Executive Summary LRI-ECO32

Environmental risk assessment of poorly soluble substances: Improved tools for assessing biodegradation, (de)sorption, and modelling:

Highly hydrophobic organic chemicals (HOCs) are characterized by a log K_{OW} above 5.5, resulting in an aqueous solubility in the µg/L-range or even lower. Owing to their high production volumes and diverse usage, these chemicals may enter the aquatic environment. HOCs tend to persist in natural environments due to their strong sorption to solid phases such as sediments, organisms, and particulate matter in general, making attempts for understanding their intrinsic biodegradability challenging. Therefore, a major part of these chemicals need to be considered as potential PBT-candidates.

Persistence assessment using standardized tests (e.g., OECD guidelines) is one of the main challenges for HOCs. Their properties often hinder a reliable experimental assessment using standard methods. For a reliable experimental determination of both persistence and biodegradability, (de)sorption effects and biodegradation in the aqueous phase have to be consequently decoupled. Mechanistic models can thus provide deeper insights in experimental results and underlying processes. In this context, the key objectives of this study were to develop novel experimental test systems for biodegradation and (de)sorption, and to test the applicability of a unified modelling approach across the spectrum of OECD biodegradation tests and our new experimental approaches for HOCs.

Two model HOCs were selected, dodecylbenzene (DDB; log K_{OW} 8.7) and pyriproxyfen (PPF; log K_{OW} 5.6). For the experimental determination of their biodegradation, different passive dosing formats were developed (PDMS coatings and silicone O-rings) and combined with single degrader strains and natural inocula. These formats provided a precise exposure control of the test substance and ensured a constant compound release to the aqueous phase over time. In parallel, the biodegradation of both model HOCs was tested in standard water-sediment systems based upon OECD 309. Additionally, abiotic desorption kinetics of the model HOCs from sterilized sediment, freshly spiked and aged, were determined utilizing silicone O-rings as infinite sink passive samplers. In all tests, ^{14}C-labelled test substance was used to trace the compound distribution to different compartments (polymer, water-sediment, mineralization to CO_2) with high sensitivity.

The modelling approach relied on the use of a unified multi-compartment model, which decouples fast and slow (de)sorption kinetics to solid matrices and describes based microbial degradation kinetics according to Monod equation. The unified model was used, in combination with the Microbial Turnover to Biomass growth yield estimation method, to simulate test substance

mineralization to CO_2 and growth of degrading microorganisms. Model predictions were calibrated against the experimental results obtained in the conventional tests and in the novel passive dosing setups. Overall, good agreement between model predictions and empirical data was shown by estimating only the ratio v_{max} / K_S. This ratio denotes the second-order biodegradation rate constant, while accounting for change in microbial abundance over the duration of tests. Different v_{max} / K_s values were shown for the selected HOCs, indicating that either limited bioavailability or intrinsic recalcitrance could explain HOCs persistence.

This study represents a first attempt of using novel test setups and a unified modelling approach for predicting reliable biodegradation of HOCs (validated with OECD 309 test results), showing promising results towards persistence prediction of organic chemicals during regulatory screening. The main conclusions of the project results are the following:

(1) Evaluating the biodegradation of HOCs (e.g., DDB, PPF) is possible by combining novel testing methods and modelling work, with assessment/simulation of multiple endpoints simultaneously.
(2) Passive dosing and passive sampling strategies can be applied to OECD based biodegradation tests (e.g., OECD 309) and abiotic desorption tests successfully.
(3) The calibrated unified model was overall capable of describing experimental results obtained in the conventional tests and in the novel passive dosing setups.
(4) Model predictions indicated that either limited bioavailability or intrinsic recalcitrance can explain HOCs persistence. Here, PPF was found to be intrinsically persistent, whereas DDB showed a rather fast biodegradation (in natural sediment inocula) which was limited by its low bioavailability.
(5) First-order rates typically derived from OECD test results and used to describe biodegradation kinetics may not be adequate due to e.g., significant changes in microbial biomass. Conversely, mechanistic models can provide deeper insights in experimental results and underlying processes. Furthermore, currently used persistence indicators (e.g., half-lives) may not adequately describe true biodegradation of HOCs, as they are influenced by bioavailability limitation.
(6) Overall, the outcome of this project raises questions about the regulatory need to clearly distinguish between biodegradation and dissipation together with the definition of a distinct terminology, particularly in the context of persistence assessment.