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Uncertainty in the river export modelling of pesticides and transformation products

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ABSTRACT

The modelling of agrochemical pollutants in the environment is burdened by numerous uncertainties. Not only parameter values are uncertain but often also the mass and timing of application. By introducing transformation products (TPs) into modelling, further uncertainty, coming from the dependence of these substances on their parent compounds and the introduction of new model parameters, is likely. The purpose of this study was the investigation of the behaviour of a parsimonious catchment scale model for the assessment of river concentrations of the insecticide Chlorpyrifos (CP) and its two main TPs, Chlorpyrifos Oxon (CPO) and 3,5,6-trichloro-2-pyridinol (TCP) under the influence of uncertain input parameter values. Especially parameter uncertainty and pesticide application uncertainty were investigated by Global Sensitivity Analysis (GSA) and the Generalized Likelihood Uncertainty Estimation (GLUE) method, based on Monte-Carlo sampling.

GSA revealed that half-lives and sorption parameters as well as half-lives and transformation parameters were correlated to each other. This means the concepts of modelling sorption and degradation/transformation were correlated. Thus, it may be difficult in modelling studies to optimise parameter values for these modules. Furthermore, we could show that erroneous pesticide application mass and timing were compensated during Monte-Carlo sampling by changing the half-life of CP. However, the introduction of TCP into the calculation of the objective function was able to enhance the identifiability of pesticide application mass. The GLUE analysis showed that CP and TCP were modelled sufficiently, but CPO modelling failed with high uncertainty and insensitive parameters. We assumed a structural error of the model which was especially important for CPO assessment. This shows there is the possibility that a chemical and some of its TPs can be modelled successfully by a specific model structure, but for other TPs the model structure may not be suitable. Concluding, this study confirmed that the introduction of TPs into pesticide fate and export modelling from hydrological catchments amplifies parameter uncertainty and model structure uncertainty.

1. Introduction

In order to control weeds and vermin, pesticides have been applied in the environment for a long time. For an assessment of their impacts on water resources – especially surface waters – a variety of catchment scale models have been developed and applied in the last decades like SWAT (Zhang et al., 2008), HSPF (Laroche et al., 1996) and AnnAGNPS (Flanagan et al., 2008). All these models consider pesticides to be completely degradable. However, pesticides are often not fully degraded but rather transformed into new substances that can be found in the environment (e.g. Battaglin et al., 2005; Olsson et al., 2013).

The main concepts implemented in current environmental fate and transport models for diffuse input of organic chemicals into rivers are sorption and degradation (Gavrilescu, 2005). Sorption is considered to be dependent on organic carbon content in soil in these models. The rate of transformation may vary between environmental compartments (e.g. plant, soil, water), or – more specifically – transformation processes such as microbial transformation or phototransformation (Mahmoud and Kümmerer,

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2012). Eventually, the combination of both concepts defines how much of the substance can be transported from the field into the river during a certain rainfall-runoff event. By implementing the dynamic formation and fate of transformation products (TP) into modelling, the mass of TP is influenced by the degradation rate of both the TP and the pesticide. Additionally, the fraction of the parent compound being transformed into the TP – the formation fraction – has to be determined in the model (Kern et al., 2011). Thus, the complexity and data intensity of these models largely increase by introducing TPs (Fenner et al., 2009).

One major difficulty in modelling pesticides and TPs in the environment is the determination of model parameter values for the above mentioned concepts. As a minimum, half-lives, soil sorption values and formation fractions are needed for all substances including TPs. As those model parameters are influenced by environmental characteristics (e.g. pH, soil properties) usually a wide range of experimental values can be found in the literature (PPDB, 2009). While parameter values are often available for pesticides from laboratory or field sampling studies, for TPs usually hardly any information about their environmental behaviour can be found. In this case, QSPR (Quantitative Structure Property Relationships) methods may be used to assess missing parameter values (Boxall et al., 2004). The models involved in the EPI-Suite (US EPA, 2012), for example, deliver a whole set of environmental parameter values. Anyway, uncertainty of these models is large (see review in Rücker and Kümmerer, 2012) and has to be considered in environmental modelling. All in all, the model prediction becomes uncertain due to the uncertainty coming from the choice of model input parameter values (Dubus et al., 2003).

Further sources of uncertainty are boundary conditions for modelling. Cryer and Havens (1999) emphasized the importance of the hydrological model for pollutant export modelling. For pesticide modelling, the temporal distribution and amount of pesticide application at the agricultural site is important as a boundary condition. Although this data is urgently required, often only rough estimations could be made and only with a huge effort (e.g. Huber et al., 1998; Melman and Bar-Ilan, 2008).

The purpose of this study was the investigation of the behaviour of a parsimonious catchment scale model for the assessment of river concentrations of the insecticide Chlorpyrifos (CP) and two of its TPs, Chlorpyrifos Oxon (CPO) and 3,5,6-trichloro-2-pyridinol (TCP), under the influence of uncertain input data. Especially parameter uncertainty and pesticide application uncertainty were investigated by Global Sensitivity Analysis (GSA) and the Generalized Likelihood Uncertainty Estimation (GLUE) method.

2. Materials and methods

2.1. Study site

The Kalil catchment (64 km^2) is located in Northern Israel and drains from the Golan Heights (1170 m.a.s.l) down to Hula Valley (70 m.a.s.l). The area is semi-arid to sub-humid with hot dry summers and mild wet winters. Precipitation in the area is on the one hand positively correlated with elevation (Rimmer and Salingar, 2006) and on the other hand convective events with a small spatial extent are common. Therefore, we used rainfall data from two stations in this study, one located in the Hula valley (75 m.a.s.l., Fig. 1) and one located at the Golan Heights (940 m.a.s.l.).

Due to its relatively high amounts of rainfall and fertile soils, the Upper Jordan River catchment, especially the Hula Valley, is highly cultivated. Particularly field crops (e.g. cotton, corn, sunflowers) and orchards (e.g. citrus, peach, apples) cover large areas in the valley (Bar-Ilan et al., 2000). In the Golan Heights there are orchards and vine-growing areas.

Data from a discharge gauging station, located at the inflow of the Kalil River to the Jordan River (Fig. 1), was used in this study to calibrate the hydrological model. The chemical sampling, however, was located more upstream. Therefore, the Hula subbasin was delineated at the chemical sampling station and the discharge sampling station (Fig. 1). In the following modelling study, the corresponding subcatchment areas (Golan; Hula) were considered for the chemical and the hydrological modelling. The rainfall station located in the Hula Valley (Kfar Blum) was taken as input for the Hula subbasin and the station in the Golan Heights (Pichman) was taken for the Golan subbasin. All meteorological data was obtained from the Israel Meteorological Service (IMS) and all hydrological data from the Israel Water Authority (IWA). Information about the chemical sampling and analysis was previously published in Olsson et al. (2013). In this study, we used 41 samples for each substance for comparison to modelling data. Since micropollutant sampling and analysis is usually much more complex than other water constituents, we considered this number to be a reasonable trade-off between feasibility and sufficient quantity for this study. A similar number of samples was used by Vezzaro and Mikkelsen (2012).

2.2. Substances and their characteristics

The organic chemicals in focus of this study were the organophosphorus insecticide Chlorpyrifos (CP) and two of its TPs, Chlorpyrifos Oxon (CPO) and 3,5,6-trichloro-2-pyridinol (TCP). Generally, CP can be transformed into CPO and TCP (Roberts et al., 1999) while CPO also is subject to transformation into TCP (Eaton et al., 2008). Bavcon Kralj et al. (2007) showed that CPO was the major TP under photodegradation of CP. TCP, however, is mainly produced by soil (microbial) degradation and hydrolysis. The little amount of produced CPO in soil is further transformed into TCP (Roberts et al., 1999). The formation fractions of these substances and processes are largely unknown. Still, the physico-chemical characteristics (persistence, mobility) are the most important information needed for environmental modelling of these substances. The parameter values summarized in Table 1 were collected from literature and give an idea about the environmental behaviour of these substances. These values served as a basis for the determination of parameter ranges.

2.3. Model theory

2.3.1. Hydrological model

In this study, two hydrological units were differentiated in the model structure: the Golan Heights in the east and the Hula Valley in the west (Fig. 1). As usual in the

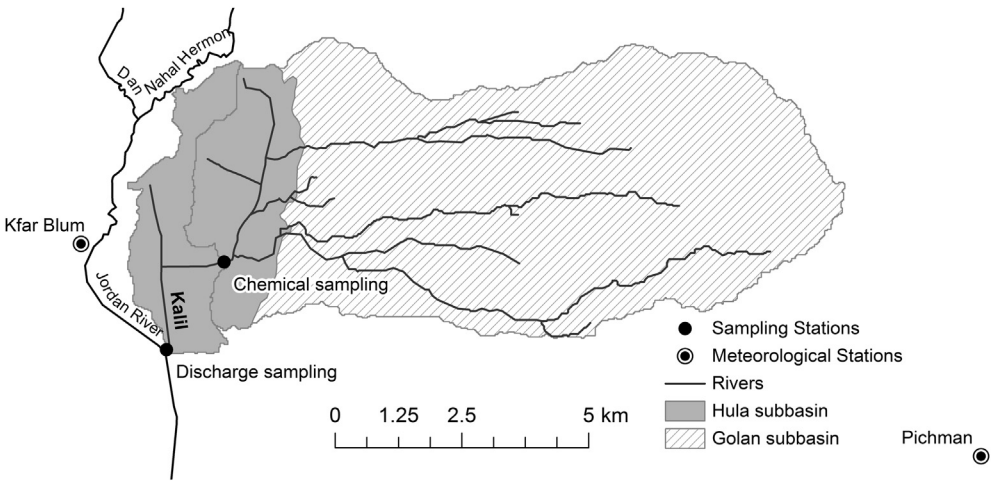

Fig. 1. The Kalil river catchment with the separation into subbasins (Hula subbasin, Golan Heights subbasin) for modelling.