LRI ECO18 – Improved strategy to assess persistence at the sediment-water interface

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A project sponsored by:

General goal

Develop recommendations on *combined testing strategies & data evaluation procedures* to derive *robust* information on the *degradation* of the *parent compounds* from OECD 308 or similar tests (308mod, 309mod, 309) that can be used *for P assessment* or *for exposure modeling* in the context of *different regulatory frameworks*.

Hypotheses of the project

- Hypothesis 1:

  Advanced parameter estimation techniques can be used to *derive degradation parameters* from OECD 308 data by *incorporating additional system knowledge* in a *transparent* manner

- Hypothesis 2:

  To obtain robust degradation data, experiments and data analysis methods need to *disentangle (bio)degradability from (reversible and non-reversible) sorption and diffusion*, and clearly *distinguish between aerobic and anaerobic conditions*

General strategy of the project

- Modeling strategy:

  Use of *advanced parameter estimation techniques* and *system descriptions of increasing level of complexity* to estimate “robust” degradation half-lives from OECD 308 data

- Experimental strategy:

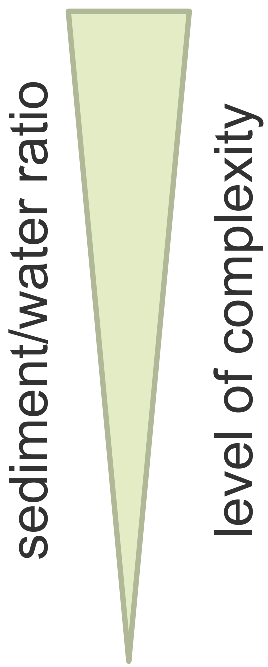
  Investigation of the behavior of *4 characteristically different chemicals* in a *suite of* complex to less complex *water-sediment systems* in a *consistent manner*

Experimental test systems

LRI ECO-18

Experimental approach

- 4 characteristically different chemicals
- suite of four complex to less complex water-sediment systems



- OECD 308 standard
- OECD 308 modified
- OECD 309 modified
- OECD 309 standard
- Water-Sediment Screening Tool (WSST)

Intentions:
- close gap between OECD 308 and OECD 309
- address some of the major points of criticism
- improve test systems regarding data evaluation

System configurations

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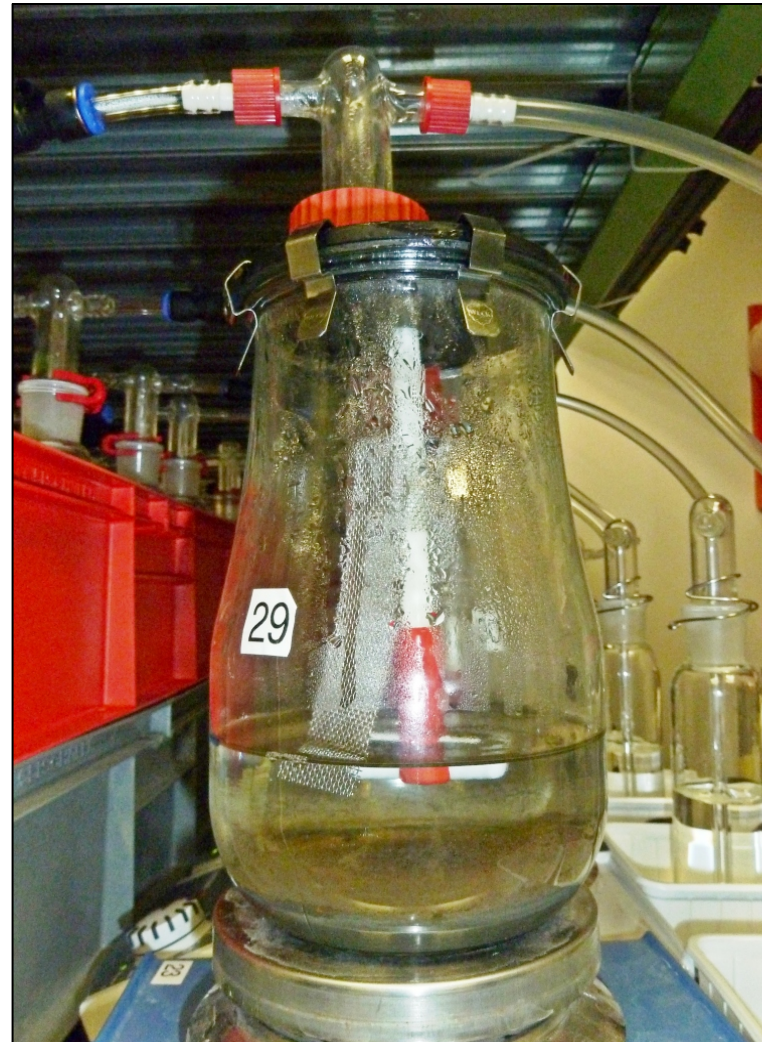
Test systems

Test system	OECD 308 (standard)	WSST	OECD 308 (modified)	OECD 309 (modified)	OECD 309 (standard)
Compartments	stratified	stratified, H_2O stirred	stratified, H_2O stirred	mixed, stirred	mixed, stirred
Water [mL]	150	500	500	300	300
- height [mm]	60	40	42	-	-
Sediment [g dw]	50	120	50	3	0.3
- height [mm]	20	10	5	-	-
- interfacial area [cm^2]	22	100	90	-	-
- Volume [mL]	45	100	45		
Water:Sediment (w/w)	3:1	4:1	10:1	100:1	1000:1
Water:Sediment (v/v)	3.3:1	5:1	11.1:1		

Test systems

OECD 308

OECD 308 mod



Test systems

OECD 309 mod

Sediment properties

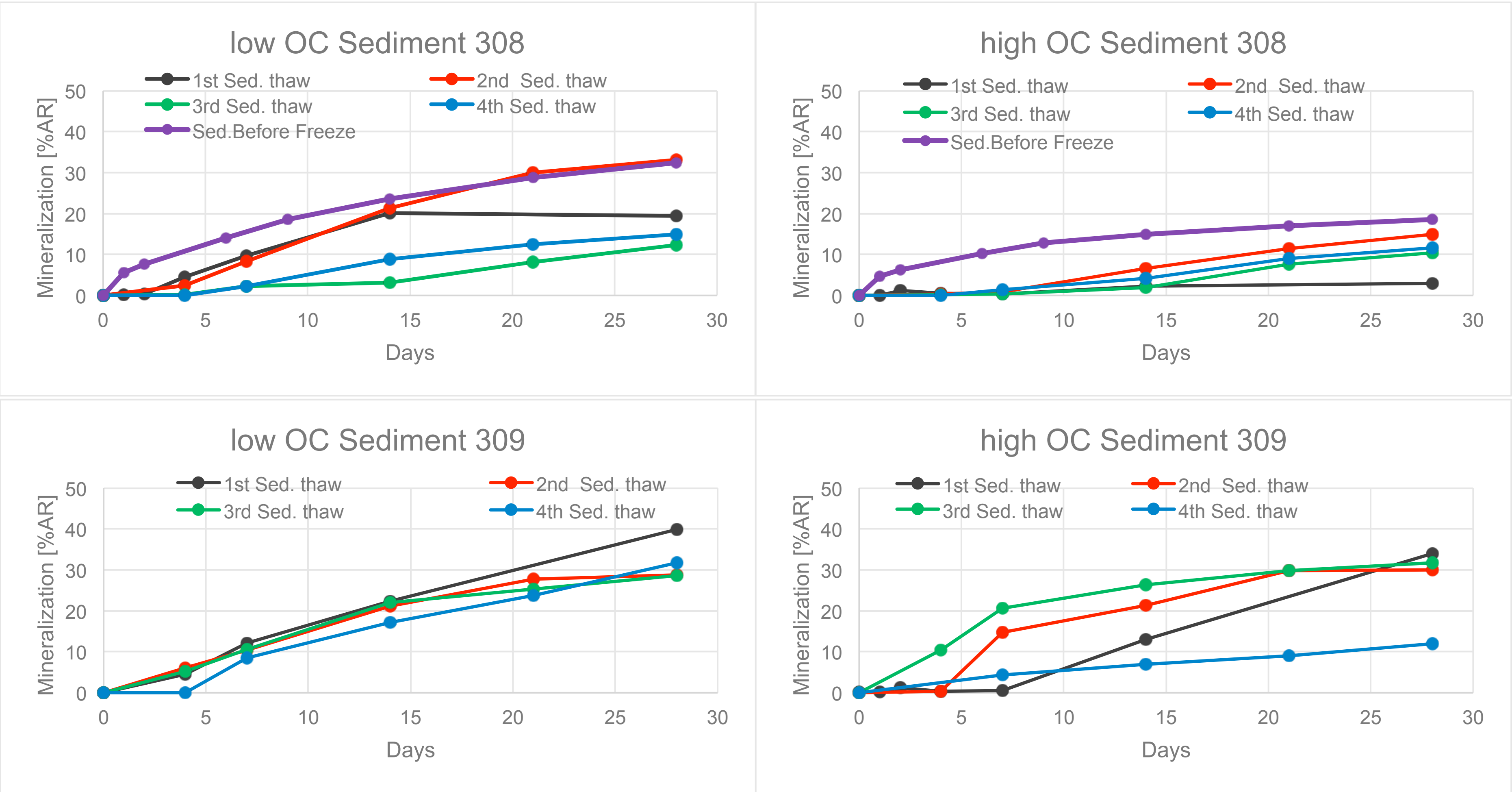
Selected natural sediments

Sediment properties	Wenne (coarse, low OC)	Wingeshausen (fine, high OC)
Sand [w%] DIN	77.5	22.9
Silt [w%] DIN	17.3	58.4
Clay [w%] DIN	5.2	18.6
TOC [w%]	0.8	7.2
pH	6.5	5.6
Dry matter [w%]	74.3	36.0
Redox potential [mV]	96.7	83.6

- Sampling: July 20th, 2012 (Wenne); August 3rd, 2012 (Wingeshausen)
- Sieving: < 2 mm
- Testing: Anilin mineralisation / fumigation / RNA-analysis, before freezing, during each test

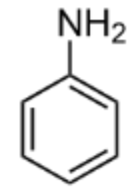
Sediment microbial activity

Activity controls (Aniline mineralisation)



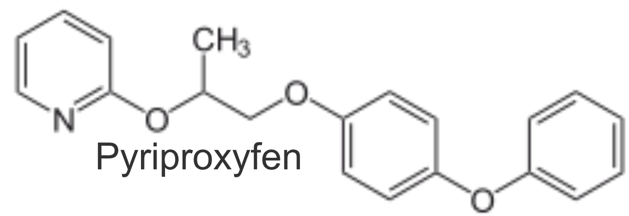
Test Chemicals

Readily degradable, weak sorption:



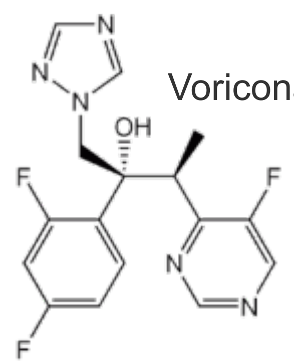
Aniline

Readily degradable, strong sorption:



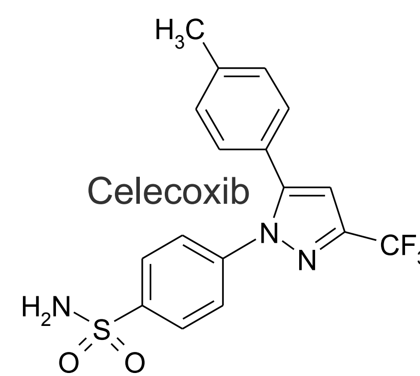
Pyriproxyfen

Intermediate degradable, weak sorption:



Voriconazole

Intermediate degradable, strong sorption:



Celecoxib

Water-sediment simulation studies

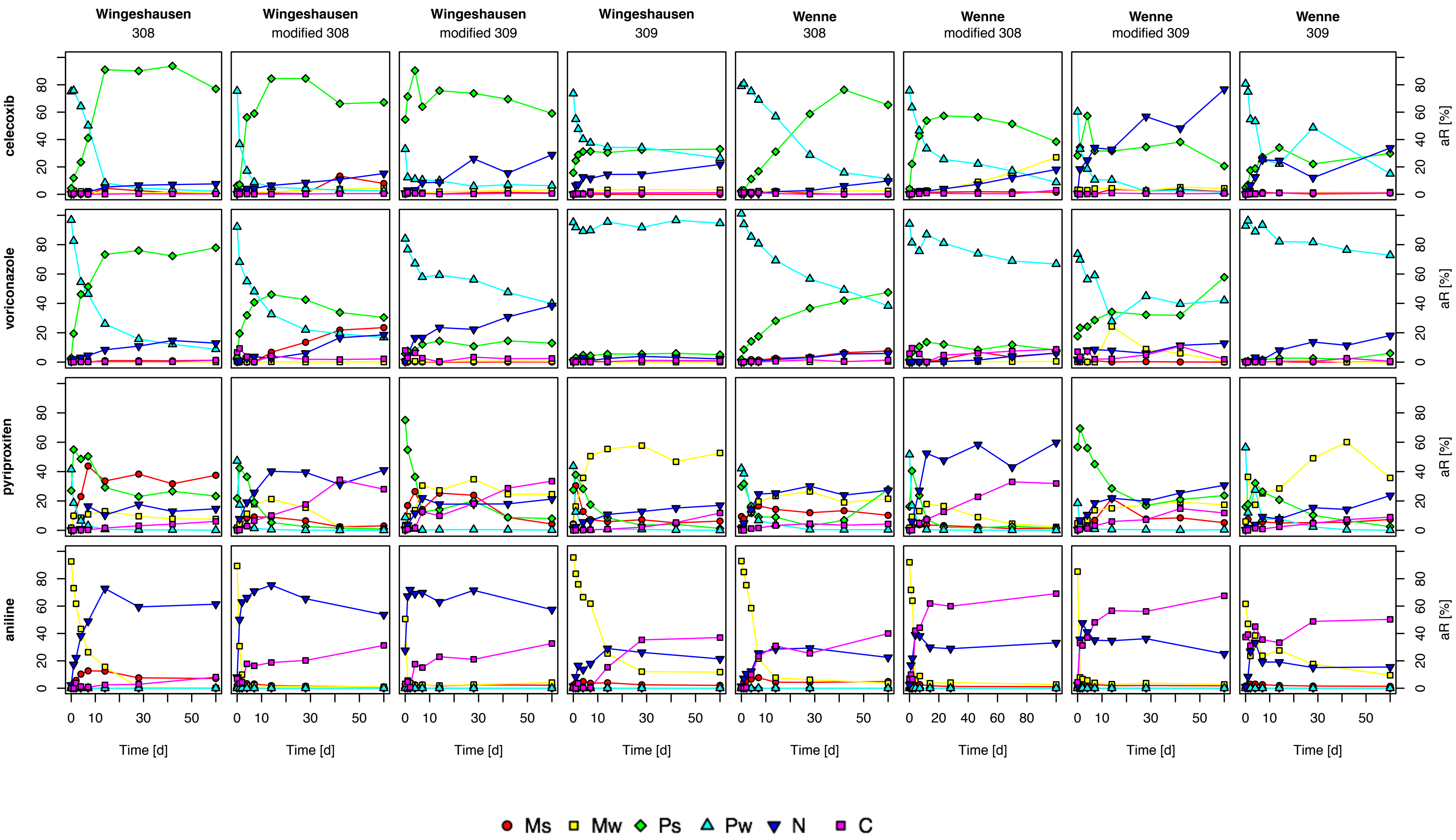
Test Performance

Initial test substance concentrations

Triggered by water solubility to avoid application of co-solvents

Starting Concentration	308	308 modified	309 modified	309
Aniline	1 mg/L	1 mg/L	0.1 mg/L	0.1 mg/L
Voriconazole	1 mg/L	1 mg/L	0.1 mg/L	0.1 mg/L
Pyriproxifen	0.1 mg/L	0.1 mg/L	0.05 mg/L	0.05 mg/L
Celecoxib	0.1 mg/L	0.1 mg/L	0.05 mg/L	0.05 mg/L

Experimental results



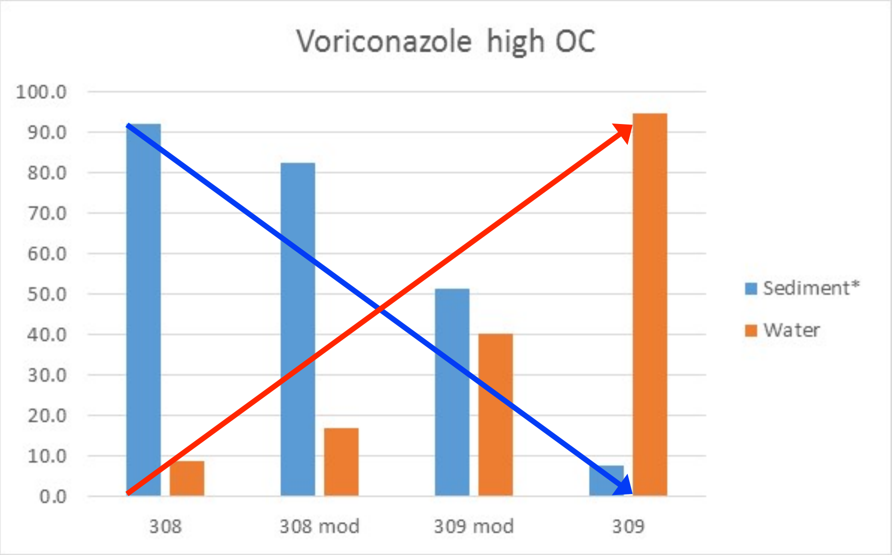
Experimental results

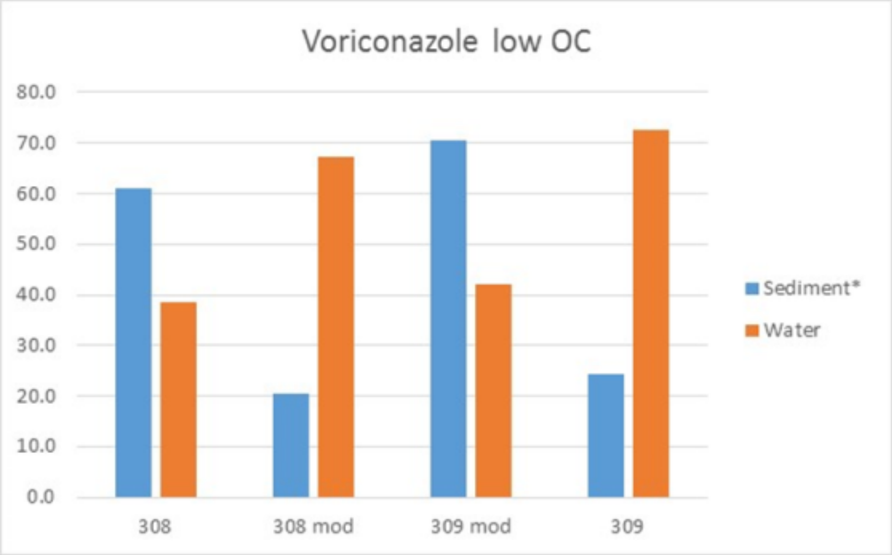
Voriconazole ⇨ main process: sorption

very low degradation, recovered radioactivity unchanged parent only

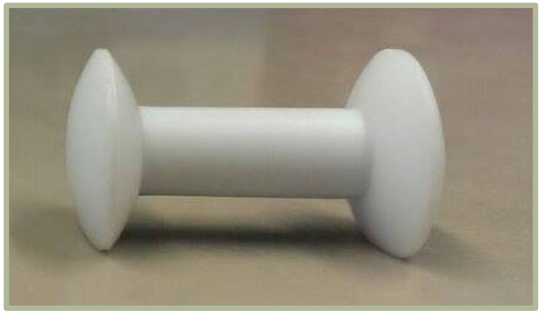
High OC Sediment: Decreasing sediment ratio = decrease of sorbed substance (extractable and non-extractable)

Low OC Sediment: No general trend. Very high sorption in 309 systems => grinding of sediment by stirring?





Shortcoming of stirred approach



Stir bars (before test)

Stir bars (after test)

up to 10% abrasion

<table>
<tr><th>Sediment properties
309 mod (stirred)</th><th>low OC
test start</th><th>low OC
60 days</th></tr>
<tr><td>Sand [w%] DIN</td><td>77.5</td><td>2.5%</td></tr>
<tr><td>Silt [w%] DIN</td><td>17.3</td><td rowspan="2">97.5 %</td></tr>
<tr><td>Clay [w%] DIN</td><td>5.2</td></tr>
</table>

Experimental Results

Celecoxib ⇨ main processes: sorption and transformation

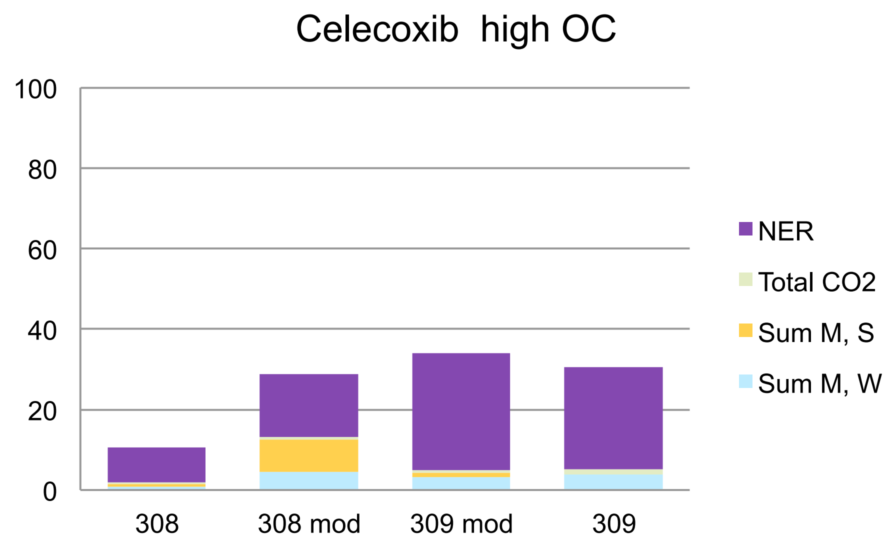
Generally same metabolic pattern in low OC and high OC systems

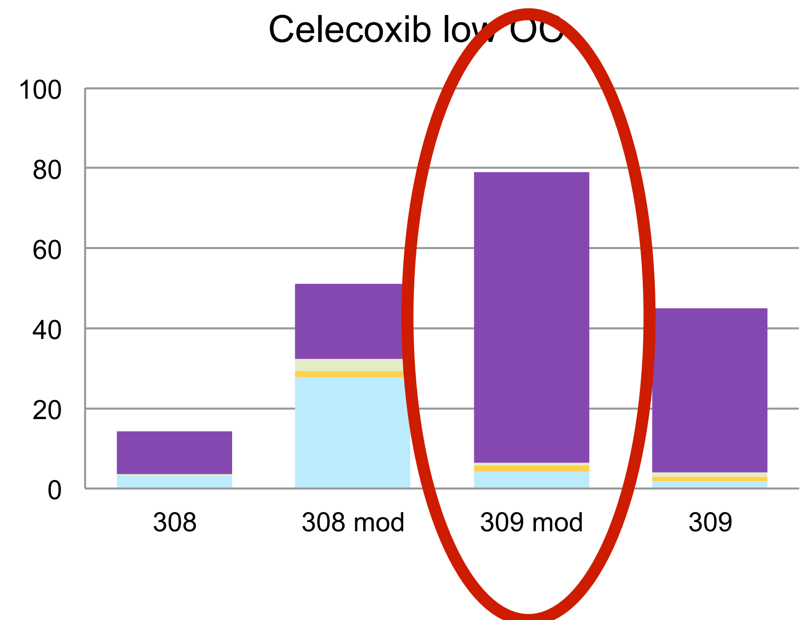
Very low mineralisation (< 2%)

Extremely high NER at 309 mod **Sediment grinding by stirring**

Extremely high „degradation“ at 309 mod

Almost complete remaining parent adsorbed to sediment





Experimental Results

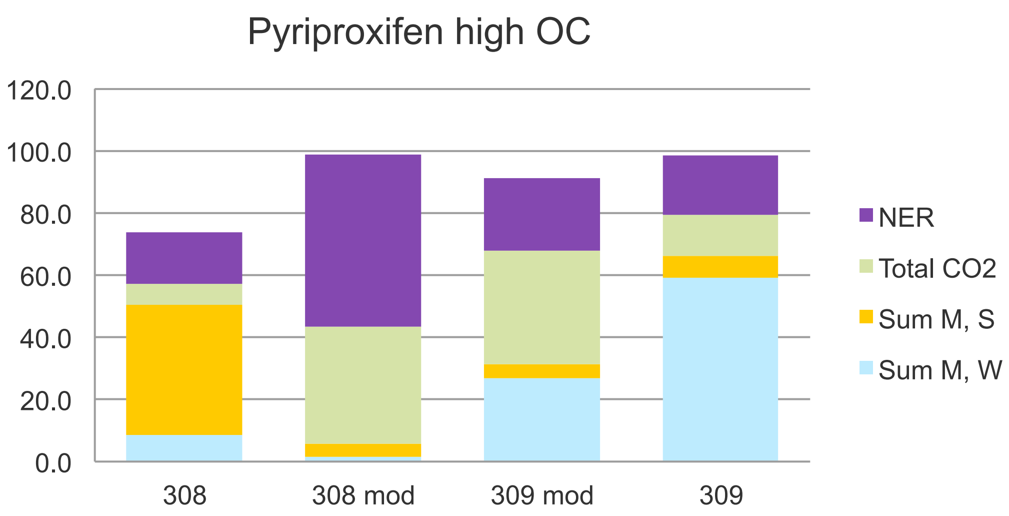
<u>Pyriproxifen</u> ⇨ increased metabolism / mineralisation

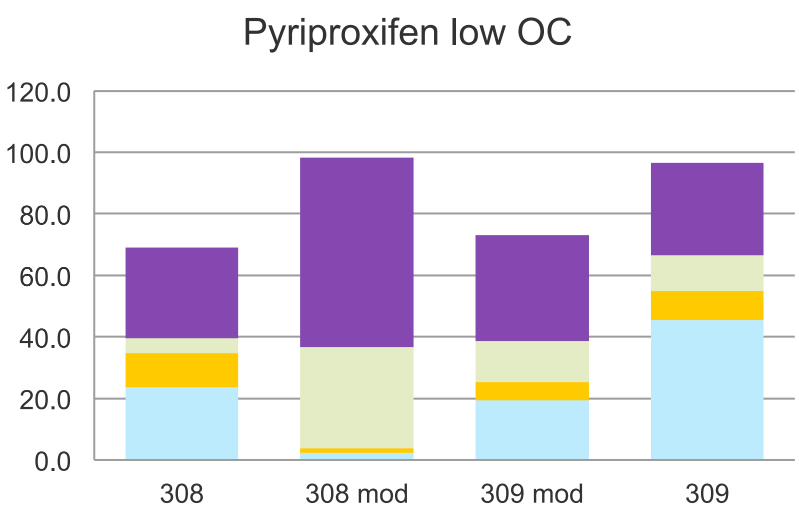
General trends in the test systems:

both sediments show comparable metabolic pattern

High OC: low degradation, but high sorption for metabolite in 308

Low OC: same trend, high degradation in 308 mod and 309



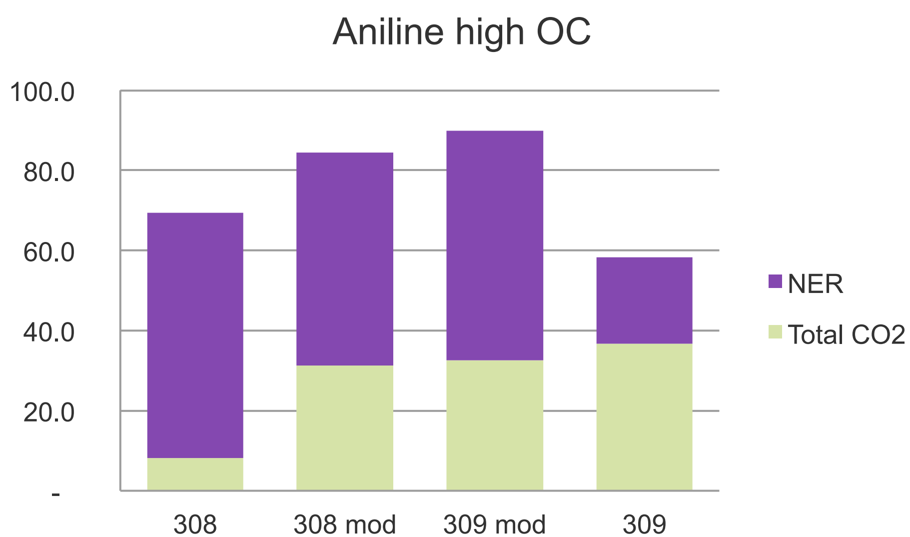


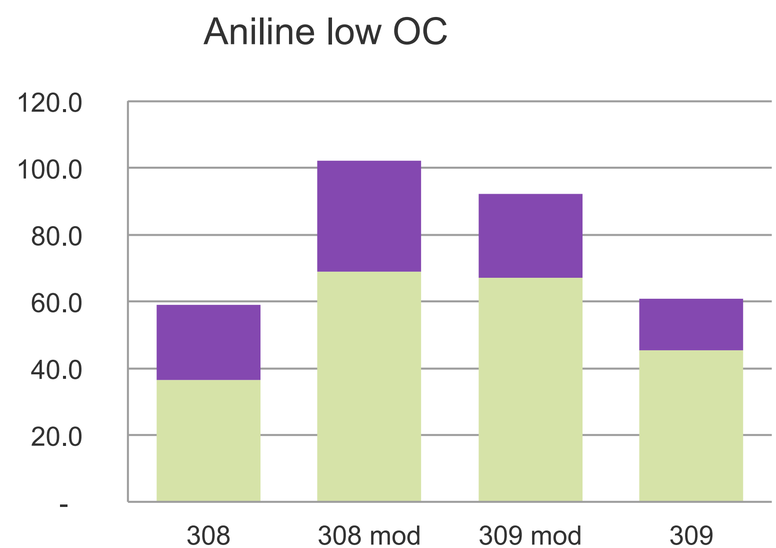
Experimental Results

<u>Aniline</u> ⇨ differences in degradation capacity

General trends (final endpoints of degradation CO_2 and NER):

308 mod. ▯ 309 mod > 309 ▯ 308 for high and low OC sediments





Aniline

High OC	OECD 308	OECD 308 mod	OECD 309 mod	OECD 309
$DT_{50,w}$ (d)	4	1	<1	10
NER & CO_2 (%)	70	85	90	59
CO_2 vs NER	CO_2 < NER	CO_2 < NER	CO_2 < NER	CO_2 > NER

Low OC	OECD 308	OECD 308 mod	OECD 309 mod	OECD 309
$DT_{50,w}$ (d)	4	3	<1	ca. 8
NER & CO_2 (%)	60	100	92	61
CO_2 vs NER	CO_2 > NER	CO_2 > NER	CO_2 > NER	CO_2 >> NER

- Extent of degradation highest in 308mod + 309mod: high inoculum density, good accessibility
- Mineralization increases over NER formation with decreasing sorption capacity

Conclusions from Experimental part

- Selected test chemicals shows a wide range of different pathways in the various test systems. Results are appropriate to indicate the relevant processes responsible for the disappearance of the parent substances
- Modified test systems (308 mod, 309 mod) generally provide improved degradation capacity compared to 308
- Stirred test systems are hard to interpret because of changing sorption properties.
  Alternatively shaking of systems?

- Next step: Parameter estimation across systems to elucidate their similarities/differences for degradation potential and interpretability of experimental data

LRI ECO18 – Quantitative Data Evaluation

Annual ECETOC Environmental Progress Review, Brussels, 12 February 2015

K. Fenner, M. Honti

A project sponsored by:

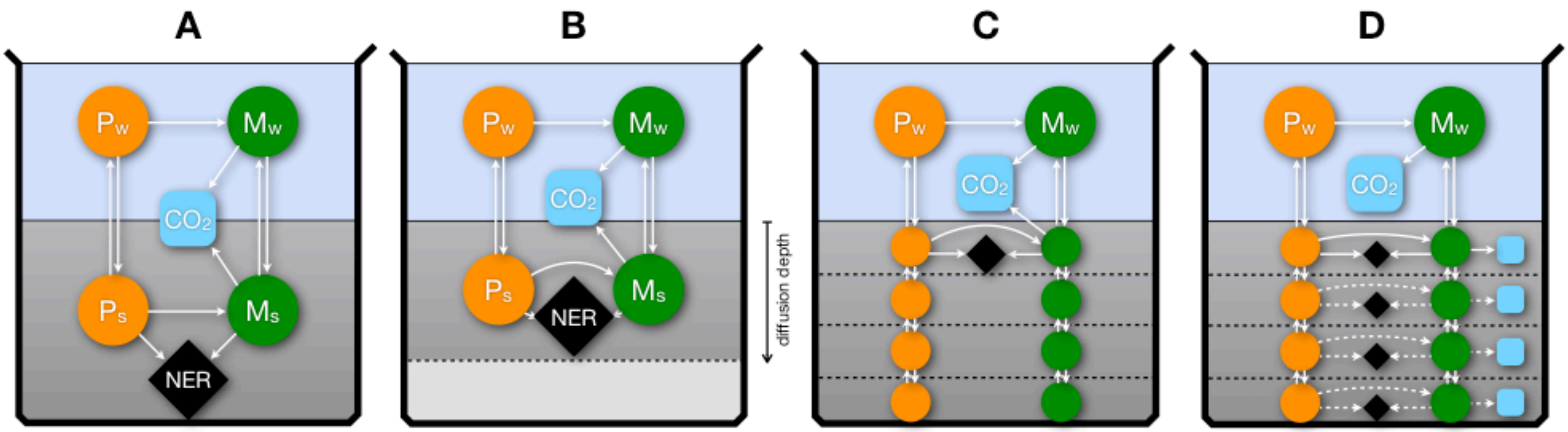
Analysis of literature OECD 308 data

Honti & Fenner (to be submitted to ES&T)

- *Problem statement*
    - OECD 308 is a complex system where transformation, diffusion and sorption are hard to disentangle.
    - Models need to describe all of these processes if meaningful degradation parameters are to be extracted from data. Such complex models suffer from parameter-identifiability issues.
- *Aims*
    - Use advanced parameter estimation techniques to come up with robust estimates for compartment-specific transformation parameters.

Analysis of literature OECD 308 data

Model versions of increasing complexity regarding sediment



Instant diffusion in sediment.

Gradual diffusion in sediment, anaerobic transformation.

Gradual diffusion in sediment, aerobic transformation.

Gradual diffusion in sediment, aerobic & anaerobic transformation.

Analysis of literature OECD 308 data

Approach

- Analysis of parameter robustness with regard to assumptions on:
  - general mechanisms
  - diffusion inside sediment (=model version)
  - transformation inside sediment (=model version)
  - system geometry

Analysis of literature OECD 308 data

Lessons learnt

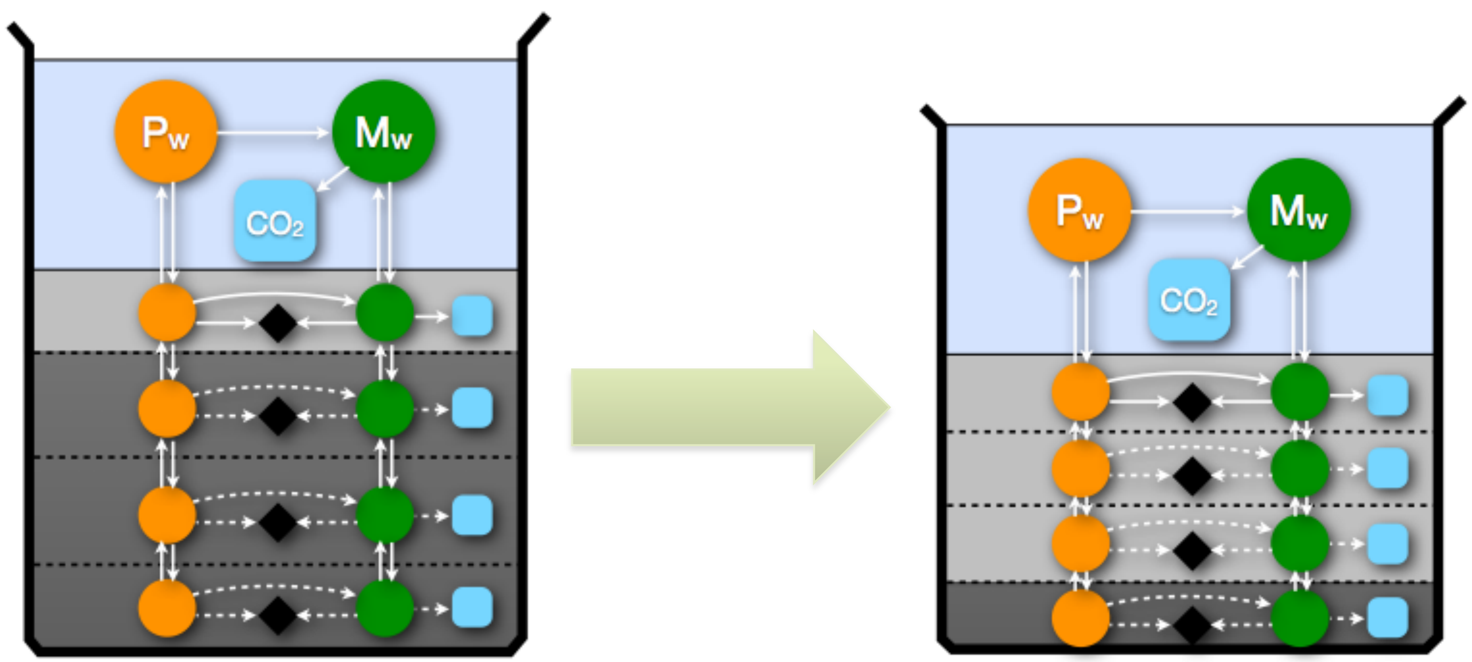
- **OECD 308 alone is not enough to derive robust compartment-specific degradation half-lives** because:
  - The ratio between aerobic and anaerobic transformation can't be estimated unambiguously
  - The extent of diffusion into sediment can't be estimated unambiguously
  - System geometry is seldom reported along with experimental data

Evaluation of own measurements

Unified model framework: 308 modified

- 308 (D) is used to spawn models for other systems
- 308 mod: less sediment, deeper aerobic layer of sediment

308 | 308 modified

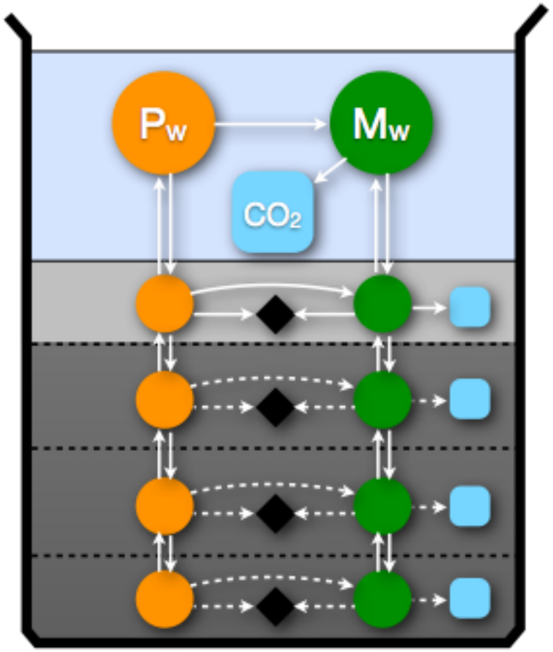


Evaluation of own measurements

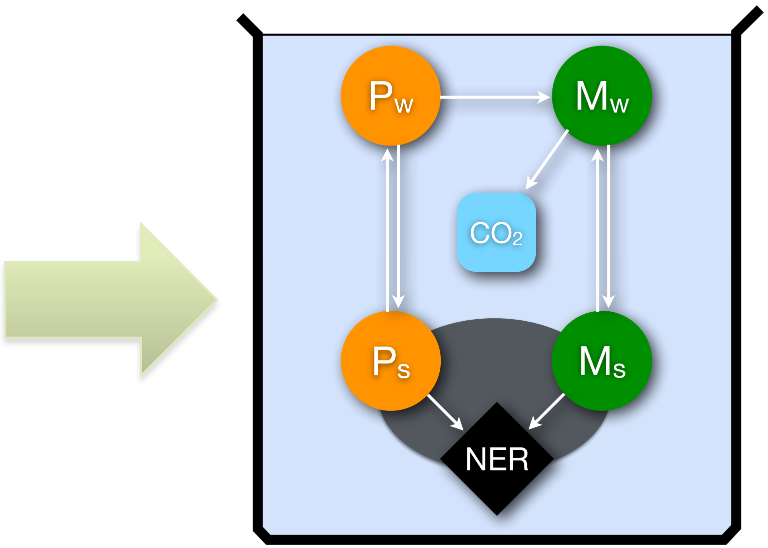
Unified model framework: 309 and 309 modified

- 308 (D) is used to spawn models for other systems
- 309s: stirred → immediate dispersal; instant sorption equilibrium?

308



309 & 309 modified



$$P_w = P \frac{1}{1 + \frac{K_{d,P}}{\mathcal{M}_{w/s}}}$$

$$M_w = M \frac{1}{1 + \frac{K_{d,M}}{\mathcal{M}_{w/s}}}$$

Evaluation of own measurements

Calibration across experimental systems

- 308 alone cannot provide robust estimates on immeasurable processes
- We have a spectrum of 4 experimental types from most (308) to least (309) sediment
- Aims: Test whether
    - (i) we can get more certainty about the transformation rate constants by calibrating across different systems,
    - (ii) this could then be used to predict the outcomes in other systems

Evaluation of own measurements

Calibration across experiments

Specific parameters

- M_w:M_s (water:sediment ratio, 309.*)
- k_{sorp}: apparent sorption rate (309.*)
- i_{grind} (309.*)
- u_{grind} (309.*)
- sediment porosity
- height of water column (308.*)
- height of sediment (308.*)
- initial values

Universal parameters

- $K_{oc,P}$
- $K_{oc,M}$
- $f_{oc,sed}$
- k_{bio}: OC-specific transformation rate for dissolved fraction in sediment
- k_{wpm}
- k_{spn}
- (transformation rates from M)
- D_P
- D_M
- ∂: relative transformation slowdown under anaerobic conditions
- (measurement error std. deviation)

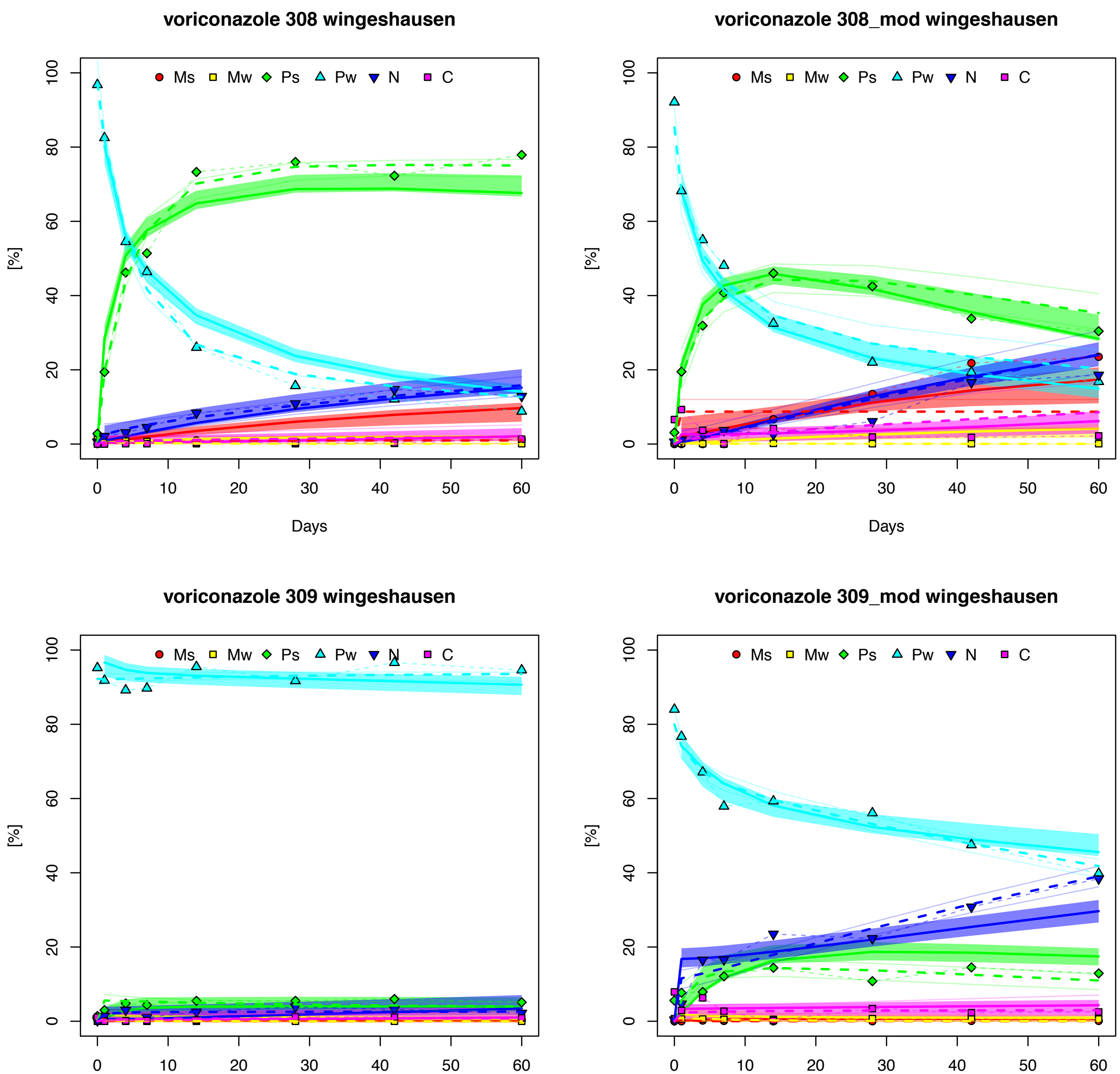
Evaluation of own measurements

Calibration across experiments

	308	308 mod	309 mod	309	Description
$K_{oc,P}$					K_{oc} of parent compound
$K_{oc,M}$					K_{oc} of metabolites
$f_{OC,sed}$					OC content of sediment
k_{bio}					OC-specific transformation rate for dissolved fraction in sediment
k_{spn}					Transformation rate from parent to NER in sediment
D_P					Diffusion rate for parent
D_M					Diffusion rate for metabolites
∂					Relative transformation slowdown for anaerobic sediment

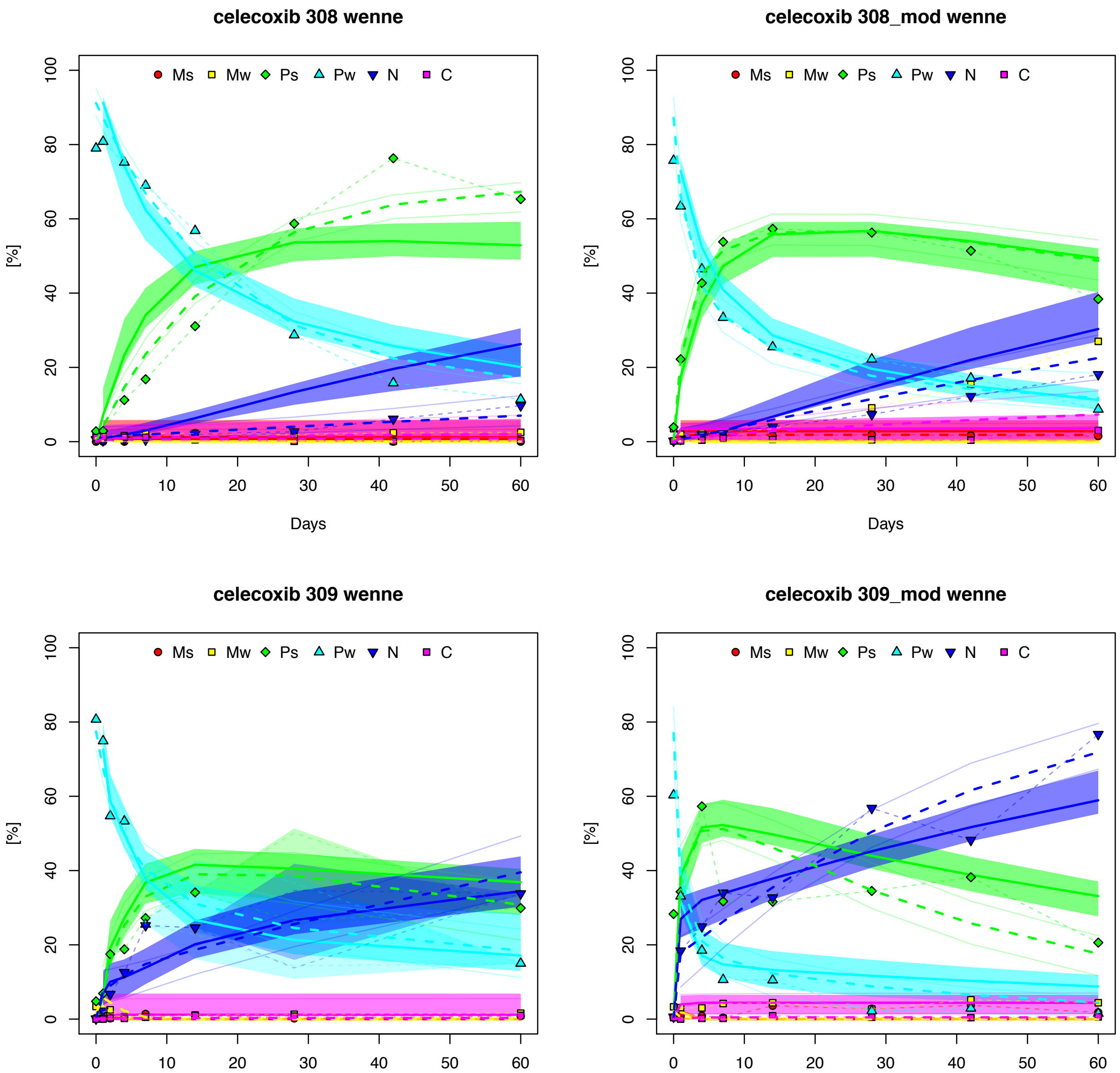
Evaluation of own measurements

Calibration across experimental systems



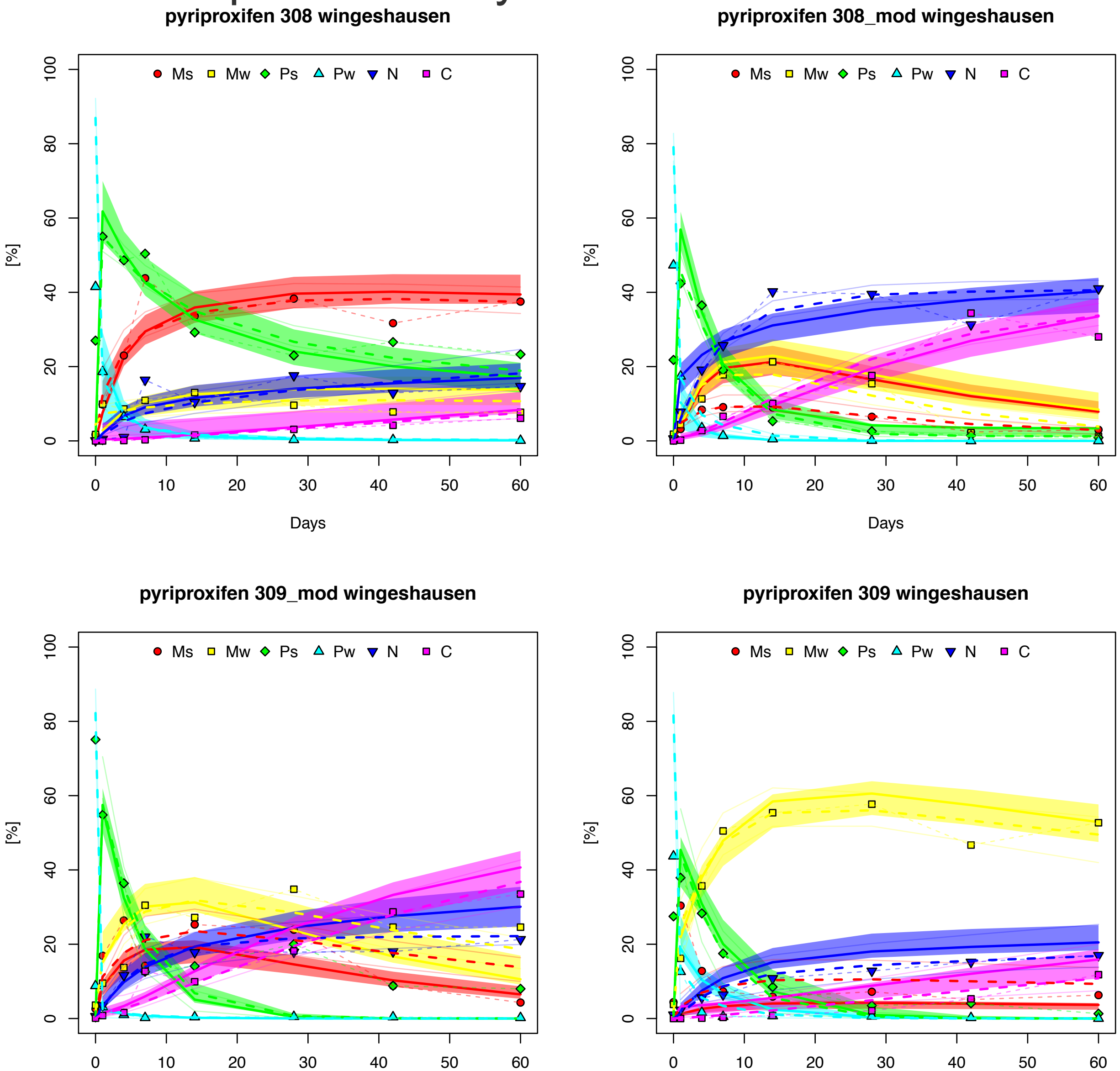
Evaluation of own measurements

Calibration across experimental systems



Evaluation of own measurements

Calibration across experimental systems



Preliminary findings

- Unfortunately explicit metabolite formation was observed only for some compounds (k_{bio}), others are complex physico-chemical experiments
- The dynamic apparent sorption capacity makes interpretation of 309/309 mod experiments uncertain
- **Cross-experiment calibration is possible**
- Uncertainty is to be analysed

Milestone plan and current status

Milestone	Status
M1. Existing data collation	Done
M2. Substance selection	Done
M3. Sediment sampling & characterization	Done
M4. Initial biomass determination	Done
M5. Sorption studies	Done
M6. Kinetic parameter estimation	Done
M7. Comparison to standard endpoints	Done
M8. WSST test conduction (aniline, vori.)	Done
M9. 309, mod 309	Done
M10. 308, mod 308	Done
M11. Evaluation of own exp. data (incl. kinetic parameter estimation)	Mid 2014 to mid 2015
M12. Comparison across test designs	Mid 2014 to mid 2015
M13. Improved testing strategy	Spring to autumn 2015

Thanks

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- Cecilia Diaz, IME
- Elena Heusner, ECT

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