Developing improved strategies to assess chemical persistence at the water-sediment interface

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Cefic LRI-ECO18

OECD 308, Limitations

Experimental issues

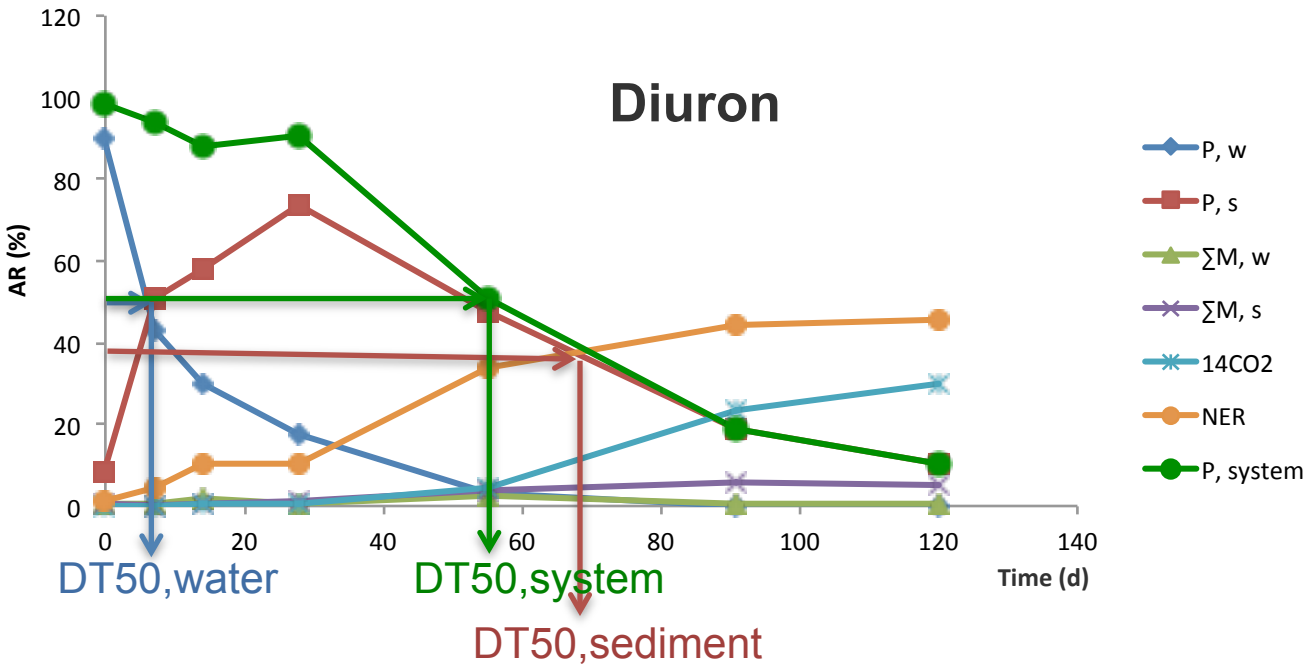
- Large experimental effort (vessels ≥ 60; labelled compounds), very expensive
- Recommended sediment:water ratio not appropriate for all compound classes/ exposure situations
- Redox gradient within sediment layer
- High sediment:water ratio shifting mass distribution excessively towards sediment

→ Sorption often dominant process, “masking” degradation

→ Extensive NER formation: Relevance in natural systems?

OECD 308, Limitations

Data interpretation



- Dynamic partitioning between solid aerobic/anaerobic phase and water during incubation
- $DT_{50,water}$ and $DT_{50,sediment}$ confound degradation and phase transfer

→ How to derive indicators of degradation (e.g., half-lives?)

Lead question

How should a test system be designed to efficiently provide robust information on degradation and persistence in sediments for chemical risk assessment?

Working hypotheses

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

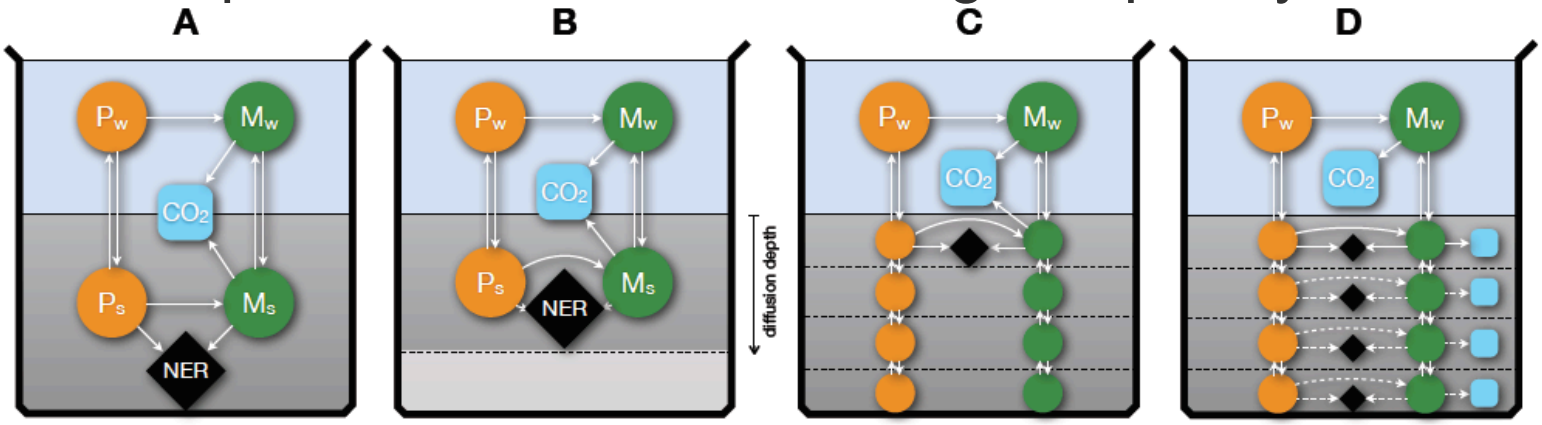
⇨ Data analysis approach

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*

⇨ Experimental approach

Data analysis approach

- System representations of increasing complexity

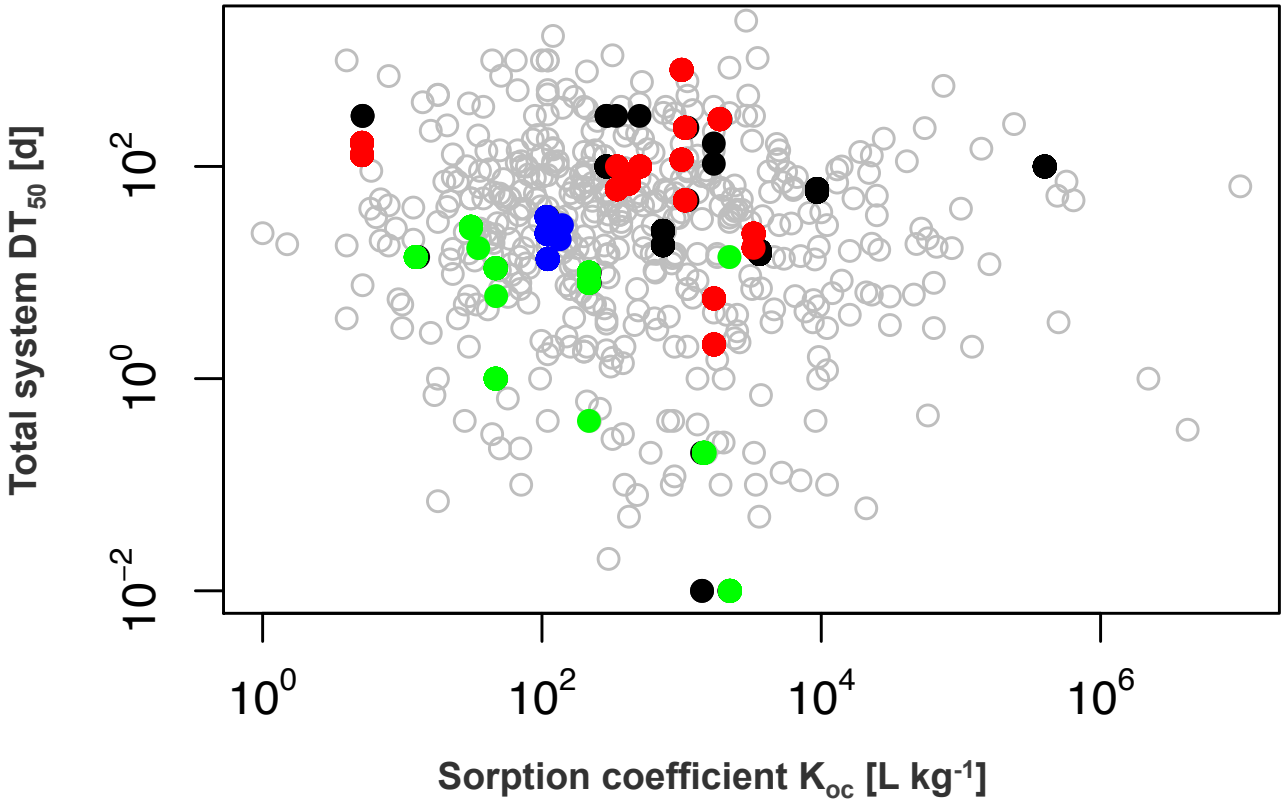


  - ➢ Metabolites as lumped pools
  - ➢ All first-order kinetics

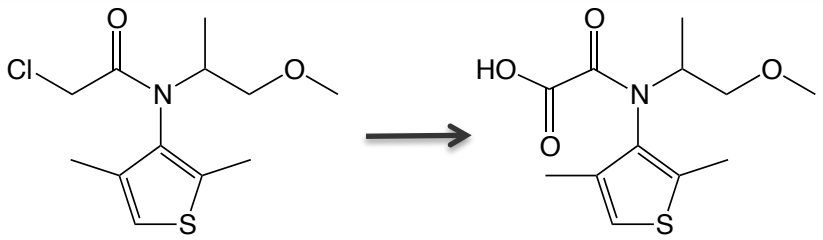
- Parameter estimation: Bayesian parameter inference
  - – (Intelligent) random walk through parameter space
  - – Yields distribution of values around area of highest posterior probability
  - – Would not converge without priors on substance properties (sorption, diffusion)

Data analysis approach, cont'd

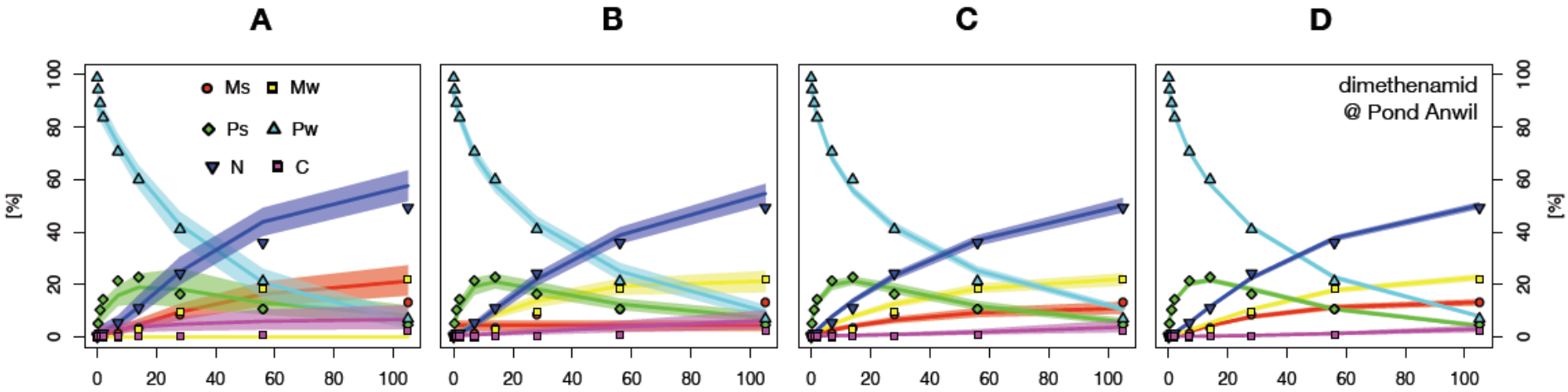
- 16 pesticides and 7 pharmaceuticals (41 data sets)
- Covering range of sorption behavior and degradability



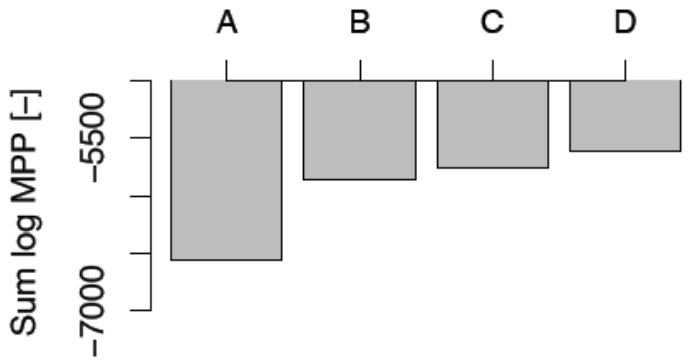
Comparison of model performance



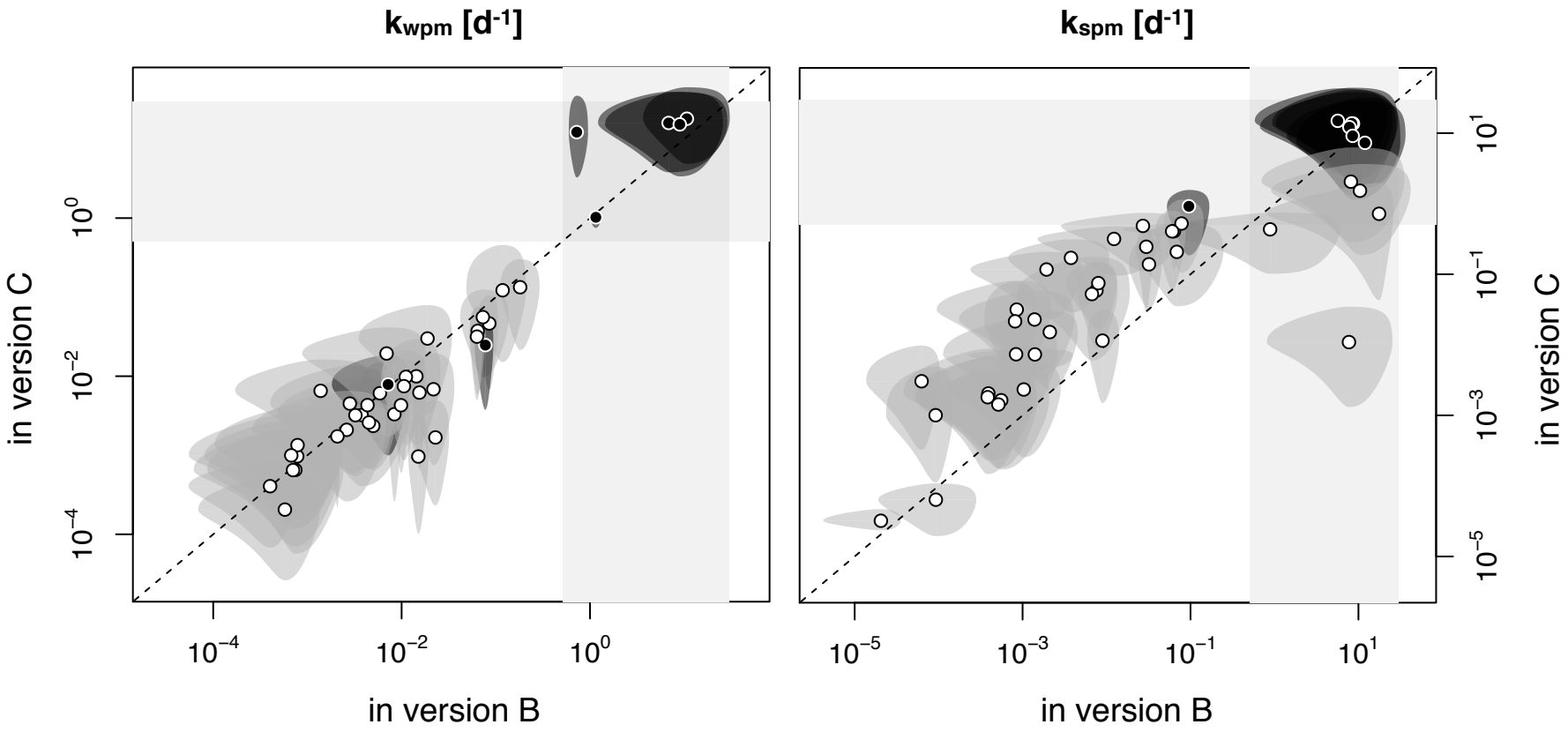
dimethenamid



Standard 2-box model (A) for half-life estimation (FOCUS guidelines) performs worst!



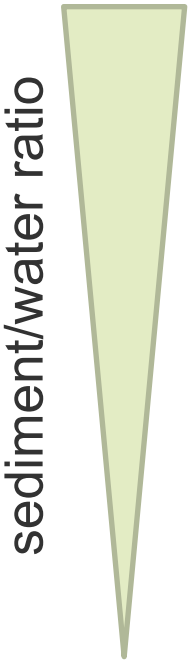
Estimation of kinetic parameters



- $DegT_{50,w}$ can be estimated robustly from OECD 308 data
- $DegT_{50,sed}$ strongly depends on model versions

Experimental approach

Use of a suite of four water-sediment systems of different complexity to investigate the behavior of four characteristically different chemicals in a consistent manner:



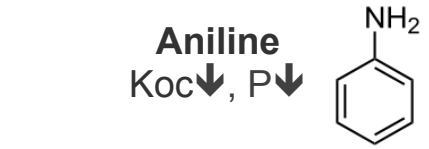
OECD 308 standard
(water:sed ratio = 3:1, not stirred)

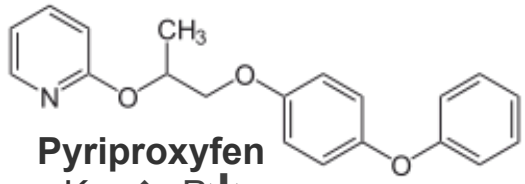
OECD 308 modified
(water:sed ratio = 10:1, stirred water)

OECD 309 modified
(water:sed ratio = 100:1, stirred)

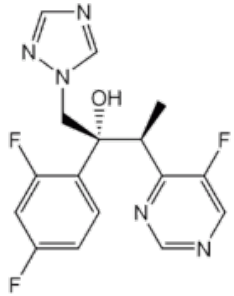
OECD 309 standard
(water:sed ratio = 1000:1, stirred)

Aniline
Koc↓, P↓



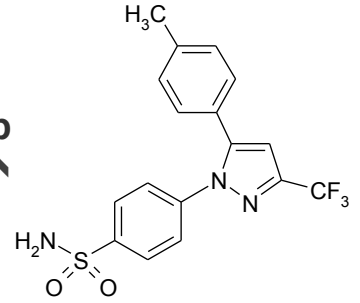


Pyriproxyfen
Koc↑, P↓



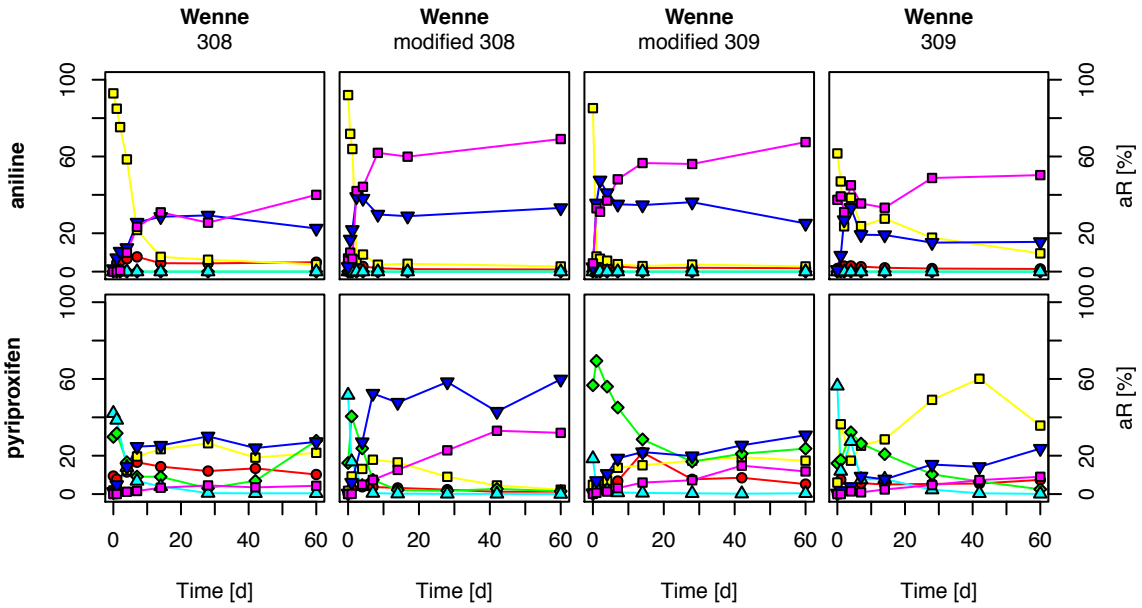
Voriconazole
Koc↓, P↑

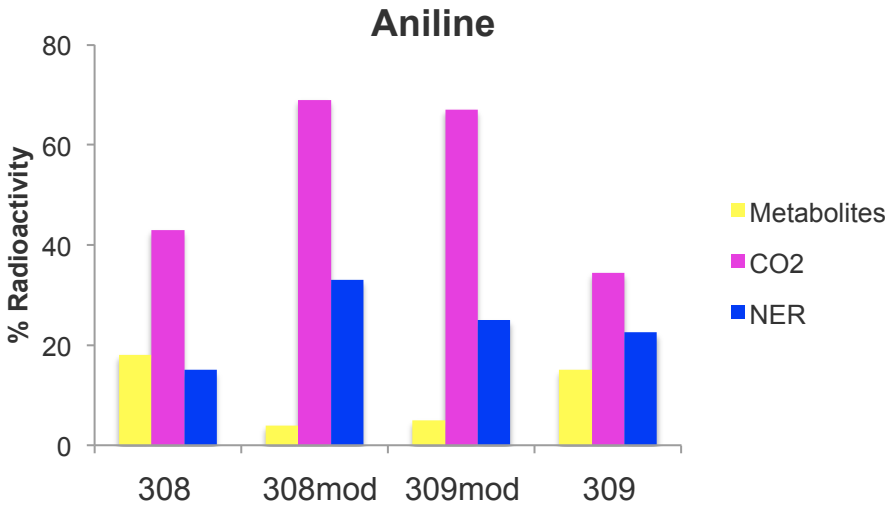
Celecoxib
Koc↑, P↑

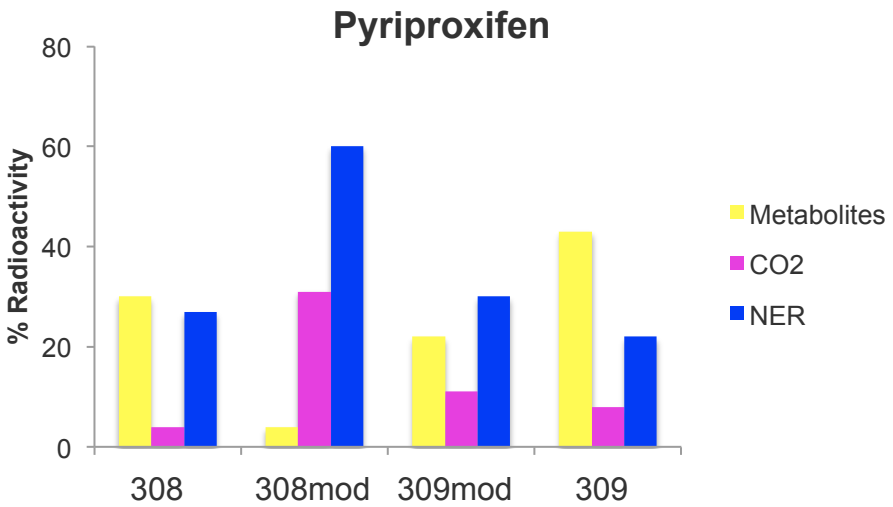


General trends in results

Low OC sediment







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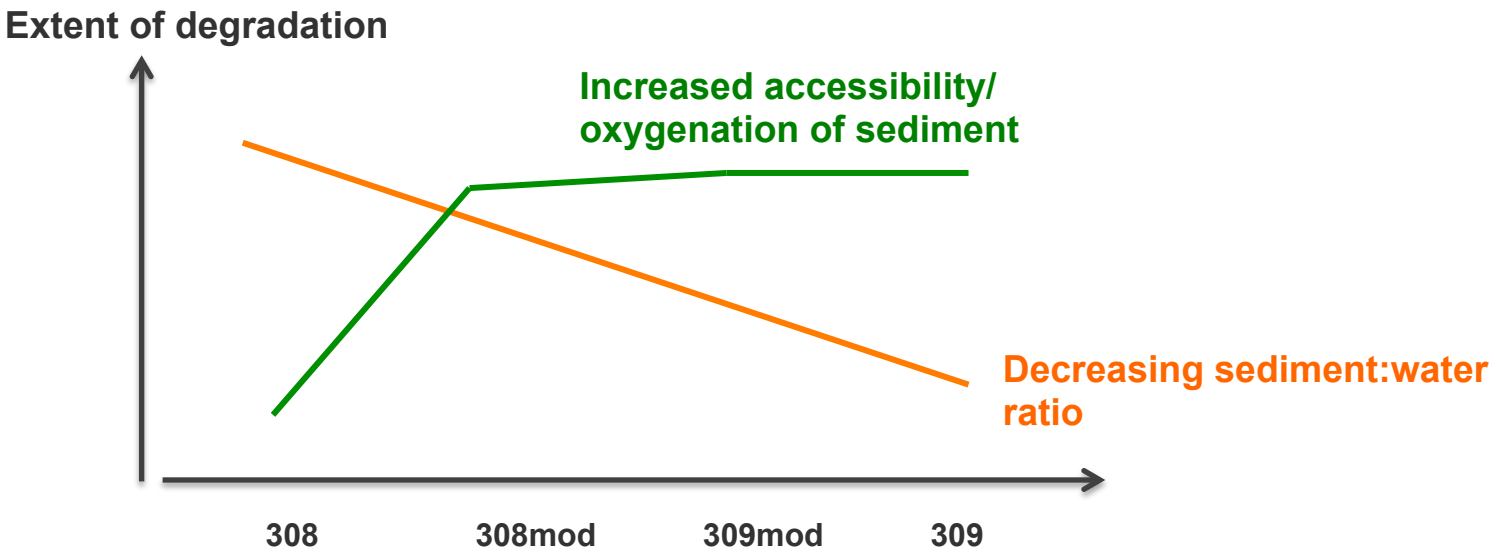

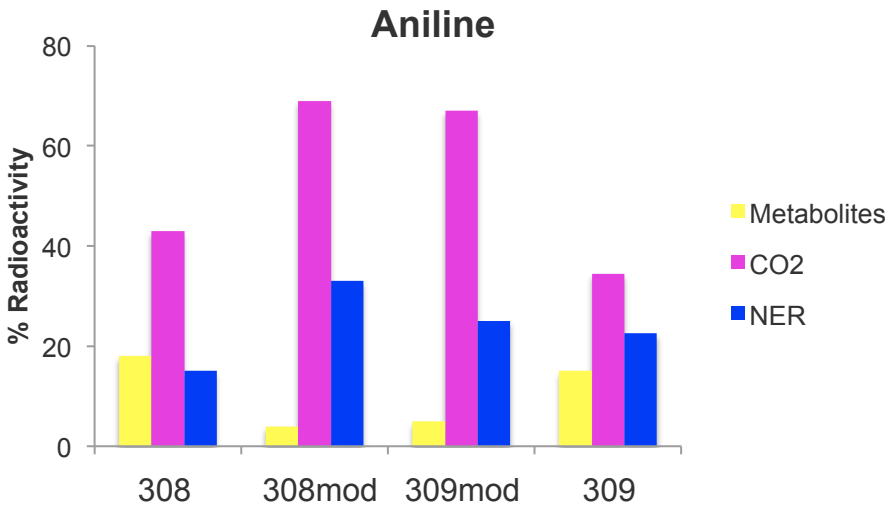

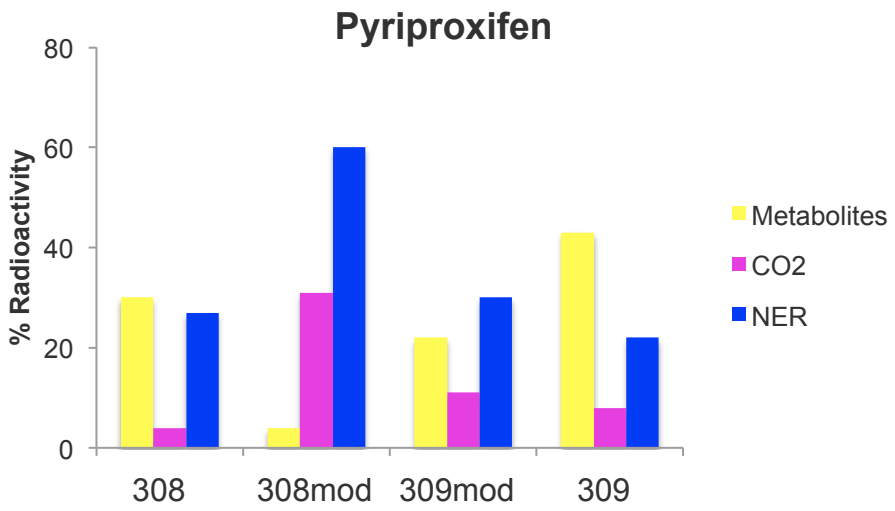

Conclusions

- Compartment-specific degradation parameters derived from OECD 308 data remain rather uncertain
- $DT_{50,system}$ provides fairly robust P measure for the specific OECD 308 exposure situation
- Modified test systems (308 mod, 309 mod, 309) provide better accessible, yet decreasing amounts of sediment
  - Maximum degradation in 308 mod and 309 mod
  - Improved interpretability in 309 systems (biotransformation in suspended sediments)
  - Non-extractable residue formation and mineralization correlate
- Parameter estimation across systems will further elucidate their similarities/differences for characterizing degradation

Thanks

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