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Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

Untangling the biodegradation of hydrophobic chemicals in OECD and novel tests using a unified modelling approach

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1. Introduction

Persistence (P) is one of three criteria (with bioaccumulation and toxicity) currently used to assess the safety of commercial chemicals in the EU under the REACH framework. Persistence is evaluated using degradation or mineralization tests in environmental media according to existing standardized guidelines (OECD tests 301, 302, 304, 307, 308, 309). However, the interpretation of test results is often challenging, due to the number of simultaneous processes and the complexity of test media. This is especially true for hydrophobic organic chemicals (HOCs, $\log K_{OW} \geq 4$), for which high persistence is explained by low bioavailability in the presence of solid matrices or by intrinsic recalcitrance. The use of radiolabeled chemicals has improved the understanding of persistence by allowing to close mass balances over the course of tests. In addition, mechanistic models can provide deeper insights in experimental results and underlying processes. To date, models have been applied only to specific OECD tests [1-2] or have focused on one fate process [3]. The core objective of this study was to test the applicability of a unified modelling approach across the spectrum of OECD degradation tests and novel experimental tests for HOCs. Through backward prediction of test results for ^{14}C-labeled HOCs, we aimed at (i) elucidating biodegradation kinetics and improving their estimation by using a new method for microbial yield calculation; (ii) determining ^{14}C fractions (mineralized, incorporated in biomass and non-extractable residue NER) at the end of tests as persistence indicators.

2. Materials and methods

The modelling approach refers to the multi-compartment unified model for sorption and biodegradation of organic chemicals [4]. Model compartments describe five possible states of radiolabeled C atoms, i.e. (i) dissolved, (ii) adsorbed to solids, (iii) sequestered in solids, (iv) mineralized to CO_2 and (v) incorporated in living or dead biomass. In this context, we predicted mineralization of test substances to CO_2, growth of degrading organisms and NER formation by using the Microbial Turnover to Biomass growth yield estimation [5]. Model predictions were fit to experimental results by manually adjusting the ratio v_{max} / K_s (describing biodegradation kinetics based on Michaelis Menten equation). Unless explicitly measured, model parameters were derived from [4]. Experimental datasets, against which the model was calibrated, were derived from aerobic mineralization tests for: (i) ^{14}C-triclosan in activated sludge [6]; (ii) ^{14}C-pentachlorophenol (PCP) in activated sludge according to OECD 301 [7]; (iii) ^{14}C-propargite in soil according to OECD 307 [1]; (iv) ^{14}C-pyriproxyfen with a single degrader strain (*P. putida*). In the last case, a novel test setup for HOCs based on equilibrium passive dosing was chosen to establish well-defined freely dissolved concentrations, account for a high compound turnover and decouple aqueous phase biodegradation from (de)sorption effects.

3. Results and discussion

Figure 1a presents model simulations and ^{14}C-CO_2 measurements for ^{14}C-triclosan at three different initial concentration levels (top) and ^{14}C-PCP (bottom). For triclosan, a good match to measurements was obtained for a relatively small range of v_{max} / K_s values (2-fold variation), indicating the possibility of describing biodegradation at different concentrations with a unique parameter set. Screening tests revealed that PCP is highly persistent, as no degradation was observed. These results are corroborated by model predictions, which also showed no degradation of PCP given that the microbial growth yield was calculated to be 0. Close agreement between model simulations and measurements (distribution of applied radioactivity) was obtained for propargite in OECD 307 test (Figure 1b). Model predictions were obtained by setting v_{max} / K_s = 55 $m^3\ g^{-1}\ d^{-1}$, indicating fast biodegradation kinetics for this substance. This further supports the hypothesis that desorption rate from soil was limiting, leading to the observation of first-order degradation kinetics [1]. Figure 1c presents experimental and modelling results for ^{14}C-pyriproxyfen in terms of total and labeled

concentration of degraders, dissolved pyriproxyfen mass and $^{14}CO^2$. A close match between measurements and predictions was obtained for v_{max} / K_s = 0.027 m^3 g^{-1} d^{-1}, which in turn indicates intrinsic recalcitrance of pyriproxyfen and was further supported by the decreasing cell number of *P. Putida* over the test.

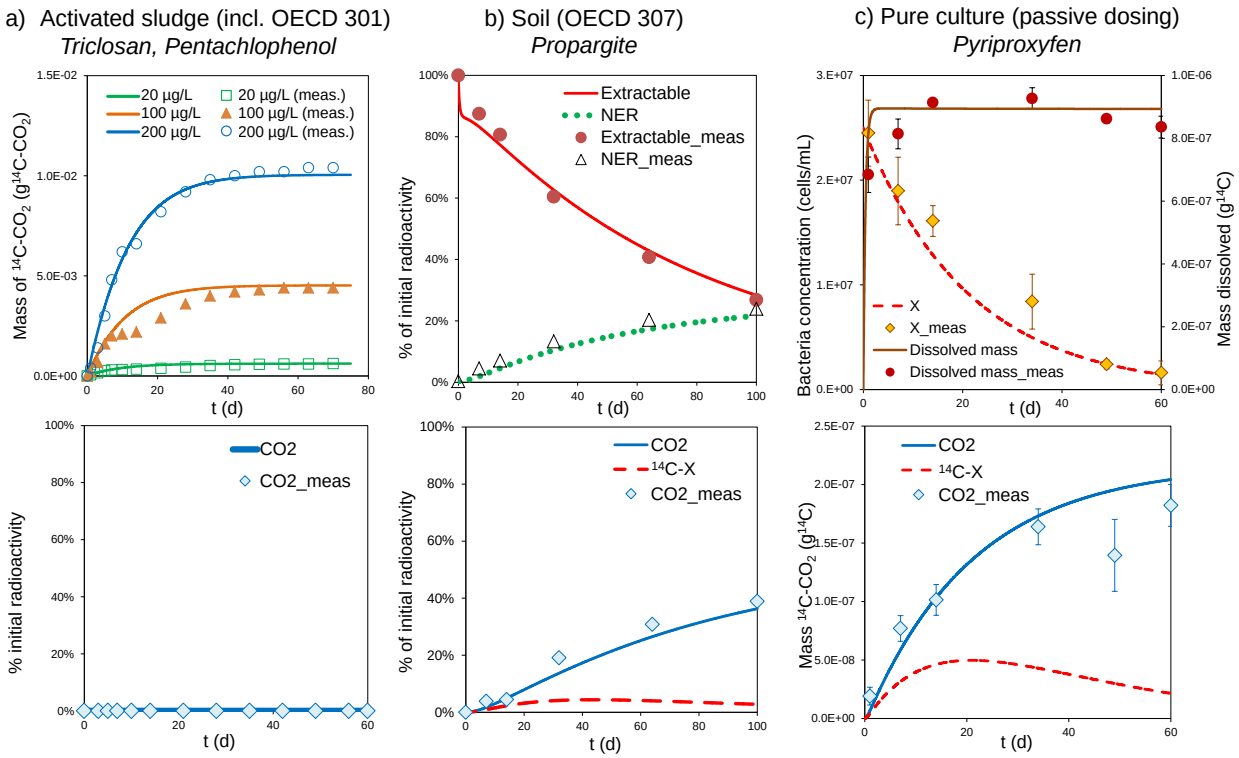

Figure 1: Modelling results (lines) and measurements ("meas", symbols) for HOCs during mineralization tests. (a) Measured $^{14}CO_2$ mass in activated sludge for triclosan and PCP. (b) Distribution of applied radioactivity in (non-)extractable residues, $^{14}CO2$ and labeled degraders (X) in soil for propargite. Measurements were readjusted to account for >100% recovery at t=0. (c) Concentration of (un)labeled degraders (X), mass of dissolved substance and $^{14}CO^2$ in single strain test with pyriproxyfen.

4. Conclusions

This study presents a first attempt of using a unified modelling approach for predicting biodegradation of HOCs in different test types, including several OECD tests. Results showed the potential of using the same mechanistic modelling approach for fate assessment across a variety of tests, making it a valuable tool for interpretation of degradation and prediction of biogenic NER formation. Ongoing research is focusing on the inclusion of transformation product formation in the model and on the determination of (de)sorption limitation in the presence of solid matrices. Furthermore, model extension with uncertainty propagation methods is envisaged to support regulatory issues in fate and turnover assessment of chemicals within REACH.

5. References

[1] Loss M, Krauss M, Fenner K 2012. Pesticide nonextractable residue formation in soil: Insights from inverse modeling of degradation time series. Environ Sci Technol 46: 9830-37.

[2] Honti M, Hahn S, Hennecke D, Junker T, Shrestha P, Fenner K 2016. Bridging across OECD 308 and 309 data in search of a robust biotransformation indicator. Environ. Sci. Technol. 50, 6865-72.

[3] FOCUS 2006. Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. EC Sanco/10058/2005.

[4] Trapp S, et al. 2017. Prediction of the formation of biogenic non-extractable residues during degradation of environmental chemicals from biomass yields. Environ Sci Technol, *submitted*.

[5] Libonati Brock A, et al. 2017. Microbial growth yield estimates from thermodynamics and its importance for degradation of pesticides and formation of biogenic non-extractable residues. SAR QSAR Environ Res 8:629-50.

[6] Federle TW, et al. 2002. Fate and effects of triclosan in activated sludge. Environ Toxicol Chem 21, 1330-37.

[7] Martin TJ, et al. 2017. Environmentally relevant inoculum concentrations improve the reliability of persistent assessments in biodegradation screening tests. Environ Sci Technol, 51, 3065-73.

Acknowledgement – This work is supported by the European Chemical Industry Council (CEFIC) in frame of the Long-Range Research Initiative (CEFIC LRI-ECO32), project "RABIT".