Persistence testing at the sediment-water interface: Too much effort for too little data?

Kathrin Fenner[1], Thomas Junker[2], Dieter Hennecke[3]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland

[2] ECT Oekotoxikologie GmbH, Flörsheim, Germany

[3] Fraunhofer IME, Applied Ecology, Schmallenberg, Germany

Introduction

Criticism of OECD 308 guideline:

- Large experimental effort (number of vessels ≥ 60; radiolabelled compounds)
- Compartment-specific *degradation* half-lives (DegT50) difficult to extract from data
- Total system half-life and *disappearance* half-lives (DT50) depend on water: sediment ratio and include other processes besides degradation
- Recommended water:sediment ratio not appropriate for all compound classes/ exposure situations; static system
- Large amounts of non-extractable residue (NER) formation because of high sediment:water ratio
- Complex multiphasic processes between thin aerobic sediment and thicker anaerobic sediment layer

Working hypothesis 1:

Advanced parameter estimation techniques can be used to quantify uncertainty in kinetic parameter estimates derived from OECD 308 data and to incorporate additional knowledge (e.g., on sorption) in a transparent manner

→ Data analysis approach

Working hypothesis 2:

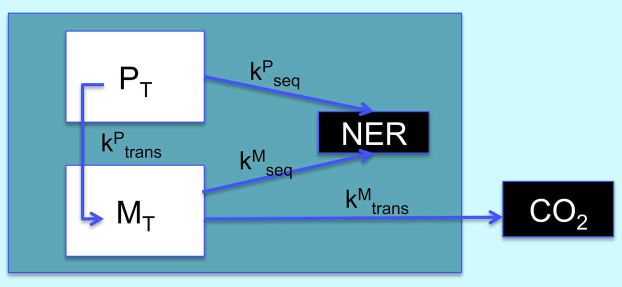
To obtain robust, i.e., experimental system-independent, degradation data, experiments need to enable disentangling (reversible and non-reversible) sorption from (bio)degradation, while clearly distinguishing between aerobic and anaerobic conditions

→ Experimental approach

Data analysis approach

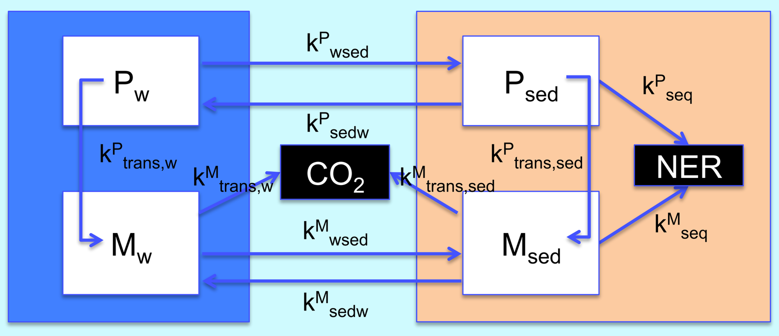
Methods:

- Use of *advanced parameter estimation techniques* and *system descriptions of increasing level of complexity* to derive transformation rate constants (i.e., degradation half-lives) and their uncertainties



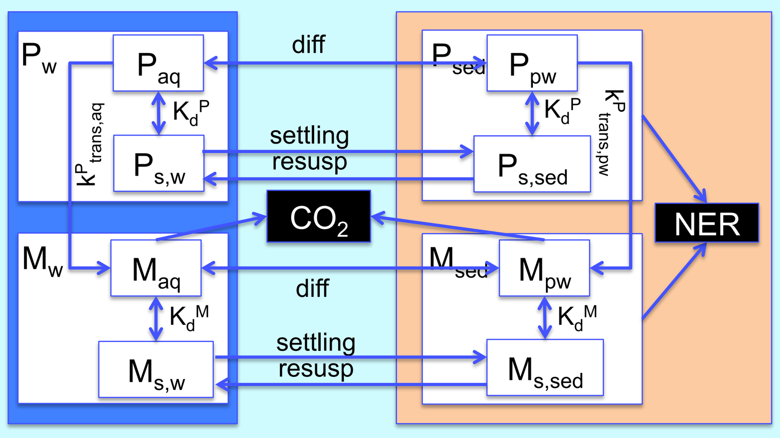
Level I

- P; ΣM_i; NER; CO_2
- Total system



Level II

- P; ΣM_i; NER; CO_2
- Bulk compartments
- Prior knowledge: $k_{wsed}/k_{sedw} = f(K_d)$

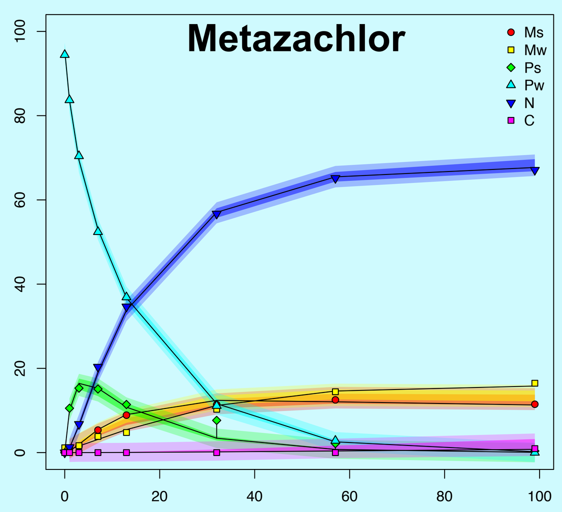


Level III

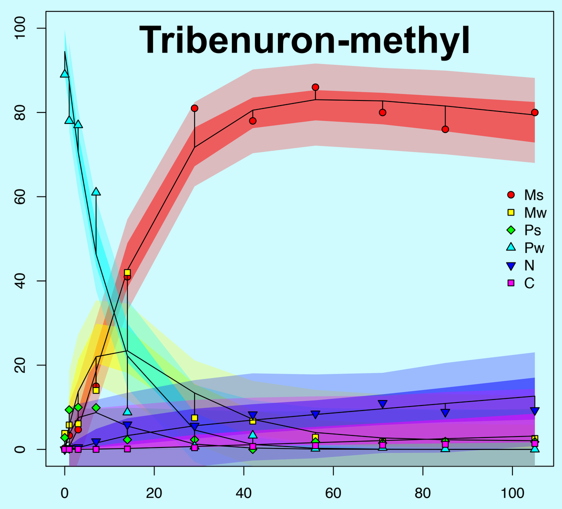
- P; ΣM_i; NER; CO_2
- Separate solid and aqueous phase pools
- Prior knowledge: $k_{wsed}/k_{sedw} = f(K_d)$ & estimates of particle settling, resuspension and diffusion rates

- Analysis of literature OECD 308 data for 20-30 pesticides and pharmaceuticals using Bayesian inference techniques (Markov Chain Monte Carlo method) (Loos et al., 2012)

Preliminary results for level II model:



Endpoint*	DAR** (d)	MCMC(this study) (d)
$DT50^P_{tot}$	13.4	nd
$DT50^P_w$	6.5	nd
$DegT50^P_w$	144	127 (47, 978)
$DT50^P_s$	3	2.4 (2.3, 3.5)
$DegT50^P_s$	nd	11.7 (8.5, 30.2)



Endpoint*	DAR** (d)	MCMC(this study) (d)
$DT50^P_{tot}$	14	nd
$DT50^P_w$	12	nd
$DegT50^P_w$	nd	8.7 (7.2, 11.3)
$DT50^P_s$	nd	ind
$DegT50^P_s$	nd	ind

* DegT50: Degradation half-lives, DT50: Dissipation half-lives, i.e., including degradation, NER formation and phase transfer processes
** EFSA Draft Assessment Reports

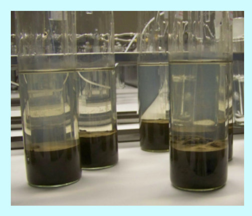
➢ MCMC allows estimating *degradation* half-lives, their uncertainties, and cases where half-lives cannot be determined with certainty from the data („ind")

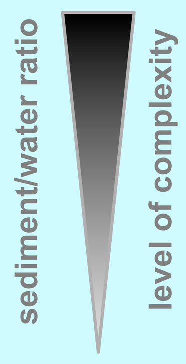
➢ Considerable differences between DT50 and DegT50 values

Experimental approach

Methods:

- Use of a suite of five, complex to less complex *water-sediment systems* to investigate the behavior of *4 characteristically different chemicals* in a *consistent manner*





OECD 308 standard protocol (water:sed ratio = 3:1, not stirred)

OECD 308 modified standard protocol (water:sed ratio = 10:1, stirred water phase)

OECD 309 modified standard protocol (water:sed ratio = 100:1, shaken)

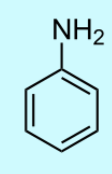
OECD 309 standard protocol (water:sed ratio = 1000:1, shaken)

+ OECD 301C modified (water-sediment screening tool)

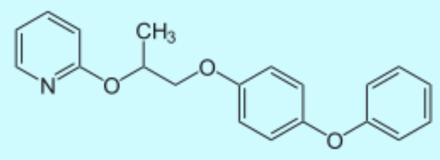
- 4 test chemicals with varying degrees of sorption and biodegradability

Name	Koc [L/kg]	Total system $t_{1/2}$ (d)	% CO2 100 d	% NER 100 d	Speciation (pH 6-8)
aniline	20-1000	nd	> 20-30	nd	Cation/neutral
pyriproxifen	4980-34200	7-10 d (extractable)	10-50	30-50	Neutral
voriconazole*	70-350	≈ 50 d (parent)	nd	nd	Neutral
tbd**	High	≥ 50 d			Neutral

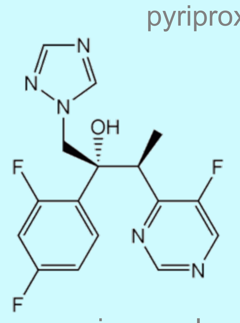
* To be confirmed with producer
** To be decided



aniline



pyriproxifen



voriconazole

- 2 natural sediments

Characteristic	Wenne (coarse)	Wingeshausen (fine)
Clay [w%] (DIN)	5.2	18.6
Sand [w%] (DIN)	77.5	22.9
Silt [w%] (DIN)	17.4	58.4
TOC sediment [w%]	0.8	7.2
pH sediment	6.5	5.6
Dry weight sediment [w%]	74.3	36.0
Redox potential sediment [mV]	96.7	83.6

Preliminary results:

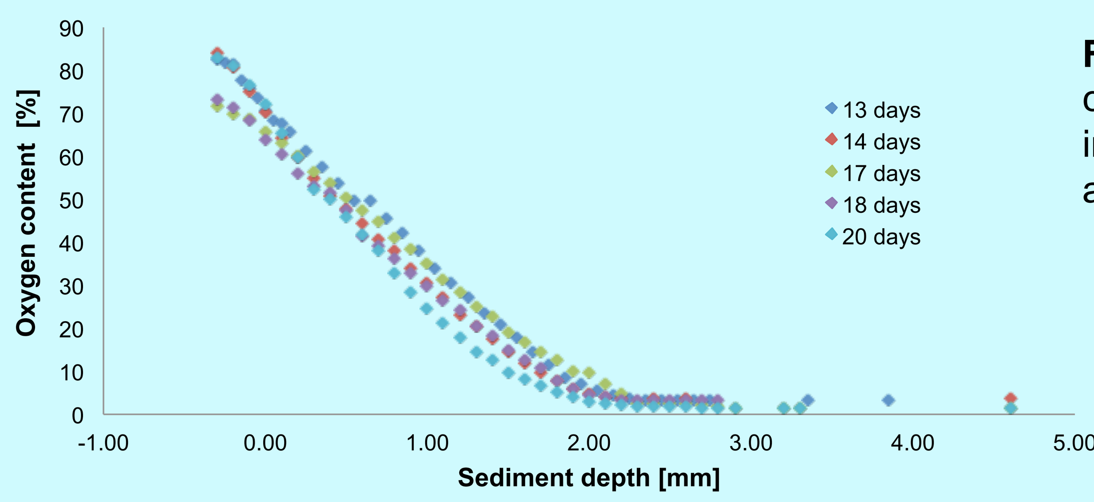


Figure 1: Depth-dependent oxygen content (relative to saturation conditions) in the coarse sediment, after different acclimation periods.

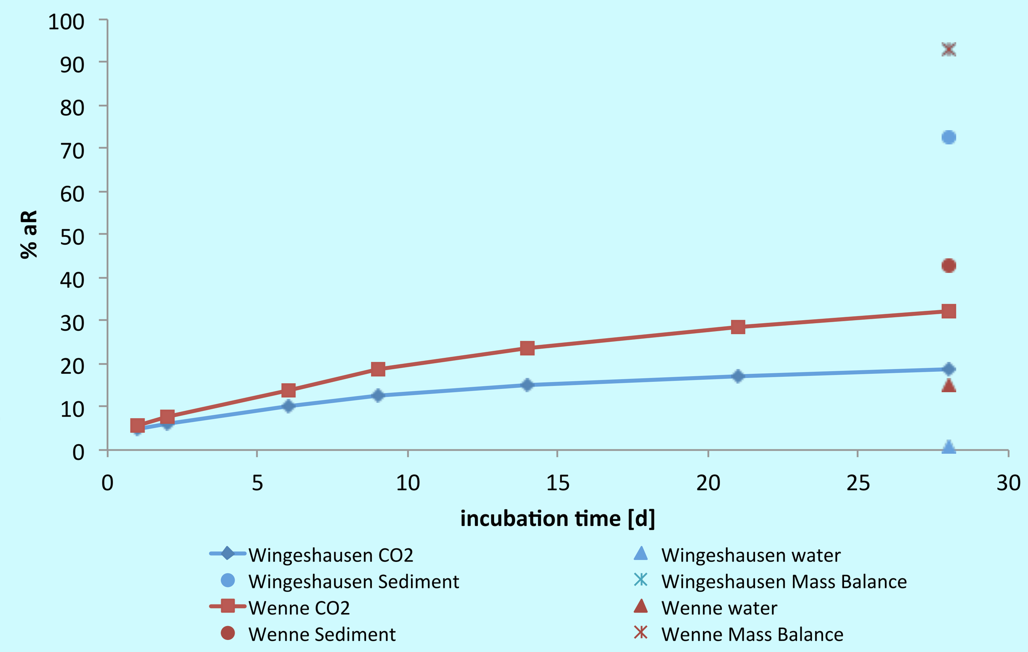


Figure 2: Mineralization of aniline in reduced 308 test design to be used as bioactivity control for frozen/thawed sediments; data given for freshly sampled sediments (reference data).

Next steps (2013-2014)

➢ Suite of 308 and 309 experiments for all four test chemicals

➢ Measurement of sediment sorption coefficients for all four test chemicals

➢ Kinetic parameter estimation for 20-30 pesticides and pharmaceuticals

➢ Comparison of estimated degradation half-lives for 20-30 pesticides and pharmaceuticals with persistence endpoints reported in dossiers

Thanks to: Mark Honti for MCMC, Rani Bakkour for discussions (Eawag)

References

Loos, M. *et al.*, 2012. Pesticide Non-Extractable Residue Formation in Soil – Insights from Inverse Modeling of Degradation Time Series. *Environ. Sci. Technol.* **46**:9830-9837.

Funding provided by:

cefic

The Long-range Research initiative