

# Estimating transformation rate constants from OECD 308 data – Opportunities and limitations of existing data

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## 1. Introduction

The OECD guideline 308 for the testing of aerobic and anaerobic transformation in aquatic sediments is an integral part of tiered testing strategies in different legislative frameworks for the environmental risk assessment of chemicals. The results of these highly laborious and costly studies are interpreted in various ways, depending on the regulatory context, but are generally used to derive persistence indicators for hazard assessment, or half-lives to be used in exposure assessment/modeling. Indicators typically derived are  $DT_{50,w}$ , which is the time for 50% disappearance of the parent compound from the water phase, and  $DT_{50,system}$ , which is the time until 50% mineralization is reached. Both of these values heavily depend on the geometry of the experimental system (water column height, sediment:water ratio), and in the case of  $DT_{50,w}$  lump together diffusion and transformation rates, which makes this indicator particularly vulnerable to different geometries of the experimental system. Overall, none of the indicators seems thus to be well suited for obtaining information on actual transformation half-lives in sediment and/or water, which would be needed for exposure modeling or to compare substances with respect to their persistence.

The FOCUS Guidance Document on Estimating Persistence and Degradation Kinetics [1] therefore suggests that estimates for actual compartment-specific degradation half-lives could be derived from the data using a two-compartment model. However, they also acknowledge that results will be very sensitive to fundamental correlations between the estimated transfer and degradation rates, unless some of the parameters can be constrained. They further acknowledge that it was not possible within their timeframe to develop simple, robust and reliable constraint procedures to estimate degradation half-lives.

In this study, we used Bayesian parameter estimation and system representations of increasing complexity (Figure 1) to assess the opportunities but also limitations for estimating degradation half-lives from OECD 308 data. Bayesian parameter estimation was preferred over frequentist approaches, because it allowed for an explicit inclusion of prior knowledge on diffusion and sorption properties of the tested compounds, and also yields information on uncertainty of estimated parameters and observed time-series. We applied the methods to existing data from OECD 308 studies for 25 pesticides and pharmaceuticals.

## 2. Materials and methods

### 2.1. Model versions

We tested four different model versions that represent the experimental system with different hypotheses. Degradation and diffusion was assumed to follow first-order kinetics in each compartment and model. Mechanisms in the water column were identical in all versions. Model A assumed instant mixing along the entire sediment depth of both parent compound and metabolite when they enter the sediment column. B accounted for slow diffusion into the sediment, calculating an effective sediment depth that increases with time [1]. C and D simulated diffusion in the sediment by splitting the sediment column into 4 horizontal compartments. In version C, degradation was assumed to take place in the uppermost boundary layer exclusively. In version D, degradation was also allowed in the deeper anoxic layers, albeit at a reduced rate.

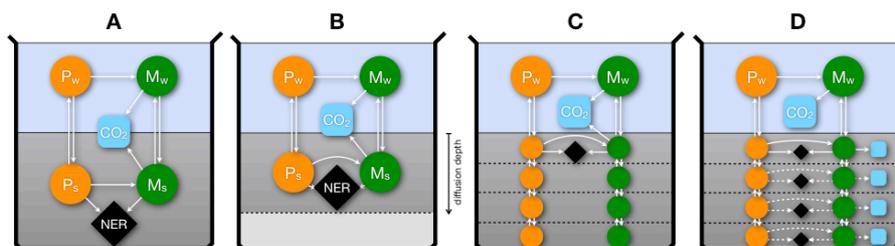


Figure 1: Water-sediment system representations of increasing complexity (models A-D) used in this study. P: parent compound; M: metabolite; X<sub>w</sub>: X in water column; X<sub>s</sub>: X in sediment; NER: non-extractable residues.

## 2.2. Prior knowledge on model parameters and Bayesian parameter inference

Existing compound-specific information was taken for  $K_{oc}$  of the parent compound and the ratio of  $K_{oc}$  of the parent and the most representative metabolite(s). Experiment-specific data was used for the organic content of the sediment. For the remaining parameters, we used expert estimations where available (e.g., diffusion coefficient in water was set to  $0.5 \pm 0.1 \text{ cm}^2 \text{ d}^{-1}$ ) and broad general priors for totally unknown quantities.

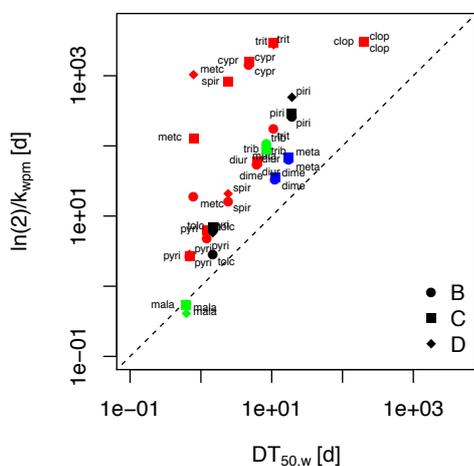
The posterior parameter distribution was sampled by Markov chain Monte Carlo (MCMC) sampling using the traditional Metropolis algorithm [2]. Parameter likelihood was calculated by assuming independent and identically distributed normal errors. The standard deviation of errors for each observed time-series was inferred together with model parameters. Three MCMC chains were generated to ensure convergence and stability, each having a total length of 200,000 rounds with 100,000 rounds dedicated for burn-in. Samples were thinned by a factor of 5 to reduce serial correlation.

## 3. Results and discussion

### 3.1. General model comparison

For version A, maximum posterior parameter probability was significantly lower or equal to the other model versions for all substances. It assumed an immediate equilibrium between the water column and the pore water, which was not confirmed by occasional pore water measurements. Version A was therefore excluded from further analysis. Versions B and C relied on conflicting hypotheses about the place of degradation in the sediment. This difference did not affect the quality of fit but resulted in very different estimations for the degradation rates in sediment. Since B allows degradation in the sediment down to the diffusion depth, the inferred rates are much lower compared to version C that limits degradation to a thin boundary layer at the sediment-water interface. Version D distinguishes two degradation rates in the sediment for aerobic and anaerobic conditions. The fit to the observed time-series and the maximum posterior parameter probability was identical to versions B and C. It was compound-specific whether degradation rates were more similar to the values of version B or C. The equal goodness-of-fit for versions B, C, and D indicates that the experimental results do not provide any evidence about the actual roles of different sediment compartments in degradation.

### 3.2. Estimated degradation half-lives



**Figure 2: Observed  $DT_{50,w}$  versus estimated degradation half-lives by different model versions. Colours indicate different groups of compounds based on initial transformation reaction. Red: slow oxidation; blue: glutathione-coupling; green: (abiotic) hydrolysis; black: other.**

With the exception of malathion, estimated  $DT_{50,w}$  was higher for all model versions than the value estimated based on the disappearance of the parent compound from the water column (Figure 2). The difference was heavily dependent on model versions and could reach up to 2 orders of magnitude for compounds belonging to the slow oxidation class. This highlights the importance of disentangling transport processes from actual degradation.

## 4. Conclusions

Models support estimation of compartment-specific half-lives, but given currently available data cannot provide any evidence about the extent of depth-dependent degradation in the sediment compartment.

## 5. References

- [1] The FOCUS guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. 2006. EC Document Reference Sanco/10058/2005 version 2.0.
- [2] Gamerman D. 1997. Markov chain Monte Carlo – statistical simulation for Bayesian inference. London, UK: Chapman & Hall. 264 pp.

## 6. Acknowledgement

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