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Modelling the first flush of pesticides and their transformation products in a Mediterranean catchment

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In natural systems, pesticides are transformed by various processes including biodegradation, hydrolysis and photolysis, mainly depending on exposure time. The transformation products are often more stable and mobile than the parent compound and can even be more toxic. In a Mediterranean environment, pesticides are usually applied in spring until the end of summer. The long dry period in summer guarantees long exposure times for pesticides and their transformation products. This study identifies a first flush of pesticides and some transformation products in a Mediterranean river by analytics and modelling. A lumped catchment scale modelling approach is introduced and applied in order to assess the mass balance of pesticides and transformation products in the field during the dry time and the release of those substances by rainfall.

The study site is a part of the Upper Jordan River, Israel, with tributaries coming from the Naftali Mountains and the Golan Heights. The Hula Valley in between is under heavy agricultural use and therefore a possible source of pesticides in surface waters. Four river points were sampled in order to get a picture of the whole catchment. Samples were analysed in the lab by GC/MS for Chlorpyrifos (CP), Chlorpyrifos Oxon (CPO), Trichloropyridinol (TCP), alpha Endosulfan (aE), beta Endosulfan (bE) and Endosulfan Sulfate (ES).

This study adapted and used the single-equation pesticide release formula by the OECD, which combines sorption and soil degradation in one equation, for the release of chemicals by rainfall. The hydrological background of the release equation consists of two linear storages fed by rain and drained by evapotranspiration, percolation and river output. The mass balance in the model considers the following substances and pathways: CP is transformed to CPO and TCP while CPO is also transformed to TCP. In the Endosulfan group, the sprayed pesticide is a mixture of 70 % aE and 30% of bE. Both isomers degrade to ES while, basically, bE can also be transformed to aE. First-order decay in combination with a formation fraction for each transformation product governed the mass transfer between the substance pools. The model was set up for the Mediterranean study site. In order to get a consistent set of parameters for each chemical group, EpiWIN and QSAR modelling was used and output for soil half-lifes and Koc were compared to ranges of experimental data.

Sampling results of the first rainfall in autumn 2009 identified a strong first flush of all substances in the CP group as well as for aE and ES. The ranking of concentrations was CPO > CP > TCP and aE > ES > bE, whereas the simulation results of pesticide concentrations in the Jordan River showed a ranking of TCP > CPO > CP and aE > ES > bE.

Considering these results it can be argued that for the Endosulfan group the modelling succeed while the CP group sampling results were not achieved by the modelling. Since the classical soil degradation approach was not applicable for this catchment, the degradation scheme (half lifes, formation fractions and pathways) was re-considered for a soil surface environment. Subsequent modelling results were more reasonable and showed the sampled order of the substance concentrations.

This study introduced successfully a first simplified catchment scale model for the transformation and first flush of pesticides and some transformation products in a Mediterranean environment. Furthermore, it revealed the importance of the natural environment for the successful parametrization of a mass balance simulation.