Department of Environmental Science

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eawag aquatic research

Environmental relevance of the OECD 309 test

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with contributions from

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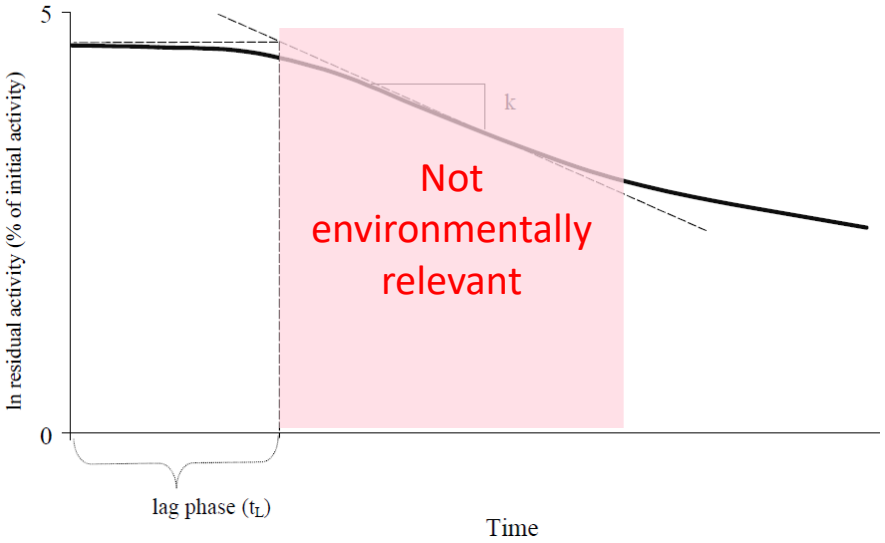
Our scientific ambition

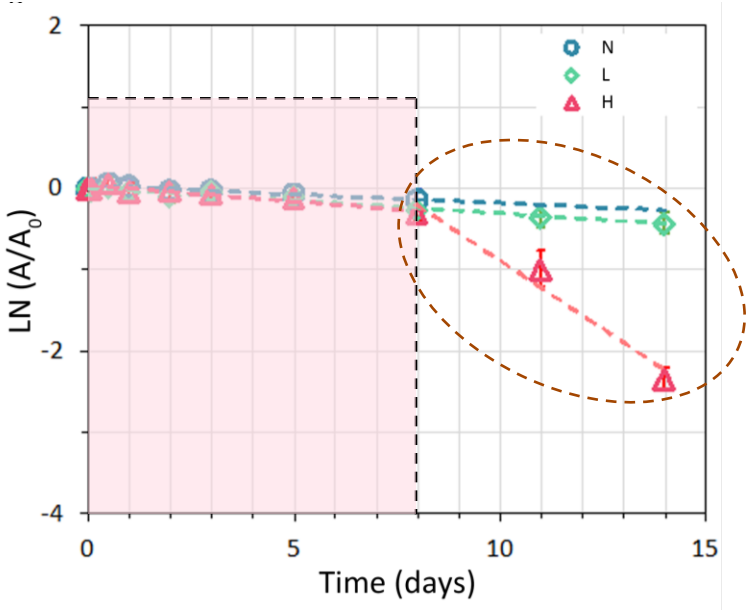
- To determine the rates of *primary* biodegradation occurring in the environment
- Very interested in environmental relevance of OECD 309
- Focus on hydrophilic substances

Biodegradation kinetics



Example of semi-logarithmic plot of data

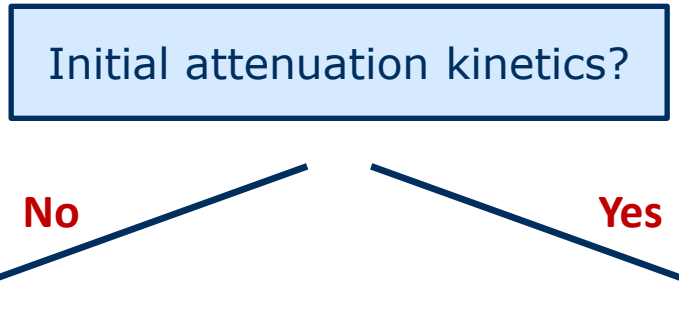
OECD. Test No. 309, 2004



Example of 5-Methylbenzotriazole

***N:** non-spike **L:** low-level spike **H:** high-level spike*

Decision Point #1



- Not environmentally relevant
- May be useful
- Should not be called a simulation test

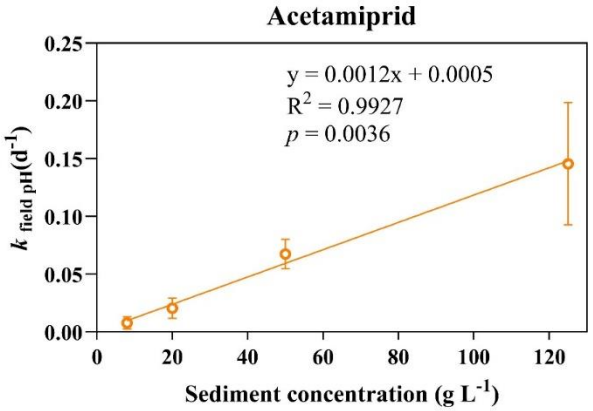
- Potentially environmentally relevant

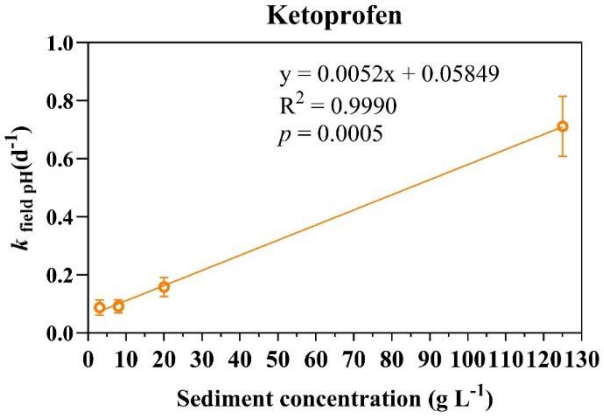
Pelagic test sensitivity

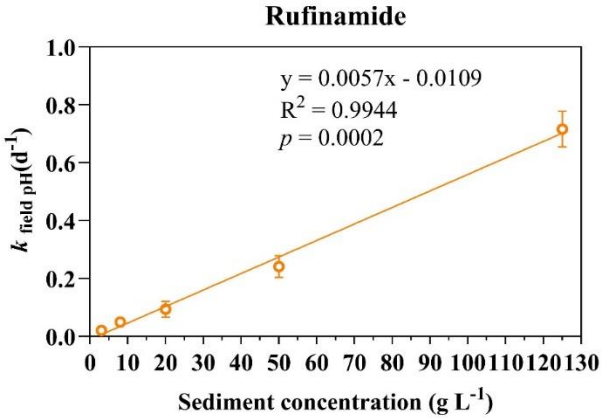
Chemicals	Half-life ($t_{1/2}$, d)
Cilastatin	2.4
p-Toluenesulfonic acid	10
Triethylcitrate	17
Bezafibrate	37
Propranolol	43
Caffeine	68
Metoxuron	81

- Water from Swedish river downstream of WWTP
- Biodegradation measured for 64 compounds (pharmaceuticals, pesticides, etc.)
- Rate constant measurable for 7 (of 64)
- Only 4 below P threshold of 40 days

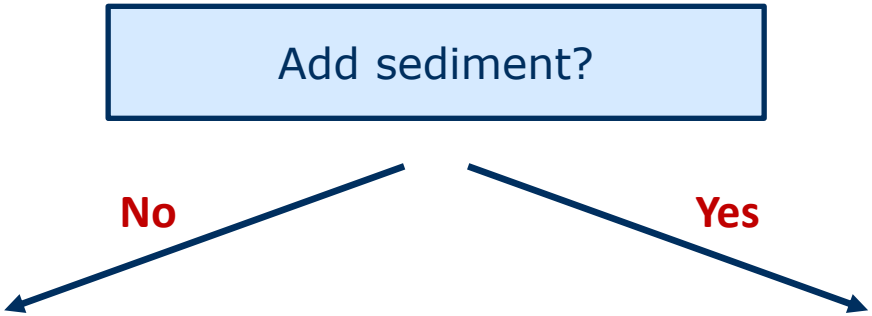
Influence of adding sediment







Decision Point #2

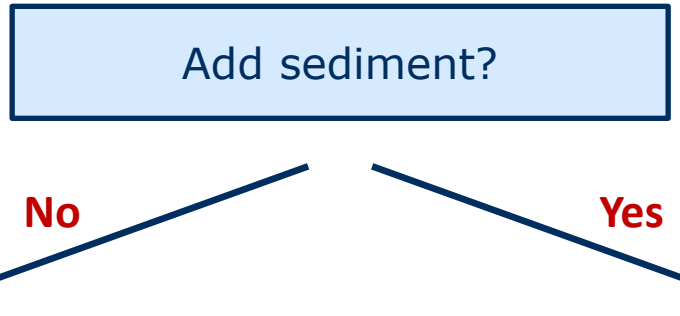


- Most chemicals persistent
- No discriminatory power
- Not useful in prioritizing
- Likely redundant vis-à-vis Ready test

Aside: Regulation misguided?

- Most chemicals persistent in pelagic test because most chemicals actually are persistent in pure water
- The microbial density is simply too low
- This implies PBT/PMT regulation of most chemicals
- Is this what we want?
- Perhaps we should be regulating based on persistence in aquatic systems – or something else?

Decision Point #2



- Most chemicals persistent
- No discriminatory power
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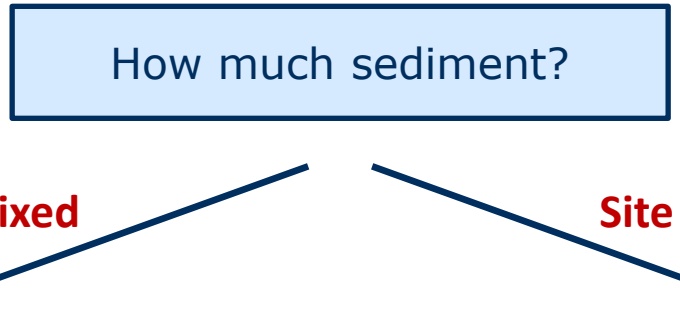
- Good discriminatory power
- Does not measure persistence in water – regulatory misalignment
- Water/sediment mixture = aquatic system?

Decision Point #3



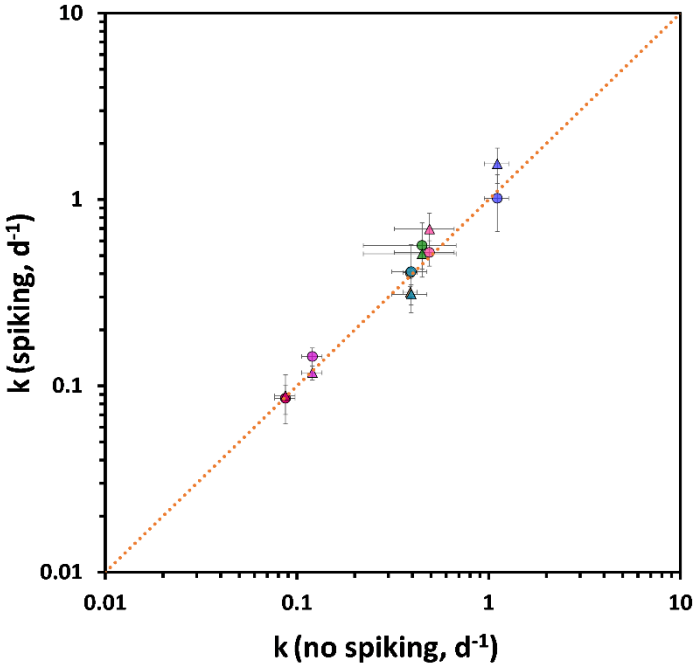
- Standardization
- Comparability of microbial activity across sites
- No comparability of half-lives (address by benchmarking?)

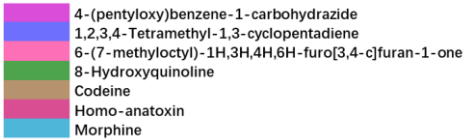
- How to choose sediment amount?
- Standardizable?
- Would allow comparability of half-lives across sites
- Environmentally relevant

Decision Point #4

Which sediment?

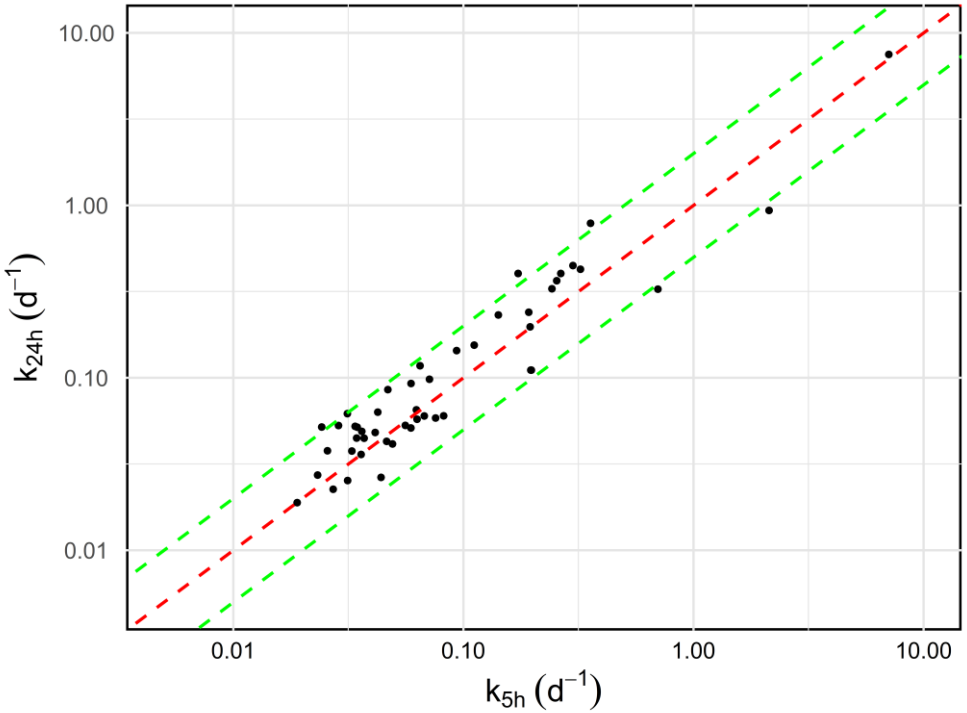
Effect of spiking on degradation of other chemicals





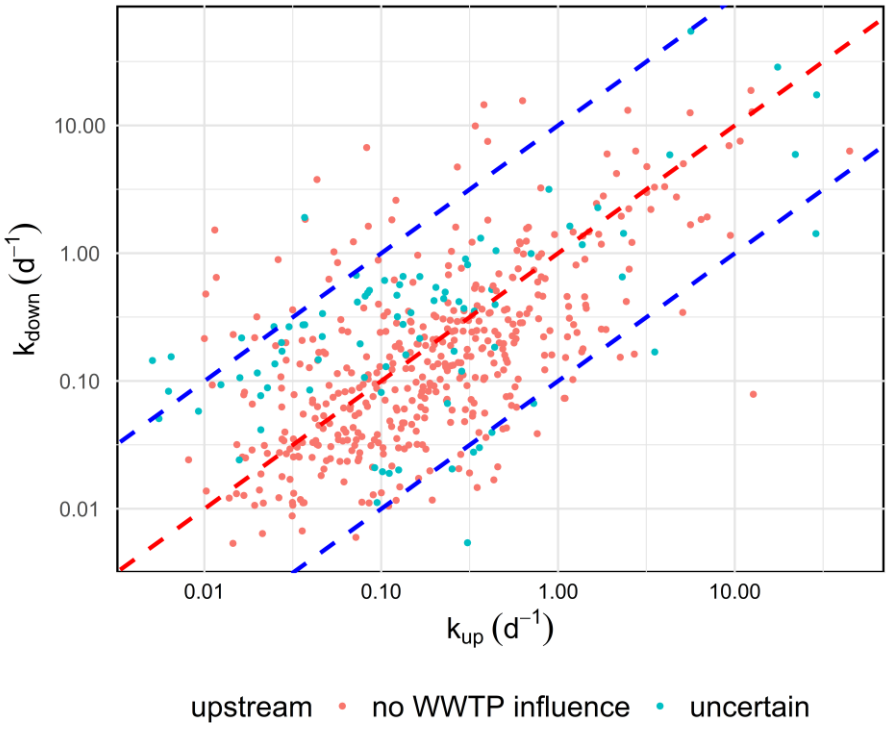
Testing multiple chemicals in the same experiment is possible

Influence of sediment storage time



- Same sample after 5 h and 24 h of storage
- Differences small

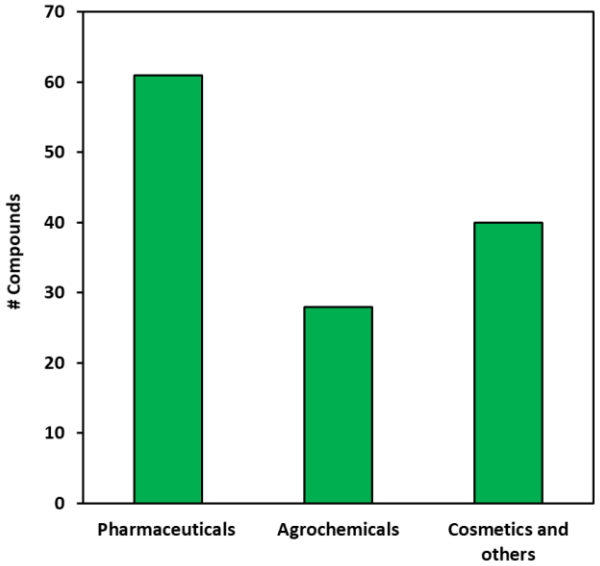
Influence of adaptation (upstream vs. downstream of WWTPs)

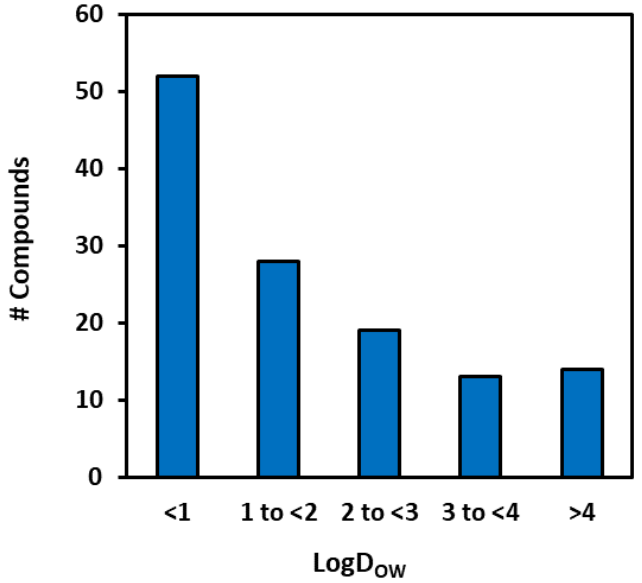


- Parallel testing upstream and downstream of WWTPs
- Upstream site "uncontaminated"
- 11 pairs of sites, up to 97 chemicals
- No systematic influence of exposure to contaminants on *k*

Test compounds

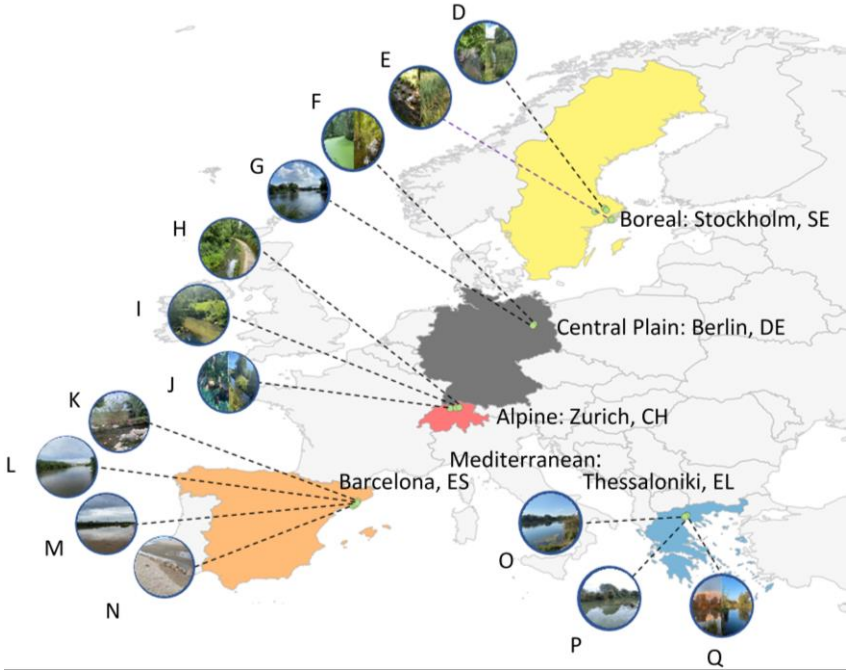
129 compounds: pharmaceuticals, agrochemicals, cosmetics, food additives, and industrial chemicals





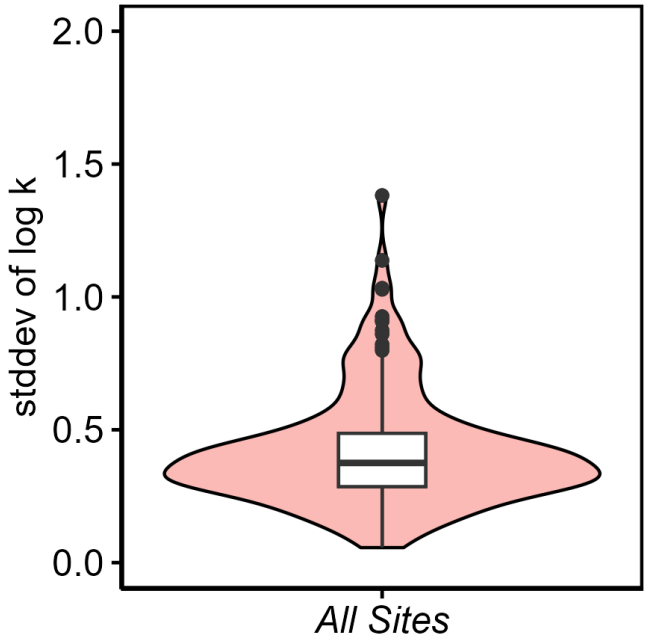
most chemicals are highly soluble in water

Spatial-temporal variability: sampling



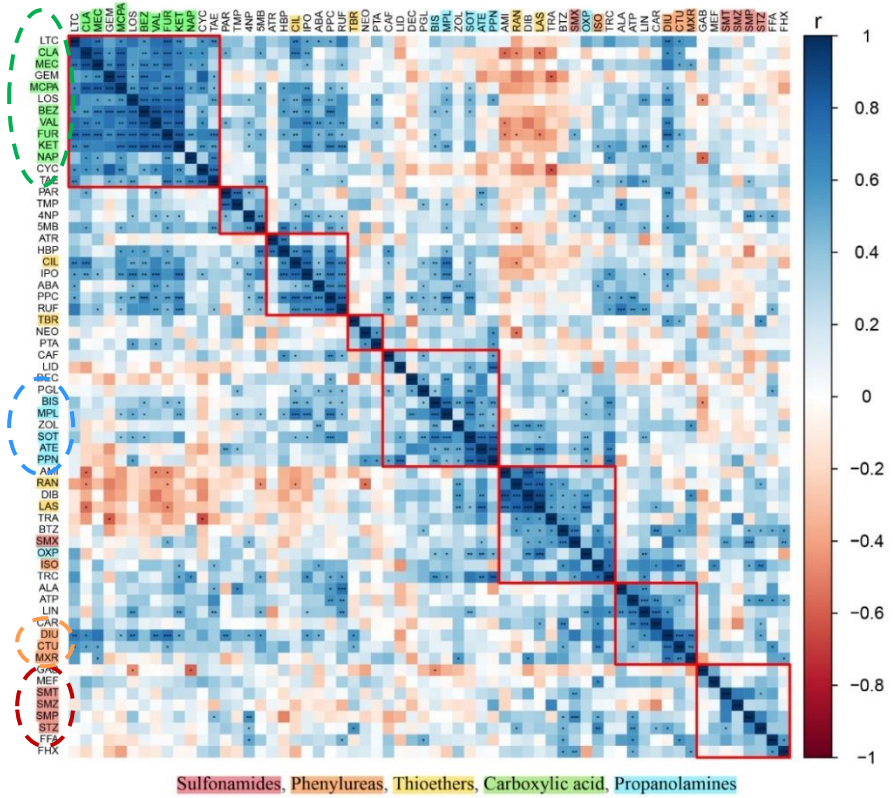
- 18 river sites across Europe
- 7 freshwater & marine sites in Australia
- Seasonality at 4 sites in Sweden
- Total of 38 experiments

Spatial-temporal variability: results



- Standard deviation across all sites.
- Only valid data (*k* significantly different from 0).
- Data range: 95% of data fall into range of 4 x standard deviation (e.g., stddev of 0.5 log units ≈ range of two orders of magnitude).

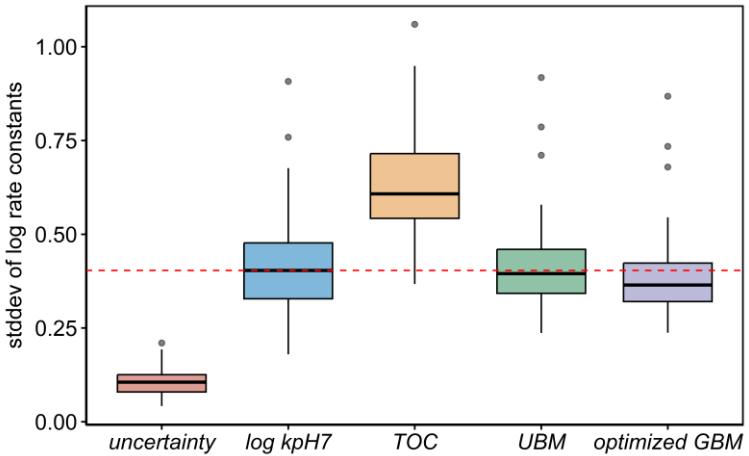
Optimized benchmarking through hierarchical clustering of the Pearson correlation coefficient of log *k*



- Benchmarking requires that test chemical and benchmark are correlated.
- Hierarchial clustering to identify if benchmarking could work for subsets of chemicals.
- 38 ecosystems (31 in EU, 7 in AUS), 62 chemicals with valid *k* in at least half of the ecosystems.

Reducing the variability via normalization or benchmarking

TOC vs. UBM vs. optimized GBM?



uncertainty: base on three replicate measurements

log kpH7: non-benchmarked data

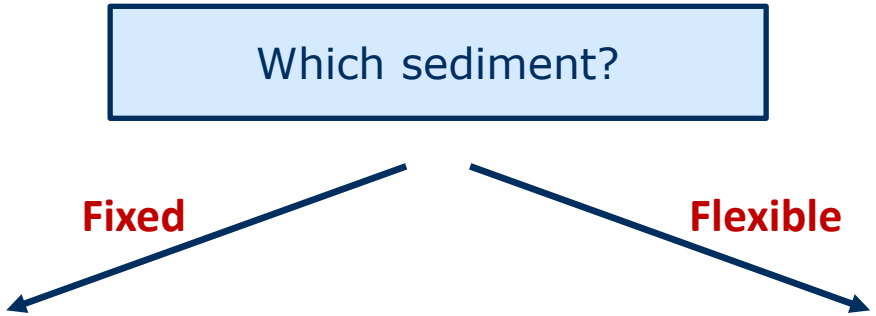
TOC: TOC normalization

UBM: best-performing chemical as universal benchmark

GBM: optimized group-based benchmarking using the best-performing benchmark in each group

- stddev of log *k* was about 4 times larger than the uncertainty in measurements
- TOC normalization **increased** the variability
- UBM had a negligible effect
- the optimized GBM reduced the variability for 87% of the compounds
- but the variability remained large (fold difference of 2.2, 95% range of factor 25)

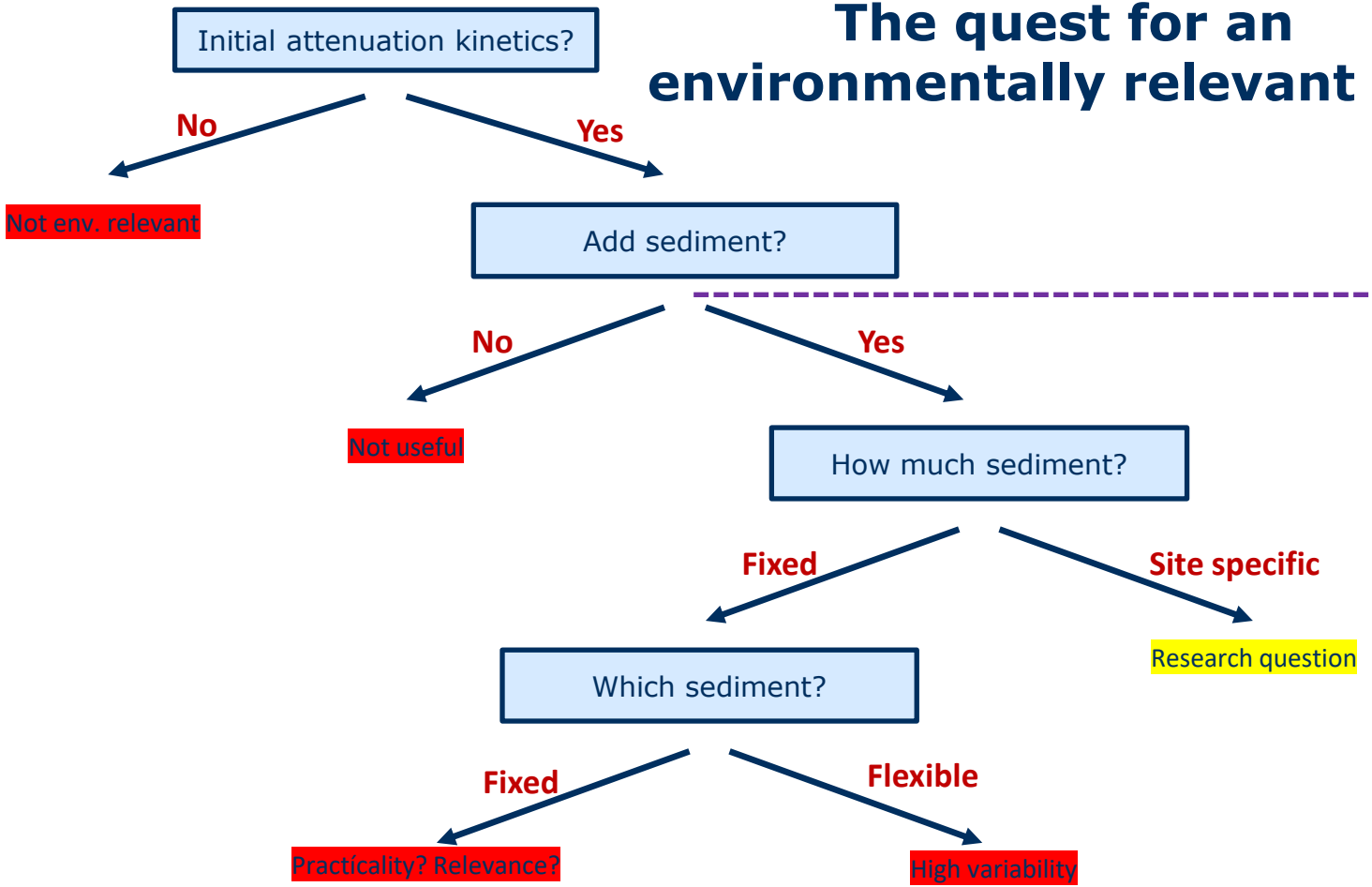
Decision Point #4



- Practical? (storage, transport)
- Seasonal variability high
- Which site is the most relevant?
- Can a simulation test evaluate a threshold?

- Large variability in test outcome
- No method to correct for variability (yet)

SUMMARY
The quest for an environmentally relevant test



Conclusions

- OECD 309 is currently not an environmental simulation test.
- Use of initial kinetics and sediment addition are required to make OECD 309 potentially relevant and useful.
- A P-criterion for half-life in water (only) is of limited use for prioritizing chemicals for regulation.
- Very large variability of biodeg rate in the environment is a fundamental obstacle for using a simulation test to assess a regulatory threshold.

References

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Tian et al.(2024): Influence of season on biodegradation rates in rivers. *Environ. Sci. Technol.* 58, 7144-7153.

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Tian et al. (in prep): Does benchmarking increase the accuracy of predicting biodegradation across aquatic ecosystems?

Li et al. (in prep): Impact of sediment concentration on biodegradation of organic chemicals in water-sediment suspensions

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