Field release modelling of pesticides and their transformation products during a first significant rainfall in a semi-arid region

Matthias Gassmann, Leibniz Universität Hannover, Institute for Water Quality and Waste Management, Water Resources Management, Callinstr. 14, 30167 Hannover, mg@warb.uni-hannover.de

Oliver Olsson, Leuphana Universität Lüneburg, Institute of Environmental Chemistry, Chair of Material Resources, Scharnhorststr. 1, 21335 Lüneburg, oliver.olsson@leuphana.de

1 INTRODUCTION

Following field application, pesticides undergo different transformation processes resulting in transformation products (TPs). As these substances are often more mobile and more persistent and can be even more toxic than the parent compounds, it is urgent to consider pesticide TPs in current research. The amount of substance transformation is strongly dependent on exposure time. In the semi-arid study site of the Hula Basin, Israel, pesticides are applied in spring. The subsequent dry summer guarantees a long exposure time of pesticides without being transported to the river. The first significant rainfall in autumn flushes parts of the substances to the stream.

The aim of this study was the dynamic modelling of pesticides and their transformation products during the dry time at catchment scale and the simulation of the release of those substances to the river during the first significant rain in 2009 in the Hula Basin.

2 METHODS

The substances in focus of this study are Chlorpyrifos (CP) with its TPs Chlorpyrifos Oxon (CPO) and Trichloropyridinol (TCP) and the Endosulfan isomers alpha (aE) and beta (bE) with their TP Endosulfan Sulfate (ES). The rivers in the basin were sampled several times at four points during the first rainfall in autumn 2009 (20.09.2009).

The model consists of a conceptual hydrological and a substance fate and release model. The substance fate model calculates the mass balance of pesticides and transformation products within a river basin considering transformation pathways between those substance and using degradation half-lives and formation fractions. The field release module calculates the release of substances to the river induced by rainfall using the runoff coefficient and the partitioning coefficient.

The conceptual substance fate model is only able to simulate one transformation process. The original equation was used with a soil degradation half-life. However, considering the Mediterranean climate, surface transformation might be of great importance and thus two scenarios were used in modelling: a surface and a soil transformation scenario. These two scenarios were combined with two application scenarios. The resulting four scenarios were then referred to as $(S1/S2)_{soil}$ and $(S1/S2)_{surface}$. Whenever possible, parametrization was done using estimation methods (e.g. QSAR) in order to get a consistent set of parameters that was not influenced by the setup and environment of experimental studies.

3 RESULTS

Figure 1 shows the results of the modelling scenarios in combination with the sampling median. The black parts of the bars depicture the inflow contribution to the total concentration, the light grey parts the basin contribution. Sampling resulted in the substance order CPO > CP > TCP in the CP group while in the Endosulfan group, only aE was found.

It can be seen that the soil scenarios overestimated the TCP contribution in relation to the other substances while CPO was underestimated. Although the surface scenarios had hardly any substance contribution, they resulted in the best relative substance distributions in the CP group. In the Endosulfan group, the soil runs had the best performance considering the relative distribution. Using the runs with the best relative contribution and multiplying all substances of a group by the same constant factor improved RMSEs from 1.2 to 0.2 µg/l and R^2s from 0.44 to 0.73 in the CP group. In the Endosulfan group, RSMEs were lowered from 0.24 to 0.02 µg/l while R^2s stayed at 1.

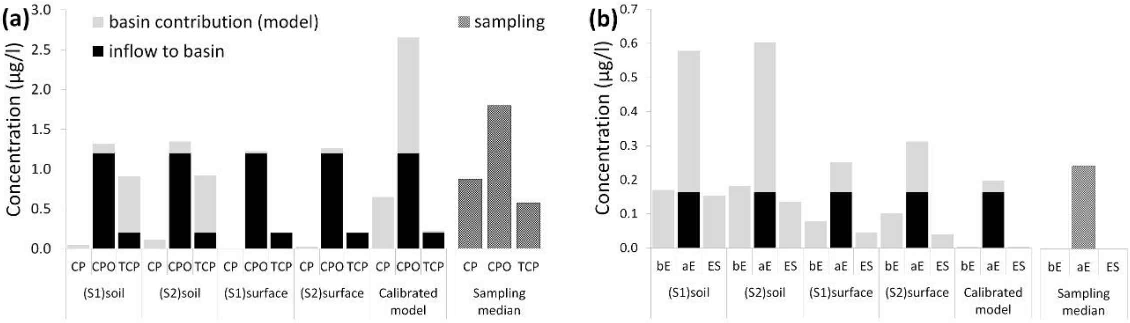

Figure 2: Modelling results of the Chlorpyrifos group (a) and the Endosulfan group (b) compared to sampling.

4 DISCUSSION AND CONCLUSION

A conceptual model was introduced for a dynamic simulation of the fate of pesticides and TPs and their release to rivers. The successful application in a semi-arid region highlighted the importance of process knowledge and subsequent parametrization if the model environment (e.g. climate) and setup (e.g. transformation process) is changed.

This model is a new contribution to simulation studies on organic chemicals and their transformation products in the aquatic environment as it works at catchment scale. It can be placed in the spatial niche between existing lake and field scale models.