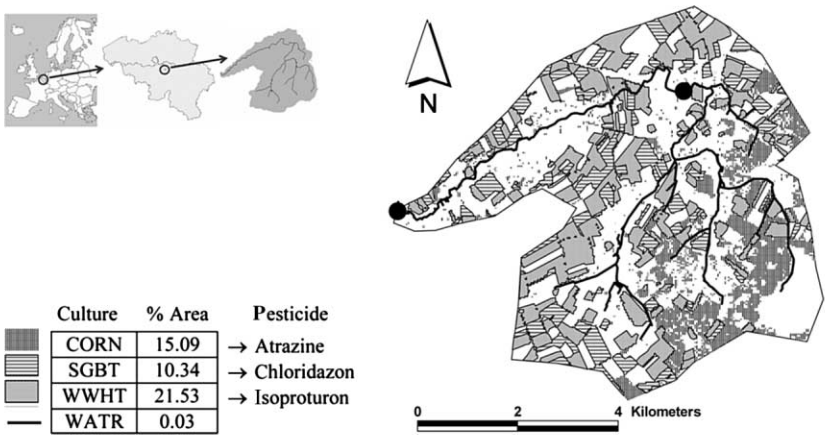

Figure 1 Situation and land use in the Nil catchment (with CORN = corn, SGBT = sugar beet, WWHT = winter wheat, WATR = water). The • represent the two measuring points

Table 1 Application periods of pesticides in the Nil catchment. (AI = active ingredient)

AI	Culture	March		April		May		June		July	
Atrazine	Corn				▨	▨	▨	▨			
Isoproturon	Winter wheat		▨	▨							
	Barley		▨	▨	▨	▨					
Chloridazon	Beets	▨	▨	▨	▨						
Diuron	Non-agriculture			▨	▨	▨	▨	▨	▨	▨	▨

transferred into amber glass bottles capped with Teflon lined screw caps and transported in cool boxes. At the lab, the samples were stored in the dark at 4°C until analysis.

Analyses of water samples were performed for at least one sample a day for each monitoring point. For the sampling station upstream, the second sample of the day was always analysed. Taking into account a residence time of about 16 hours between the two sampling stations, every first sample of the day at the mouth of the river was analysed. Once the results of the screening analyses were available, periods showing high peaks of pesticide concentrations were selected. For these periods, the two remaining samples per day were analysed as well, both upstream and downstream. Analyses were performed for the herbicides atrazine, chloridazon, diuron, isoproturon, lenacil and simazine.

Undisturbed sediment samples were taken twice (17 May, 29 June) by means of a macro-core and were immediately frozen on the field with CO_2-ice. This way, the sediment samples could be easily transported avoiding any disturbance. Once in the lab, the samples were sliced and analysed for pesticides in pore water and on the sediment.

Analysis

Water samples. 25 ml of the water samples was filtered through a 0.45 μm filter. 10 ml of the filtered water was spiked with 10 μl Mie-Or-C13atrazine-004 and extracted with an on-line SPE unit (Merck-Hitachi OSP-2A with C18 phase). Desorption was performed with a mobile phase. By means of an automated transfer, the pesticides were then analysed by LC-MS/MS. The pesticides were detected in multiple reaction monitoring mode (MRM) using positive ion electro-spray. The on-line SPE LC-MS/MS method is a very appropriate tool to monitor polar pesticides in surface waters. The method allows the interference-free determination of pesticides at low cost, with a high throughput of samples.

Soil samples. First the sediment slices were weighed. Next, the pore water and the sediment were separated by applying vacuum over a 0.45 μm filter. The amount of extracted pore water was measured. The pore water could be further analysed as described for the water samples. The remaining sediment was weighed and then dried at 40°C. The dry sample was again weighed so that the amount of pesticides originating from the not completely extracted pore water could be recalculated afterwards. 15 g of soil was mixed with Na_2SO_4 and extracted by sonication with acetone. The organic solvent was then evaporated. Water and methanol were added (9:1 v:v) during sonication. Following this, the procedure was similar to that previously described for water samples.

Results and discussion

Herbicides in the water compartment

The results for the different pesticides in the water compartment were plotted versus time, together with the rainfall events which occurred. For the pesticides studied, a wavy course could be determined, as is represented in Figure 2 for chloridazon and atrazine. Periods with frequent pesticide peaks for each of the compounds correspond with their

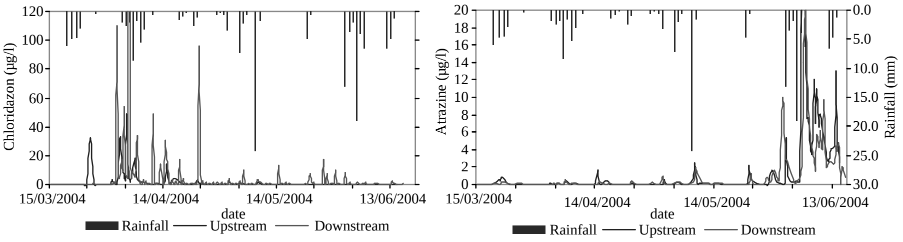

Figure 2 Measured concentrations of chloridazon (left) and atrazine (right) at the mouth and upstream in the river Nil during spring 2004

application period. The highest pesticide concentrations could be found in the river after rainfall events due to runoff and even more important in the absence of rain immediately after application, e.g. through the clean-up of spray equipment, leaking tools, processing of spray waste and this on paved surfaces. On Figure 2 such an event can for instance be seen for chloridazon around 14 April. Approximately 70% of the load of pesticides passing through the river is coming from these direct losses.

The graphs representing the water column show that it is a highly dynamic system. Routine monitoring networks from environmental agencies base their pesticide determination in rivers on a three-monthly sampling by filling a bucket. As could be seen from this study, this method will never give a realistic view of what is happening in the river. By using passive accumulating devices, at least an averaged value could be determined over a certain period of time which much better represents the history of the water system.

The high concentrations themselves also deserve special attention. The allowed maximum concentration in Flemish rivers for basic water quality amounts are 2 µg/l for atrazine and 1 µg/l for the sum of chlorinated aromatic amines. Both the concentrations for chloridazon and for atrazine frequently exceed these standards. The maximum concentrations detected during the monitoring campaign for chloridazon and atrazine were respectively 300 µg/l and 40 µg/l. The PNEC for atrazine determined by Klein *et al.* (1999) by means of the COMMPS procedure amounts to 0.8 µg/l. This PNEC is frequently exceeded and toxic effects are probable. An ecotoxicity test for repeated pulse exposures could give a more realistic idea about the toxic effects of these strongly varying pesticide concentrations. This is currently being investigated.

Herbicides in the pore water

Analysis of the pore water revealed that the dynamics in the pore water are in agreement with the application period of the appropriate pesticides. As can be seen from Figure 3, the chloridazon concentration decreases from May to June in pore water. The application period for chloridazon lasts from March until the end of April. The same can be seen for atrazine, as the application period for atrazine is most intensive during June.

Concentrations of pesticides in the pore water are about a factor of two smaller compared to concentrations in the water column. Fast pesticide peaks passing in the overlaying water column have only short residence times and consequently, not enough time to interact with the pore water.

Herbicides on the sediment

On the sediment, a similar trend can be found. Here too, the dynamics are in agreement with the application schemes (see Figure 4). There is a decrease with depth and there are some irregularities due to stones present in the sediment slices.

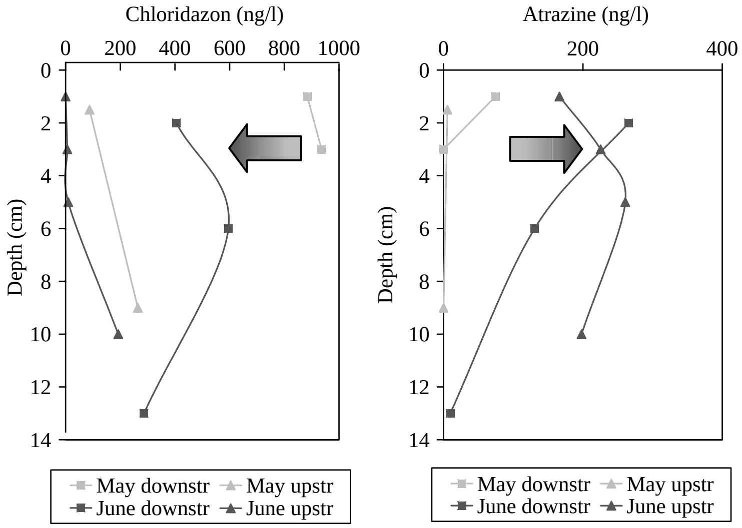

Figure 3 Measured concentrations of chloridazon and atrazine in pore water of sediment samples, taken at the mouth and upstream in the river Nil on 17 May and 29 June

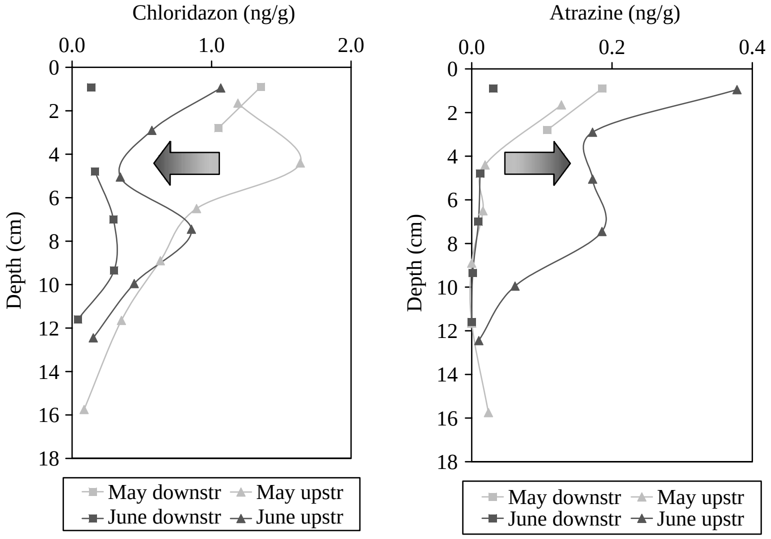

Figure 4 Measured concentrations of chloridazon and atrazine in the sediment, in samples taken at the mouth and upstream in the river Nil 17 May and 29 June

The observations found in pore water and sediment can be explained through combined processes, i.e. diffusion, biodegradation, burial and chemical processes. Further insight in the importance of each of these processes can be gained by dynamic modelling. This research is currently in progress (Deksissa, 2004; De Schepper, 2005).

Conclusions

The water–sediment is a highly dynamic system which shows hourly variations. This information should be borne in mind during the set-up of monitoring campaigns. Monitoring campaigns for pesticides should be fine-tuned to: the application period of the respective pesticide, and the climatic conditions in the area. To be sure that the pesticide is detected, continuous sampling systems are preferred over grab/bucket sampling; due to high sampling costs, alternative sampling systems such as passive devices can be used in combination with models. In the water column, the irregular course can be attributed to run-off and direct losses. The direct losses contribute 50–70% of the pesticide load passing through the river. Only permanent sensitization of farmers regarding this issue resulted in the past (years 2000–2001) in a significant decrease of pesticide loads in the river. When this sensitization campaign was finished in 2002, pesticide loads in the river immediately increased (Beernaerts *et al.*, 2002). The contribution to the water column coming from pore water is negligible but may be very important for benthic organisms.

Besides, it seems that neither K_{OC}-values nor low-level Mackay models are able to predict the dynamic partitioning of pesticides over the compartments of a water system. These results underline the need of a dynamic model predicting pesticide concentrations to give insight in the importance of the different processes influencing the behaviour of pesticides. This work is currently in progress (De Schepper, 2005), starting from the dynamic model for chemical fate developed by Deksissa *et al.* (2004).

Finally, the intensive monitoring campaign showed frequent exceedance of the standards with possible effects on organisms in the river.

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