Benchmarking the persistence of organic micropollutants

in large European rivers

Budapest University of Technology and Economics

MŰEGYETEM 1782

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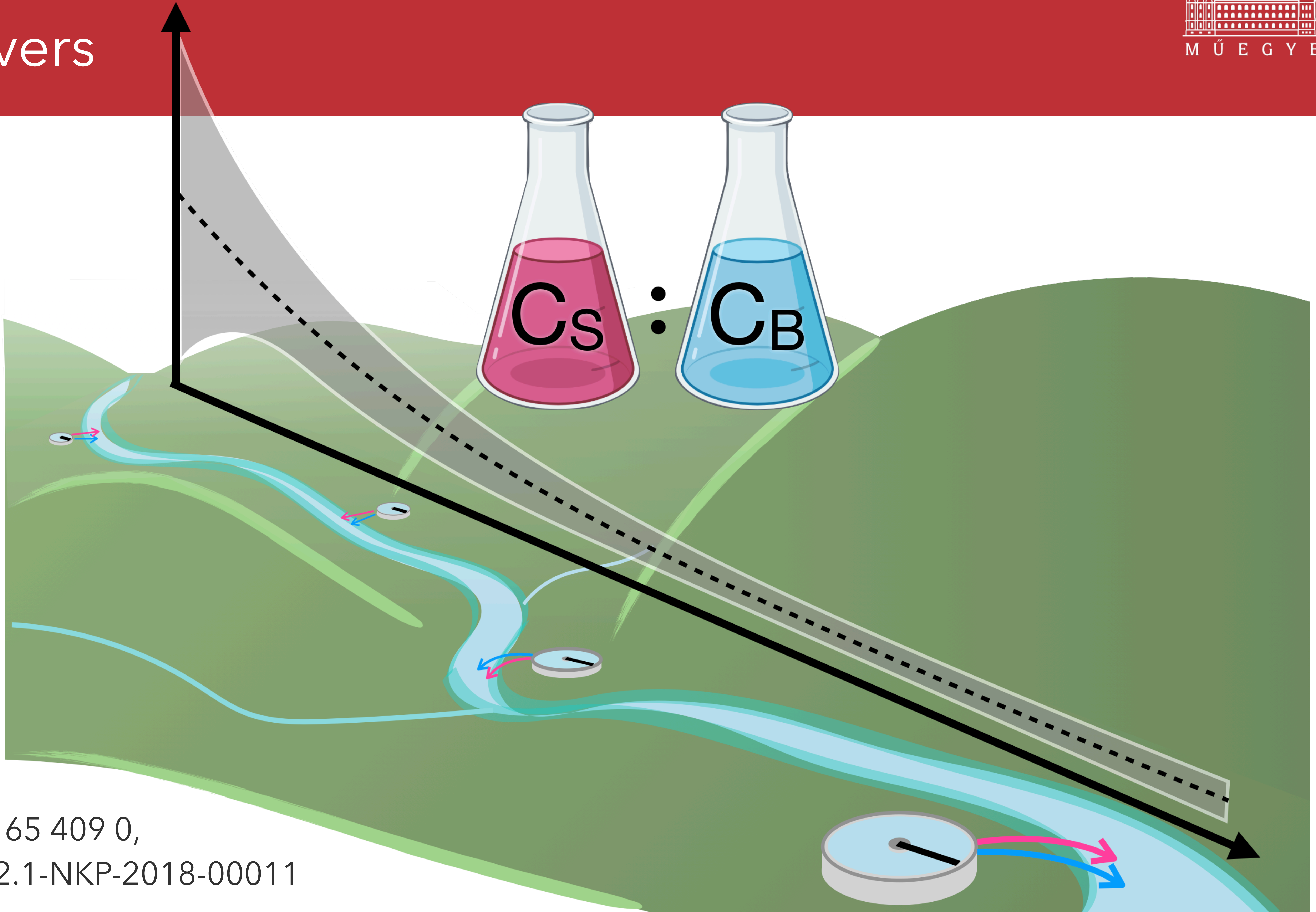

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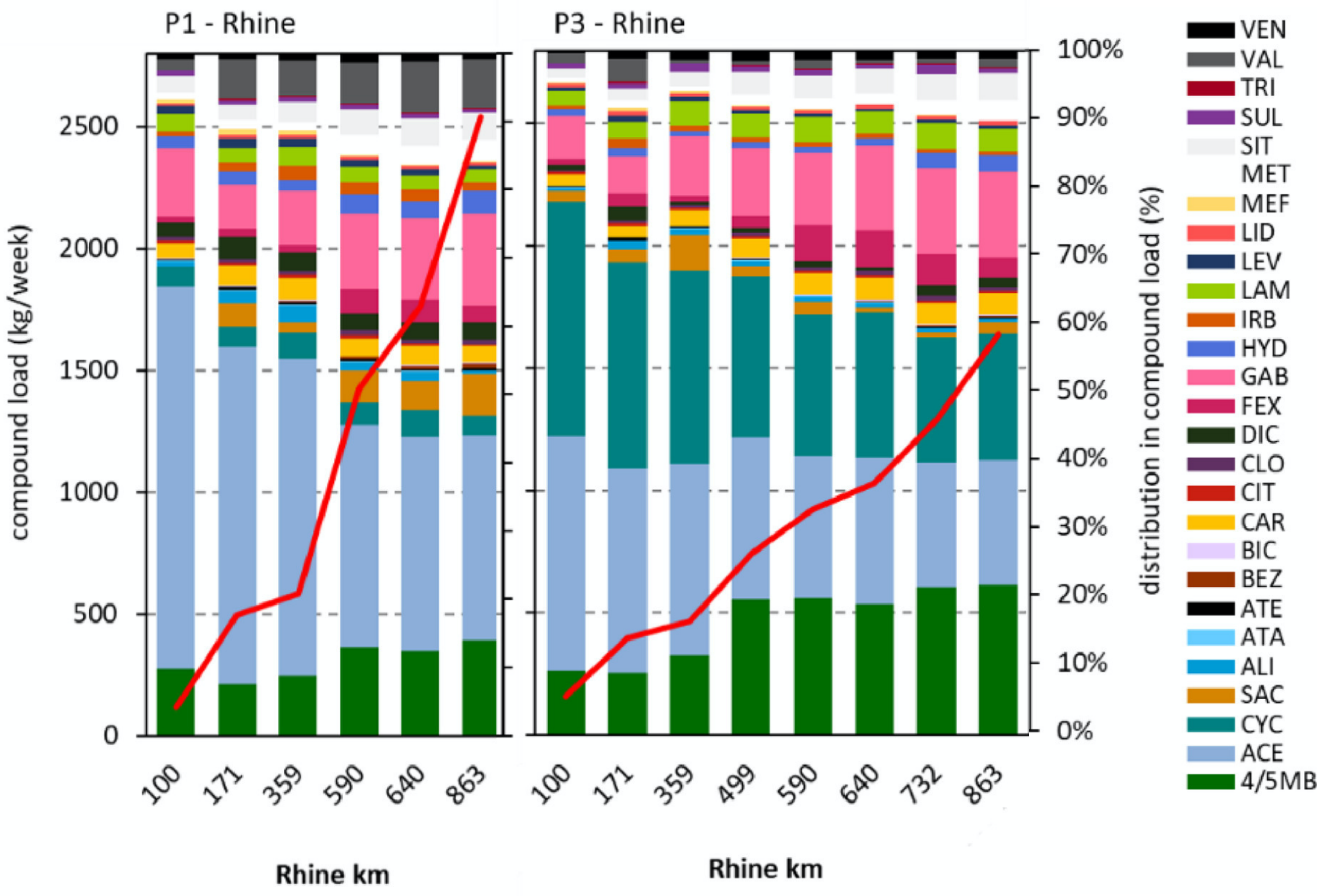
Which organic micropollutants?

Active pharmaceutical ingredients (APIs)

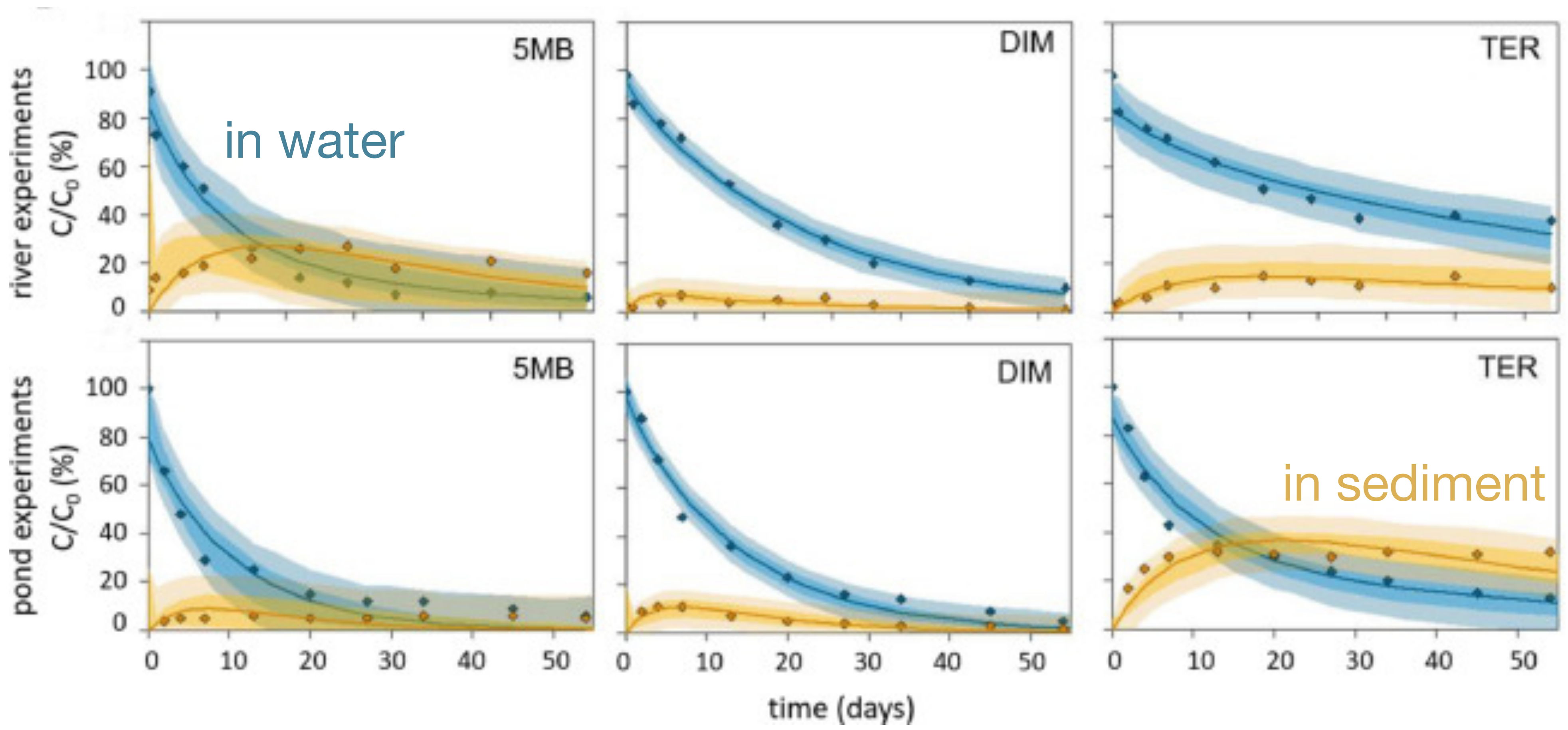
- APIs: ubiquitous organic micropollutants
  - popular or used for chronic diseases: ~continuous emissions
  - 100s detected in most European rivers
  - bioactive by design → potentially harmful for ecosystems and non-targeted humans

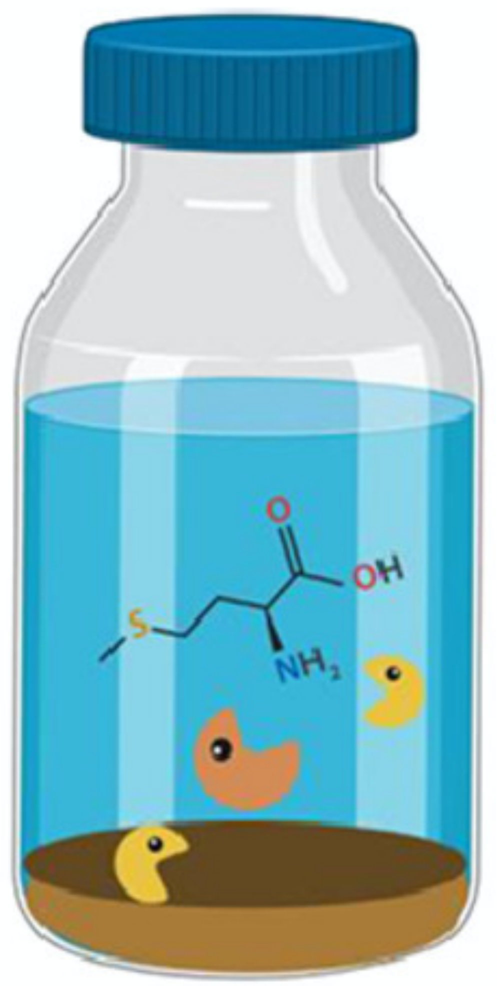


- Covered by EU REACH regulatory framework (Registration, Evaluation and Authorization of CHemicals)
  - PBT (persistent / bioaccumulating / toxic) assessment obligatory to identify hazardous compounds
  - Persistence testing by “simulation” lab experiments

Persistence testing

- Globally standardised "simulation" lab experiments
  - Testing of ready biodegradability, hydrolysis, etc.
  - OECD guidelines 308 and 309
    - 308: biotransformation in water-sediment systems
    - 309: biotransformation in water

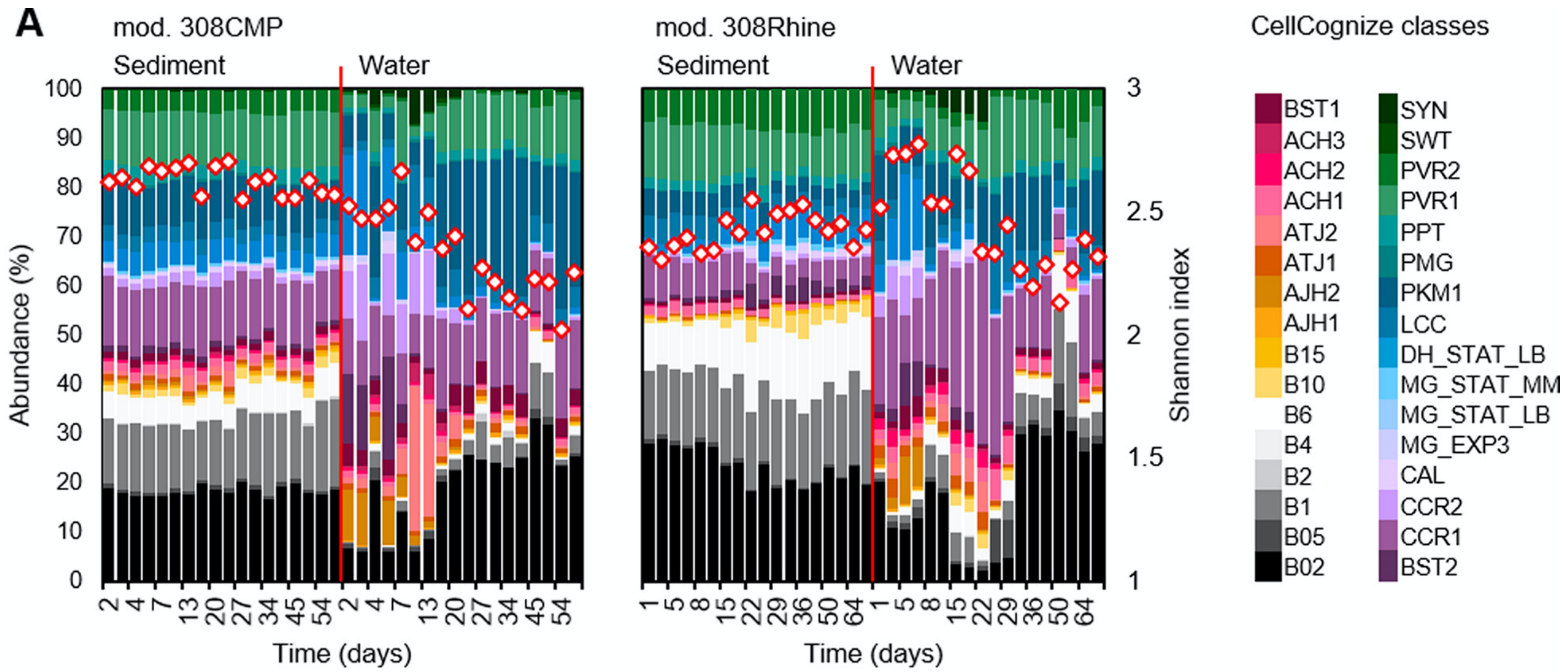


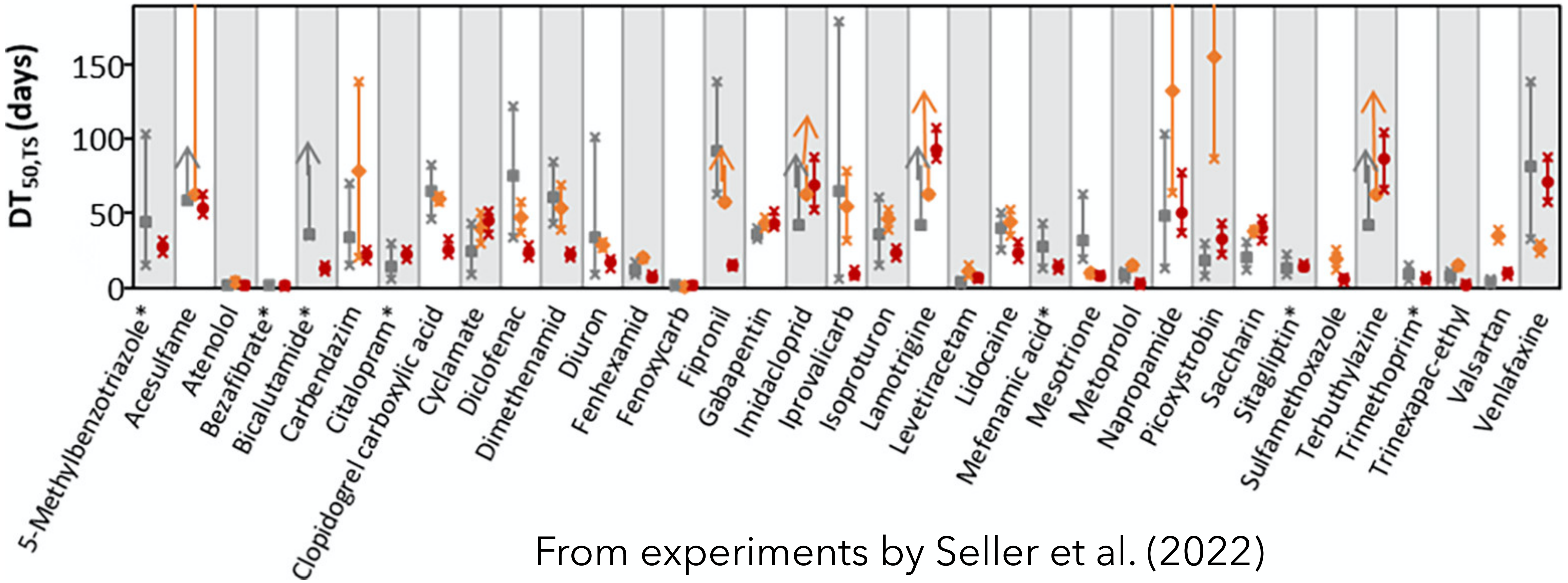


Relevance of laboratory persistence

- Lab systems vs. “the environment”
  - representativity
    - water:sediment ratio
    - redox conditions
    - microbial composition
  - reproducibility
    - microbial composition

- **Real environmental persistence can be learnt from field data**
  - **but how?**

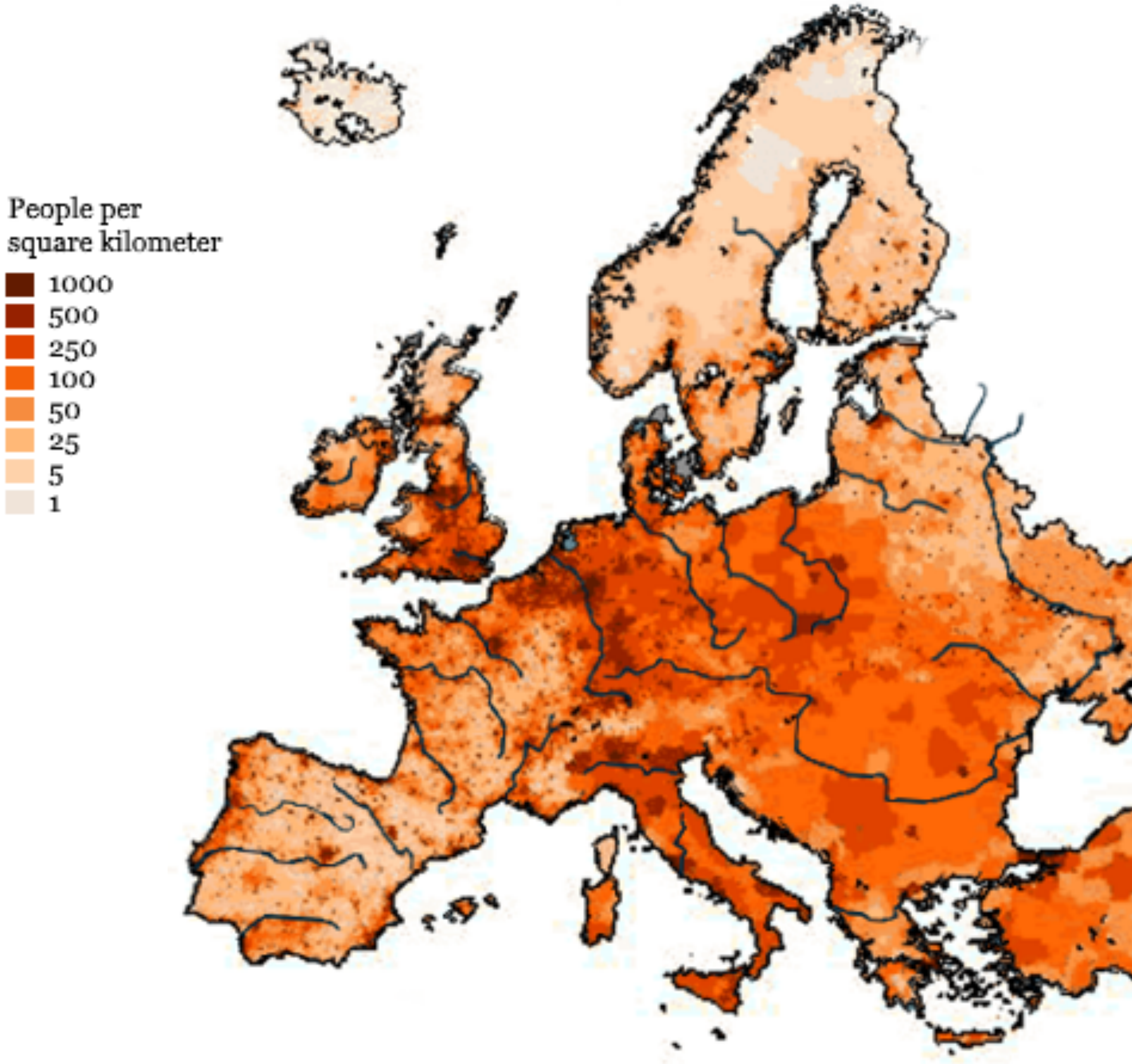




From experiments by Seller et al. (2022)

Why large rivers?

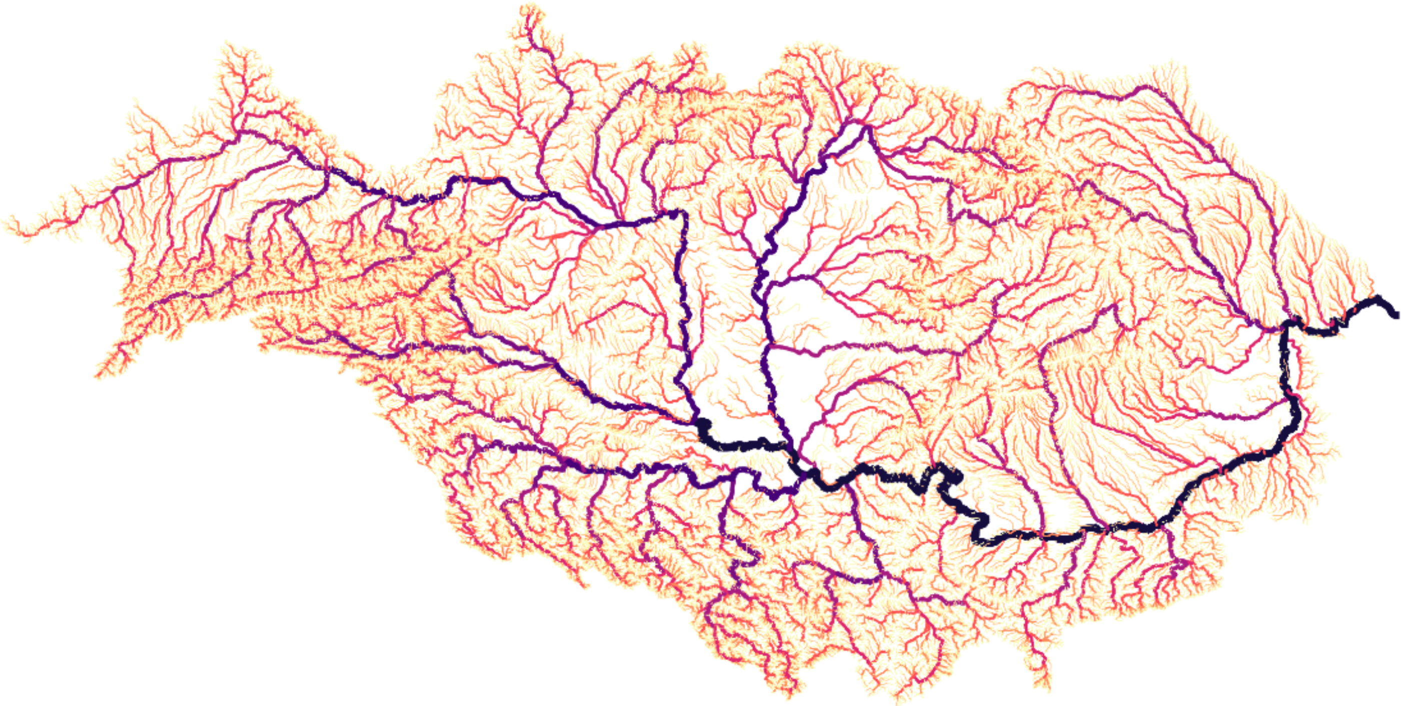
- Connect some of the most populated inland regions
- Transport most of the inland pollution into the seas
  - Large emissions require large dilution capacity
- Possess enough residence time to expect visible effects of transformation (nP behaviour)
  - Scaling properties of stream networks → water covers most of the travelled distance in large rivers



Complexity of large rivers

Analysing the fate of APIs in large rivers: need a catchment-scale approach

- Large rivers: huge stream network (~~river continuum~~ vs. stream graph)
- Thousands of (unknown) emission sources (WWTPs)
- Expressed environmental gradients of all kinds
- Anticipated high diversity in biotransformation potential

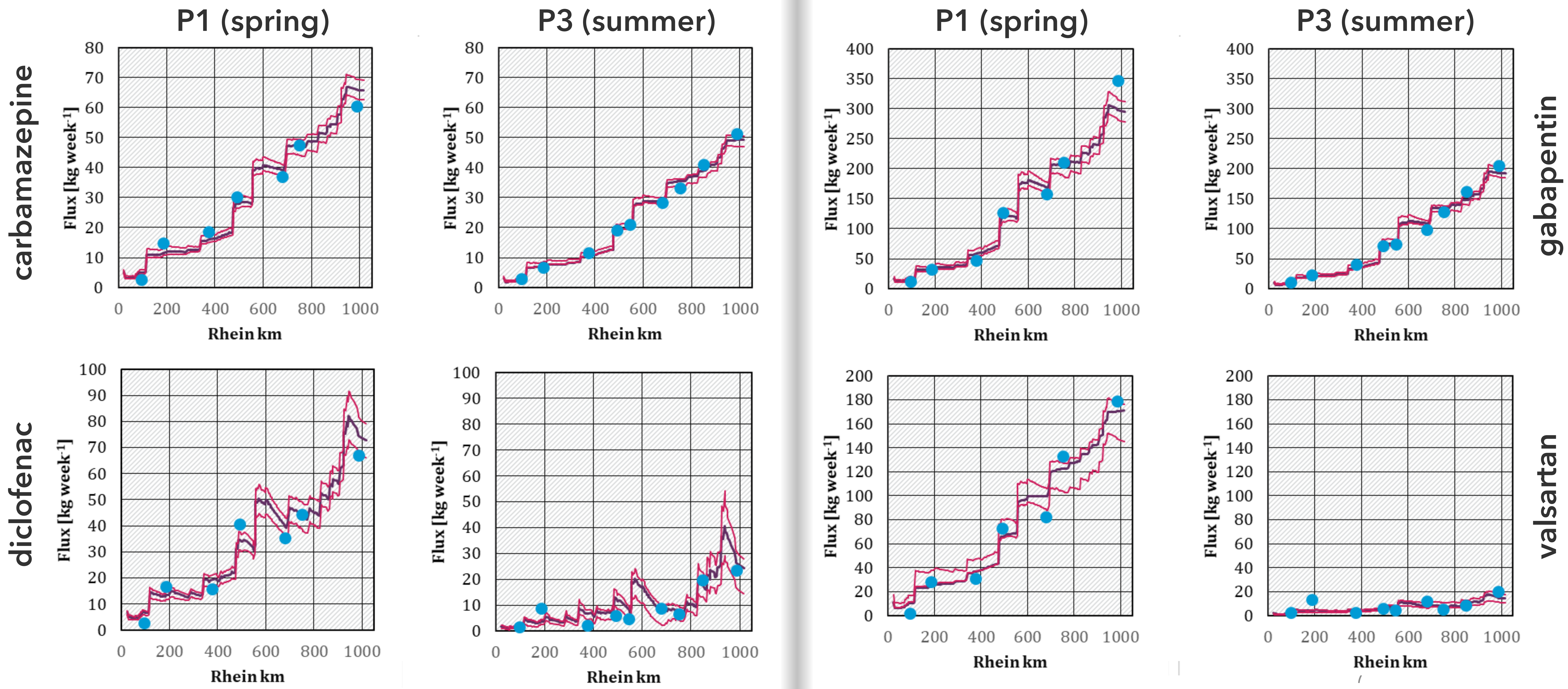


138 013 stream segments

Degradation in the Rhine (IKSR SMPC data, 2017)

Detailed API transport and degradation model by Seller et al. (2023)

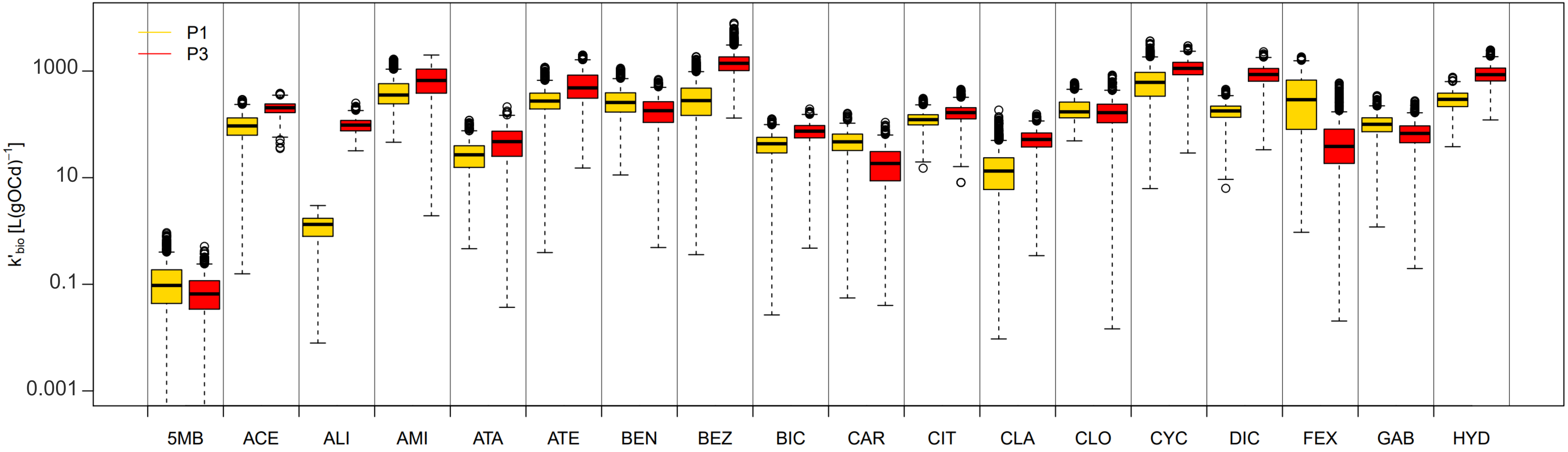
● Measurement ═ Model



Lessons learnt from modeling the Rhine catchment

- Model describes observations, but
  - assessed (bio)transformation is conditional on
    - emission data
    - sediment conditions
    - stream section geometry
  - transformation rate (~persistence) is rather uncertain

Need a less explicit approach…



Persistence benchmarking in a lake

Zou et al. (2014), Zou et al. (2015), McLachlan et al. (2016)

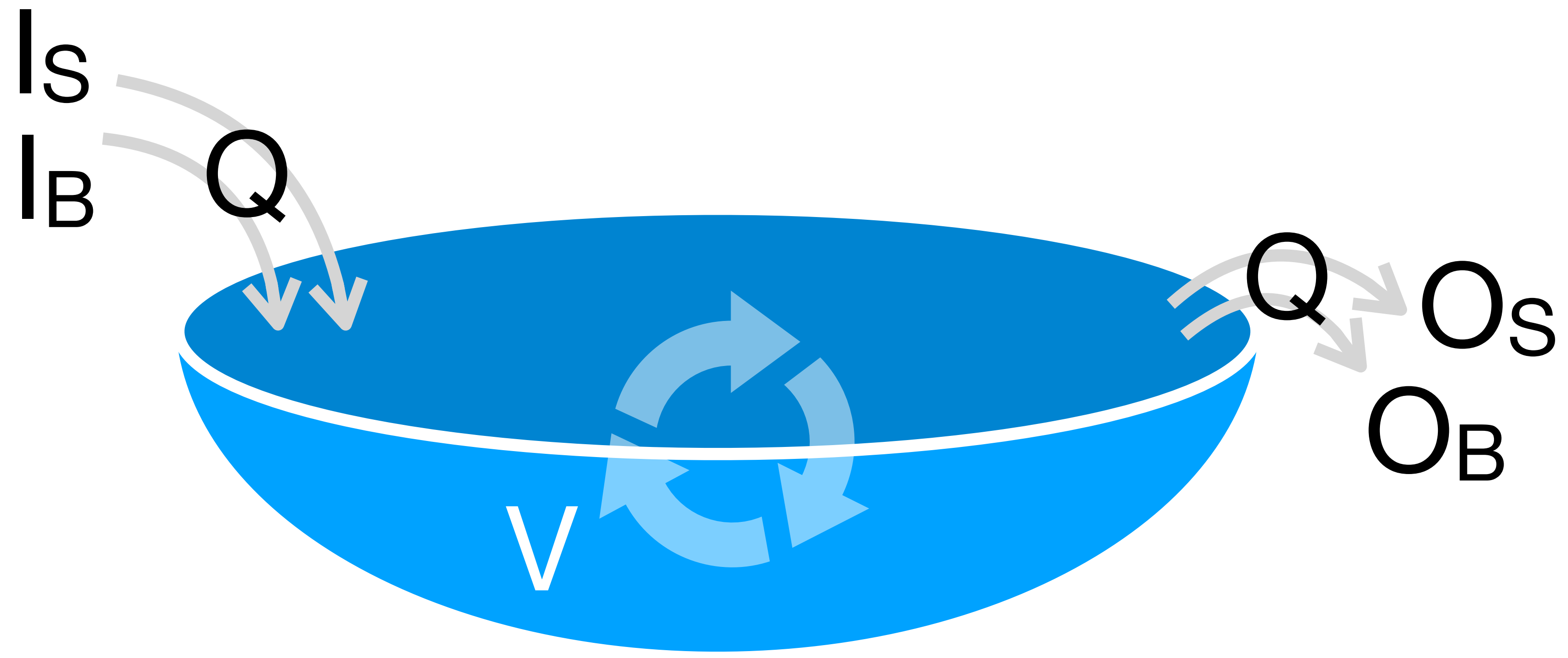
Theory: *Making a full mass balance model in a lake can be avoided by using benchmarks that only differ from the analysed compound in the factor/property of interest.*

For persistence: a conservative benchmark compound (B) can be used to estimate the degradation rate constant (k [d^{-1}]) in steady state.

In a lake with a single continuous source, the degradation rate constant of a non-conservative substance (S) can be estimated as:

$$k_S = \frac{\frac{I_S/I_B}{O_S/O_B} - 1}{\tau}$$

where I is input concentration [g m^{-3}], O is outflow concentration [g m^{-3}], τ is hydraulic residence time [d].



$$\frac{I_S Q}{I_B Q} = \frac{O_S Q + k O_S V}{O_B Q}$$

$$\frac{I_S}{I_B} = \frac{O_S}{O_B}\left(1 + k\tau\right)$$

Lakes vs. large rivers

Differences in transport and emission sources

- Lake = single black-box reactor with known inputs and output.
- Rivers have an expressed direction of transport and MANY, often non-measured emission points (incl. direct emissions and tributaries).
- The approach could be applied to a shorter section with modification for lateral transport, but
- a simple mass balance between a pair of points (=input, output) is problematic: it seems impossible to find a reach that (1) does not have significant inputs in between, (2) is long enough to show noticeable degradation, and (3) has very precise measurements at the endpoints (w.r.t. the expected removal).
- Nevertheless: we may have many observation points along the river, so we can look inside the system (grey box approach).

Dissipation in a river

Single source case

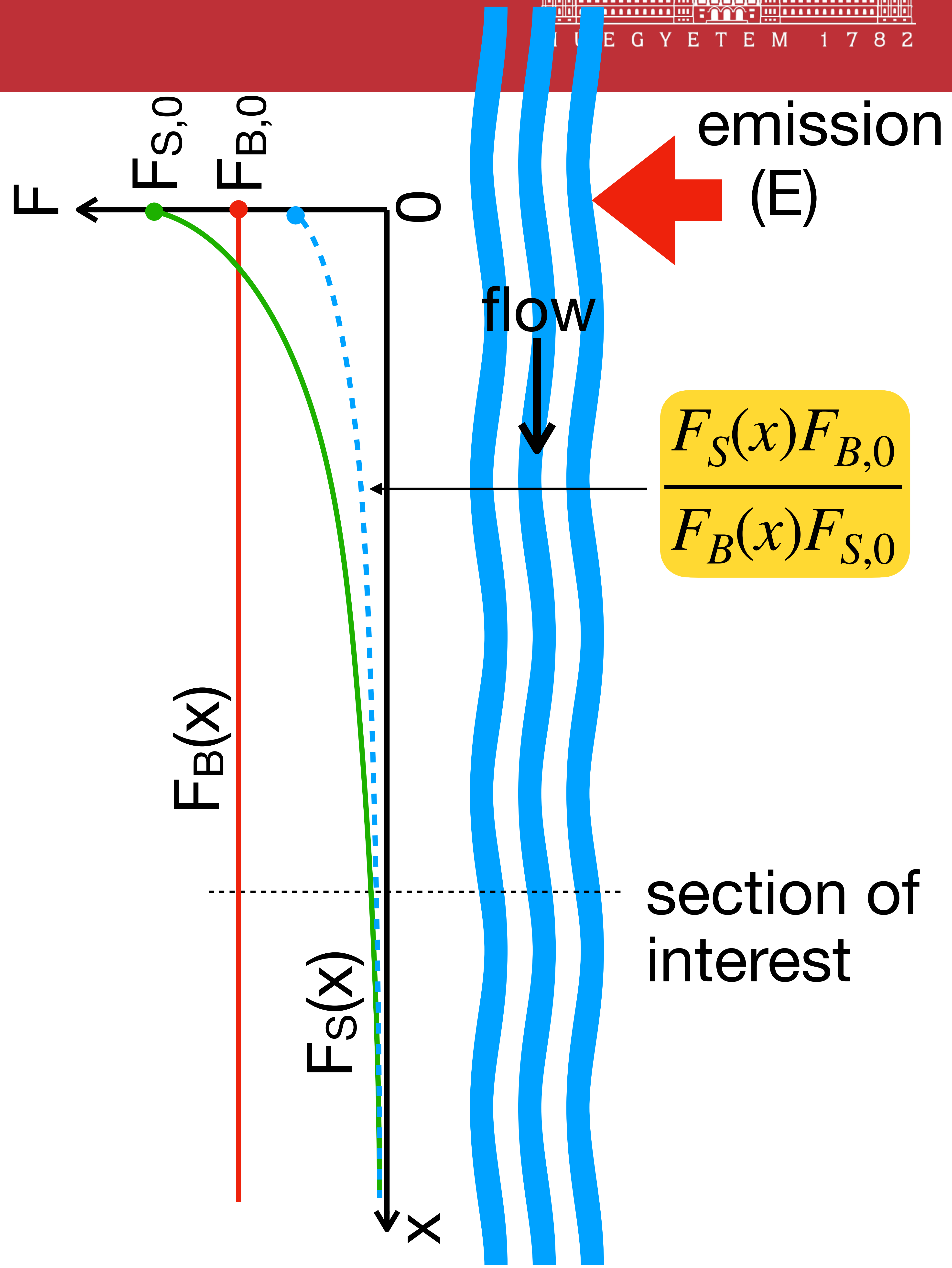
Use fluxes to avoid dilution effects.

With instant mixing and dissipation, the longitudinal flux profile:

$$F(x) = F_0 \exp\left(-k'x\right)$$

where F is flux [g d^{-1}], x is the longitudinal coordinate [km], and k' is the longitudinal dissipation constant [km^{-1}]. Making the benchmark:

$$\frac{F_S}{F_B}(x) = \frac{F_{S,0}}{F_{B,0}} \exp(-k'_S x), \quad \text{so then} \quad k'_S = -\frac{\log\left(\boxed{\dfrac{F_S(x)F_{B,0}}{F_B(x)F_{S,0}}}\right)}{x}$$



Dissipation in a river

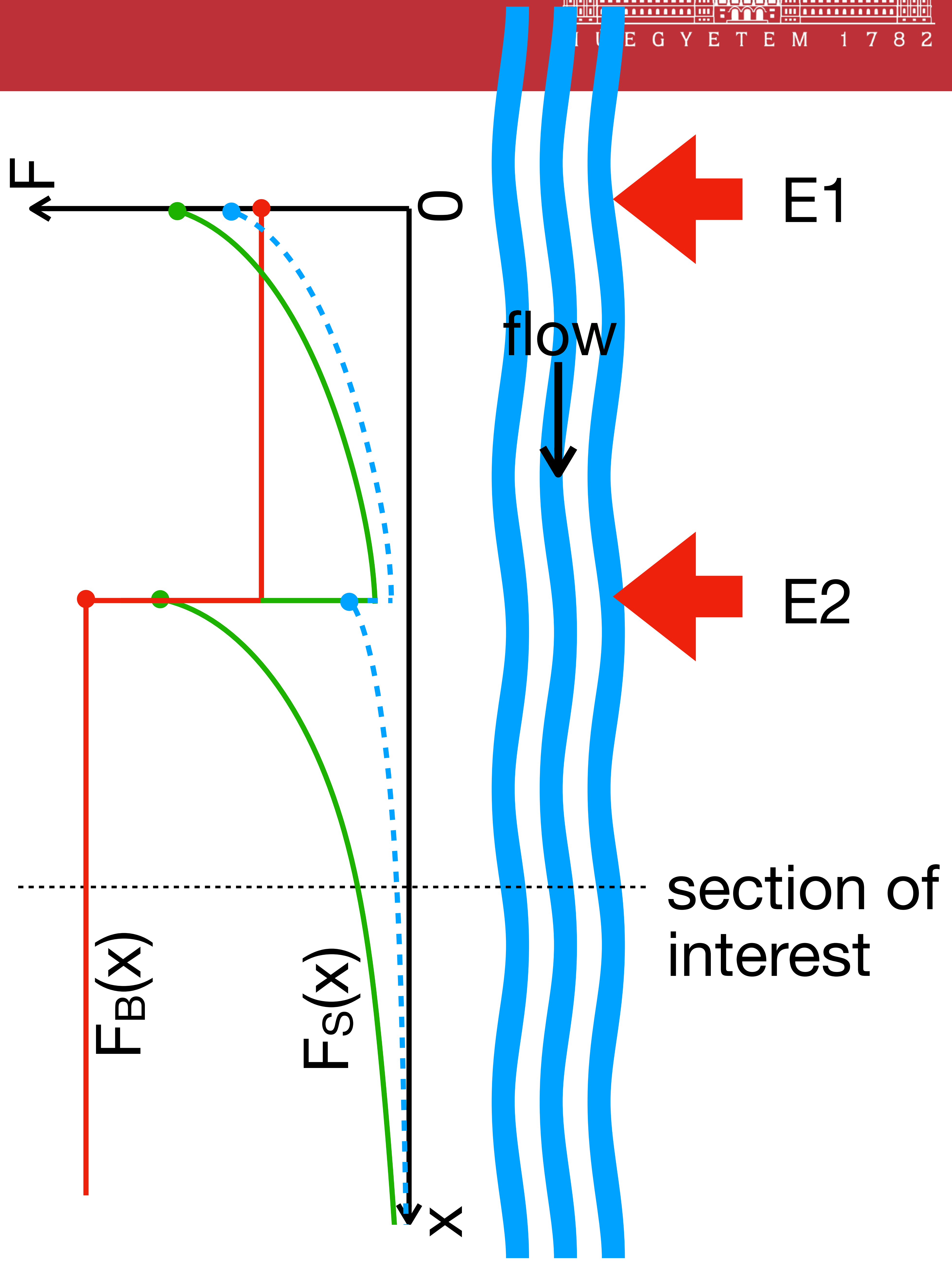
Multi-source case

Multi-emissions complicate longitudinal flux patterns.

Variable momentary ratio between F_S and F_B, need to know magnitude and position of sources

$\dfrac{F_S(x)F_{B,0}}{F_B(x)F_{S,0}}$ no longer simplifies to $\dfrac{F_S(x)}{F_{S,0}}$

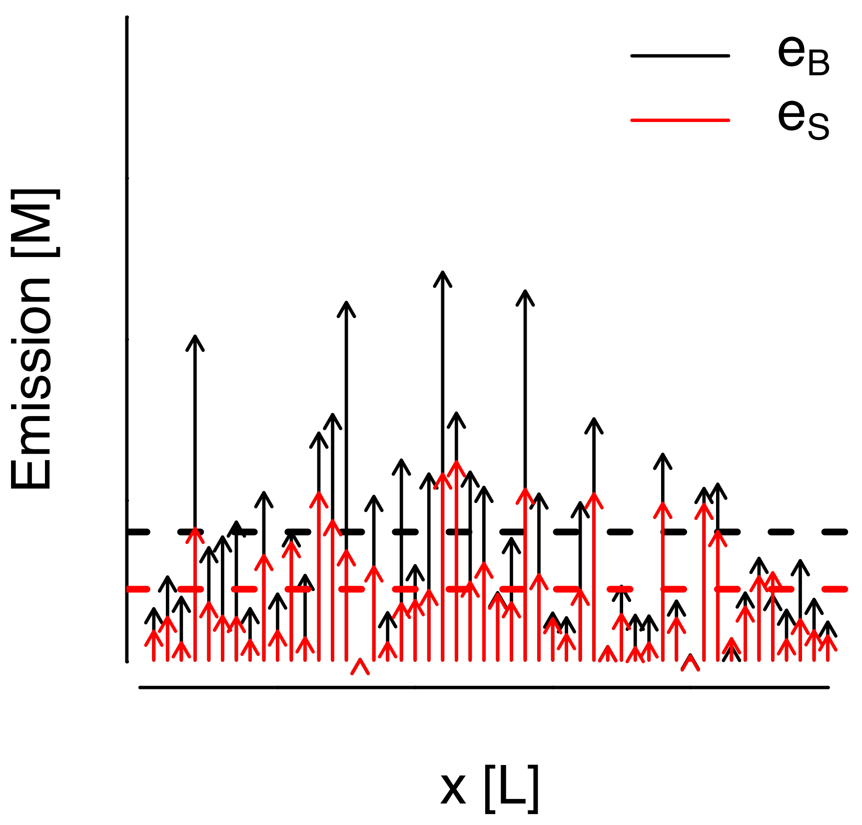
Not a viable method.

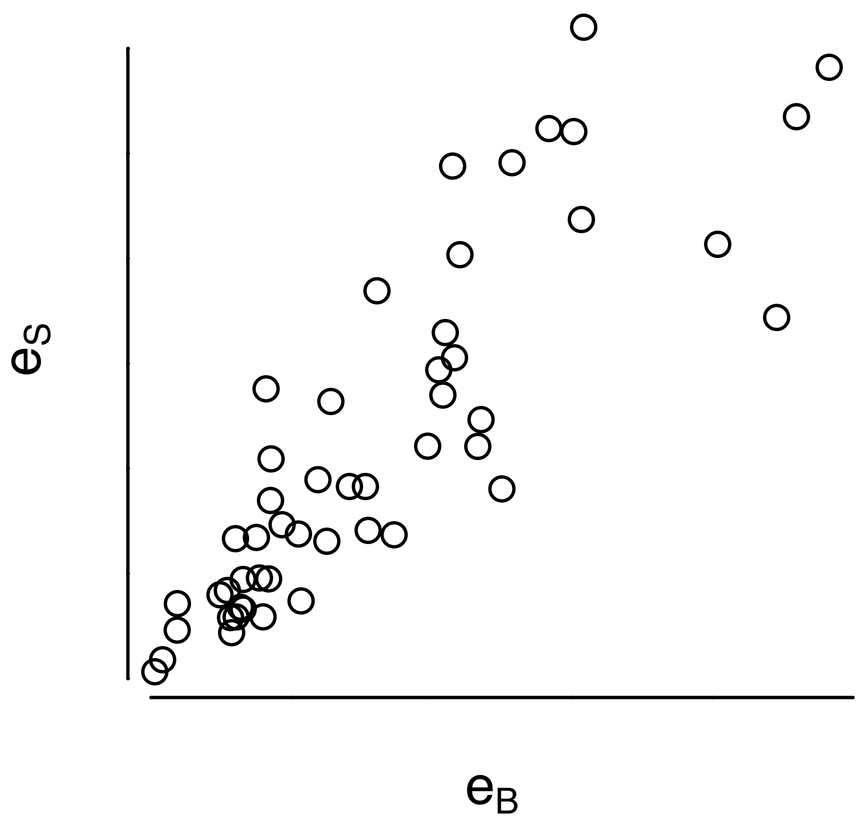


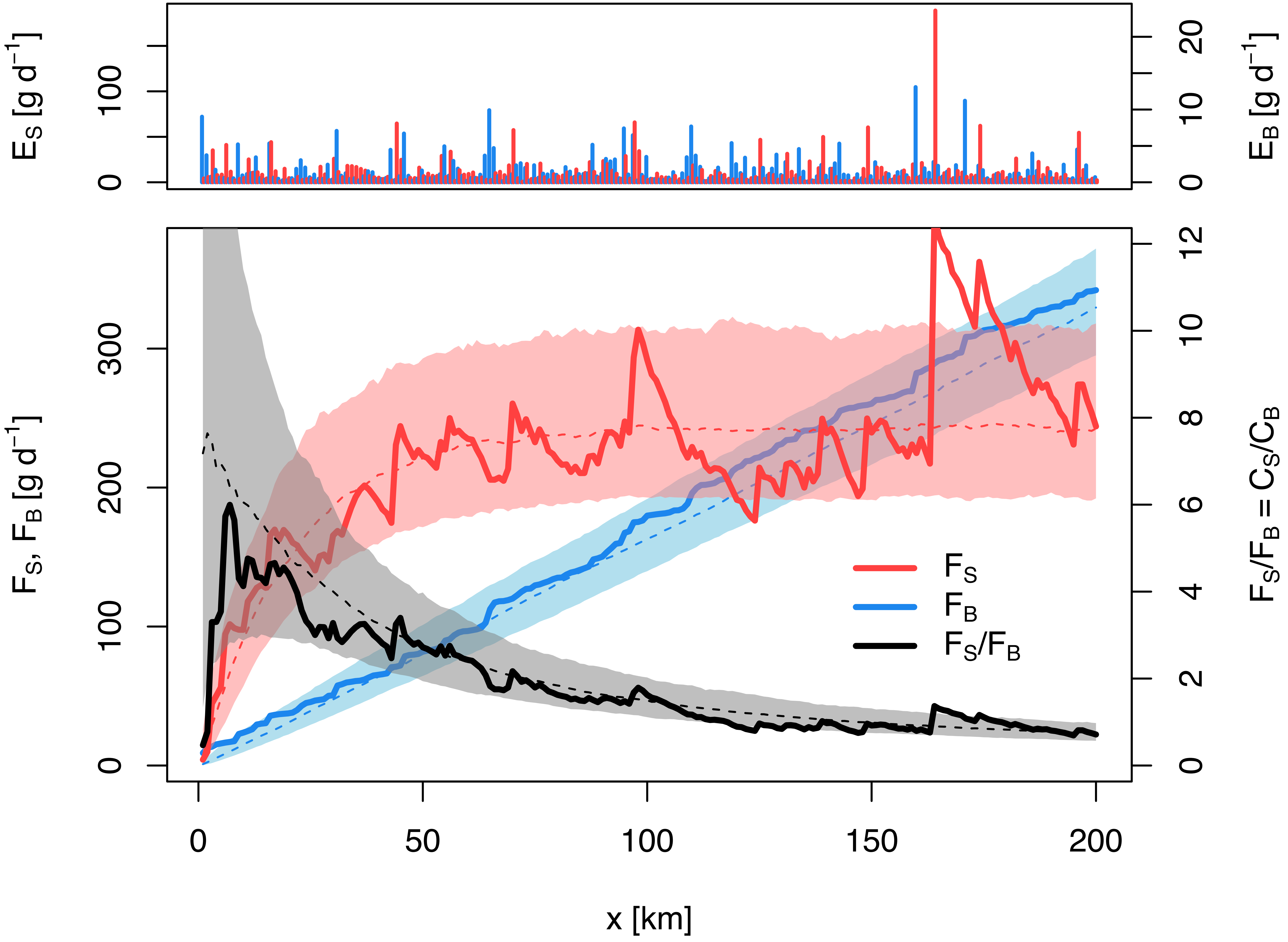
Dissipation in a river

Multi-source case

- Assume that emissions are unknown stationary stochastic processes with some cross-correlation and a steady mean-ratio
- Don’t have to know single emissions or properties of E_S or E_B







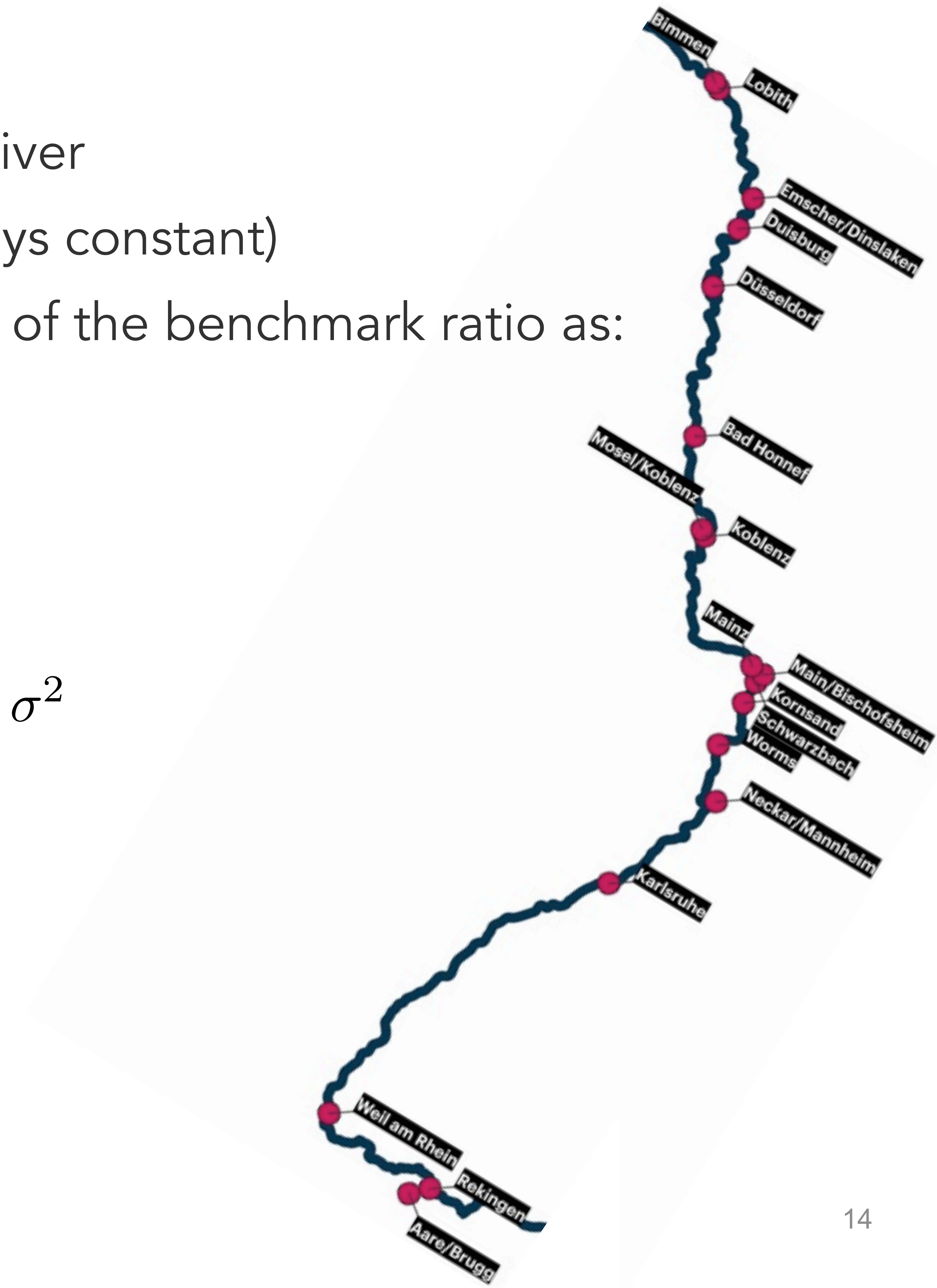
Benchmarking from longitudinal river data

- Suppose that fluxes of compounds S and B are measured along a river
- (Emissions of S and B are spatially variable, but their <u>mean</u> ratio stays constant)
- Then for a conservative B one can deduce the statistical properties of the benchmark ratio as:

$$\mathsf{E}\left[\frac{C_{\mathsf{S}}}{C_{\mathsf{B}}}\right] \approx \frac{v}{k_{\mathsf{S}}}\left(1-\exp\left(-\frac{k_{\mathsf{S}}}{v}x\right)\right)\left(\frac{\alpha}{x}+\frac{\beta}{x^2}\right)$$

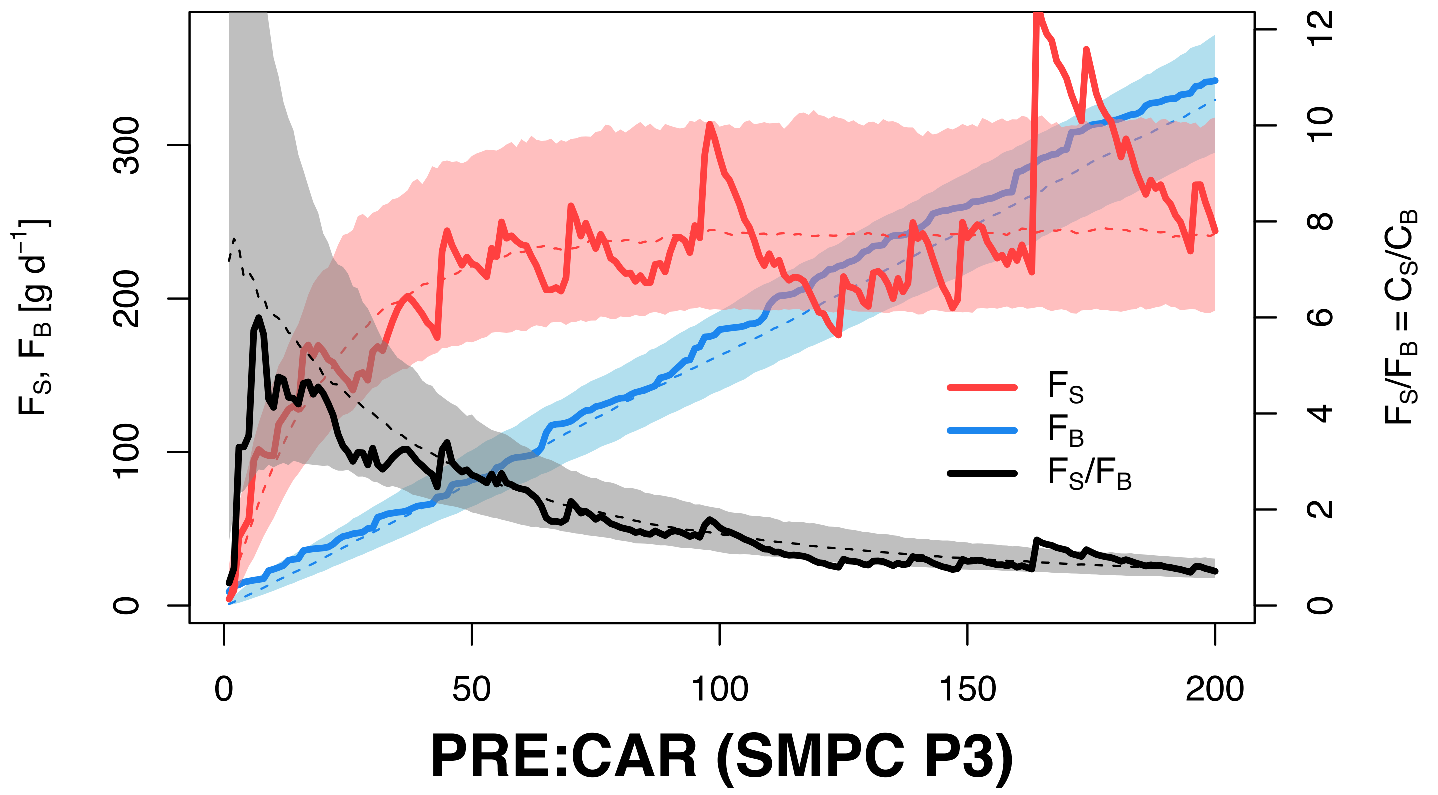
$$\mathsf{Var}\left[\frac{C_{\mathsf{S}}}{C_{\mathsf{B}}}\right] \approx \frac{v}{k_{\mathsf{S}}}\left(1-\exp\left(-\frac{k_{\mathsf{S}}}{v}x\right)\right)\left(\frac{\gamma}{x^2}\left(1+\exp\left(-\frac{k_{\mathsf{S}}}{v}x\right)\right)-\frac{\delta}{x^3}\right)+\sigma^2$$

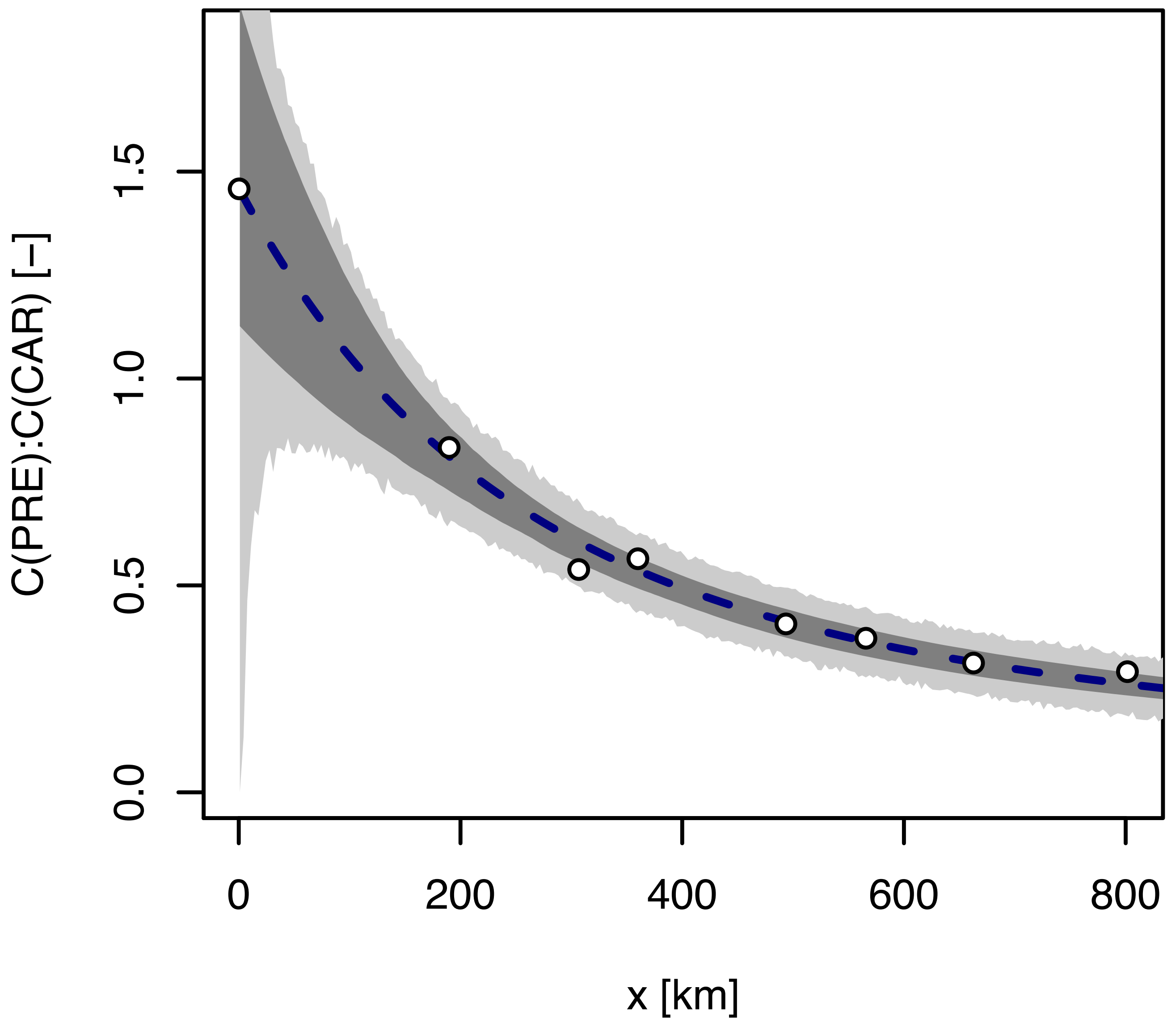
- where x [km] is the distance downstream, v is flow velocity [km d^{-1}]
- k_S [d^{-1}] is the dissipation rate of S ($k_S' = k_S/v$ [km^{-1}])
- α, β, γ, and δ are unknown constants, σ is the observation error

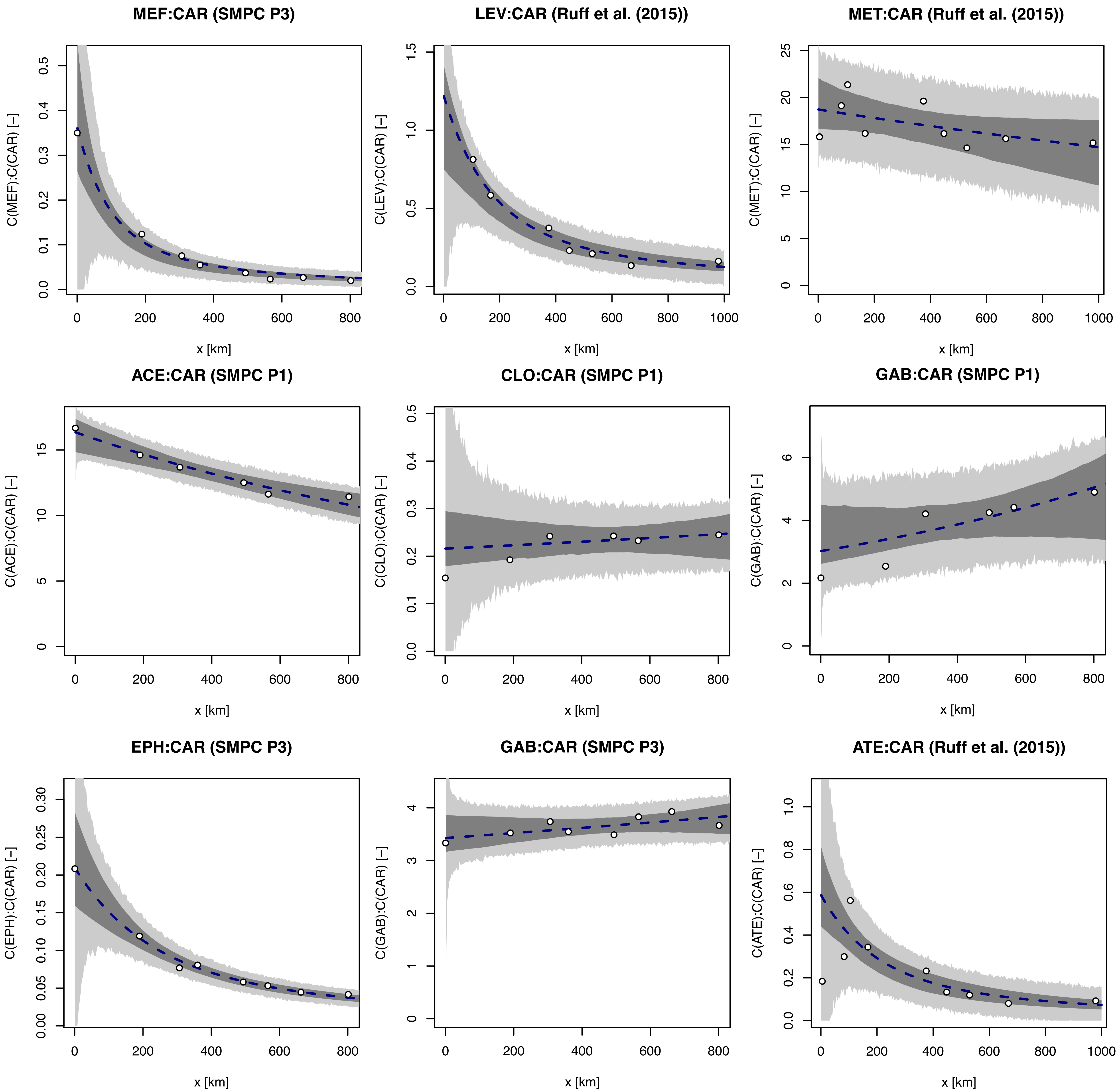


Benchmark ratio under homoscedastic emissions

Demo and Rhine (B=CAR)







Danube: heteroscedastic emission rates

- JDS3 and JDS4 data
- Economic and cultural gradient
    - Cannot assume emission processes to follow the same distributions along the entire river
    - Need to split the river into homoscedastic sectors (which boundaries?)
    - Can only solve for expected value for a homoscedastic benchmark compound:

$$\mathrm{E}\left[\frac{C_\mathrm{S}}{C_\mathrm{B}}(x)\right]_j = \sum_{l=1}^{j-1}\left\{\frac{\alpha_l}{x}\exp\left(-\frac{k_\mathrm{S}}{v}\left(x - X_l\right)\right) - \exp\left(-\frac{k_\mathrm{S}}{v}x\right)\right\} + $$

$$+\frac{\alpha_j}{x}\left(1 - \exp\left(-\frac{k_\mathrm{S}}{v}\left(x - X_{j-1}\right)\right)\right)$$

Data source: ICPDR, CCM.
© European Commission, JRC, IET, 2014.

Benchmark model fits for Danube

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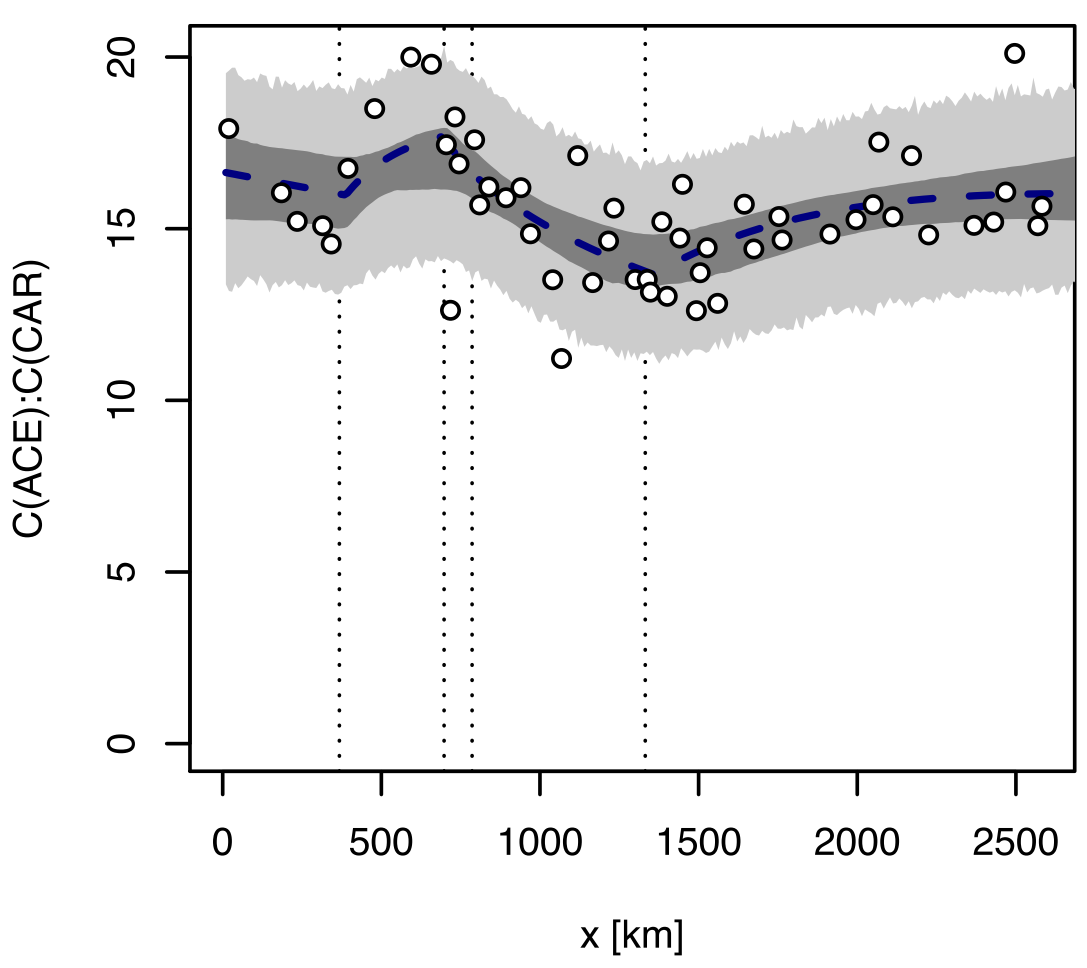
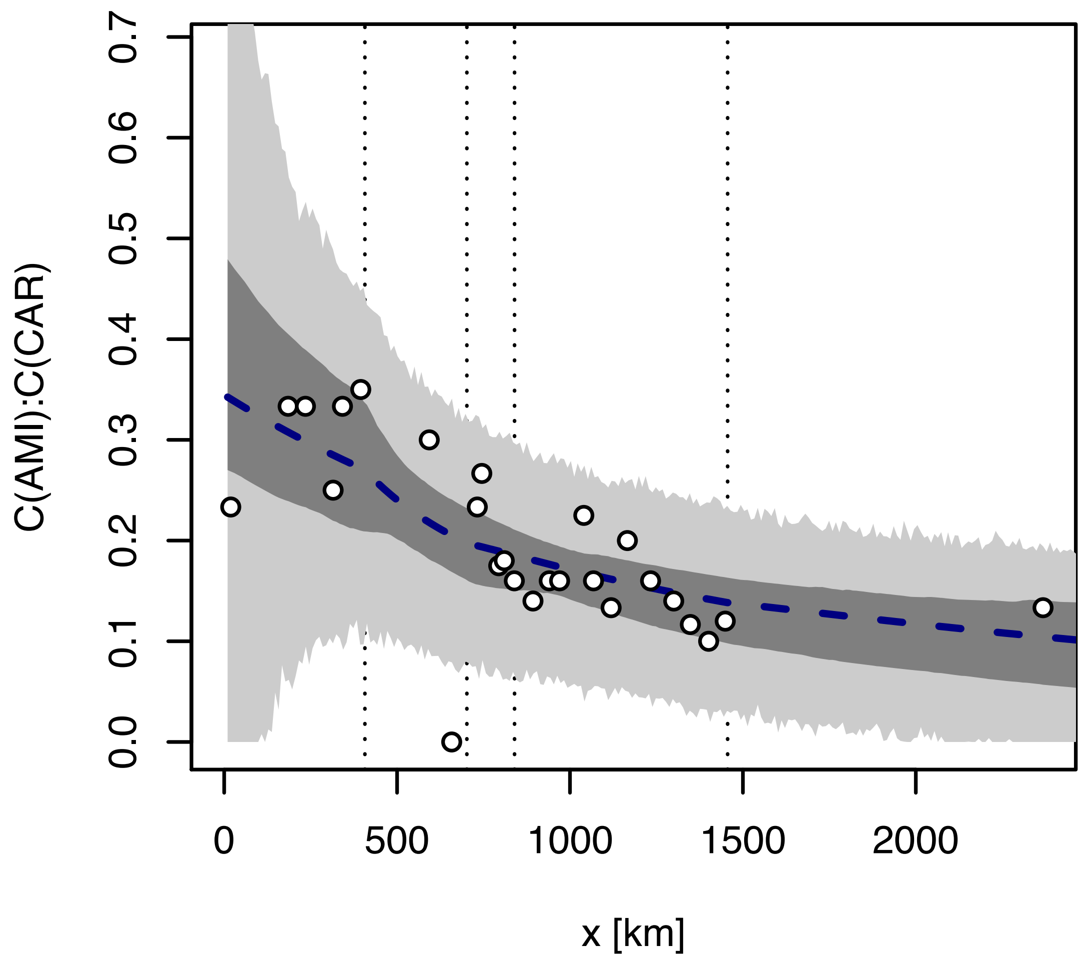
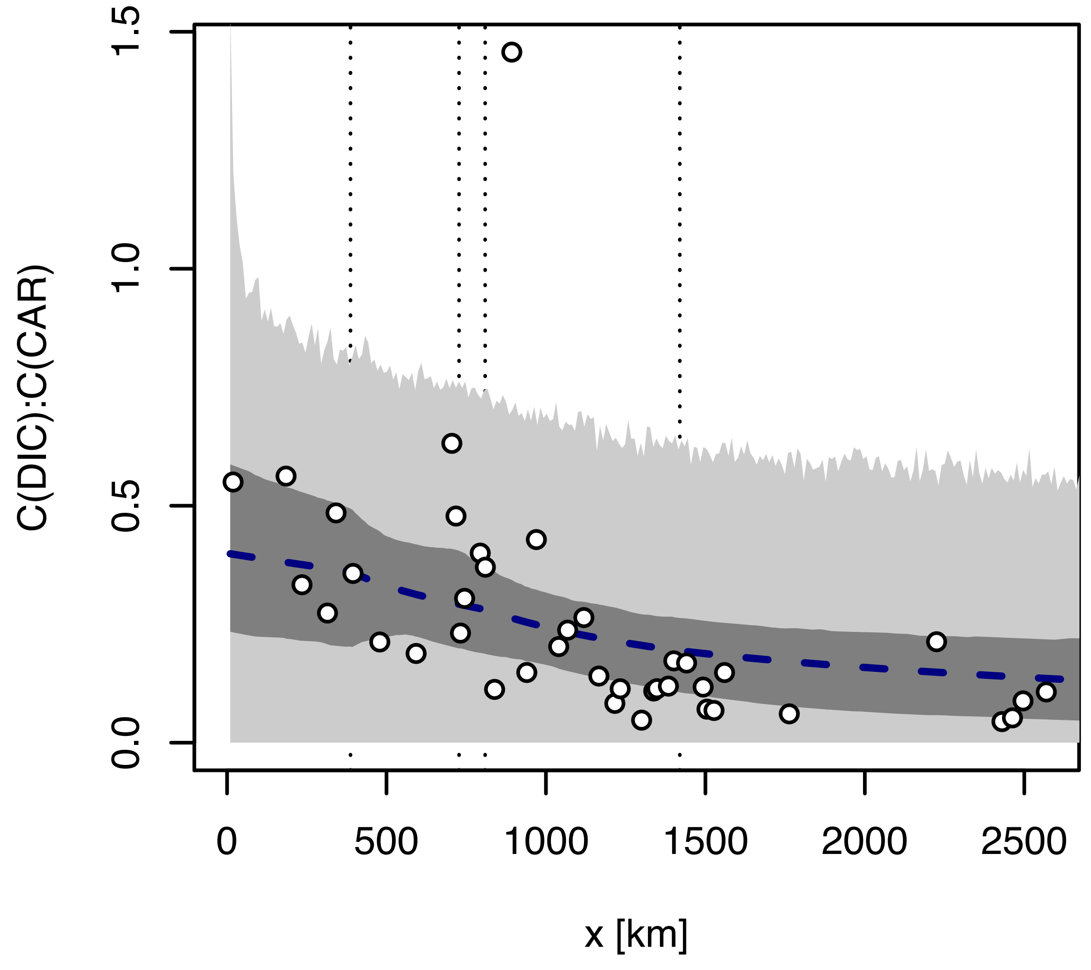
ACE:CAR (JDS3)



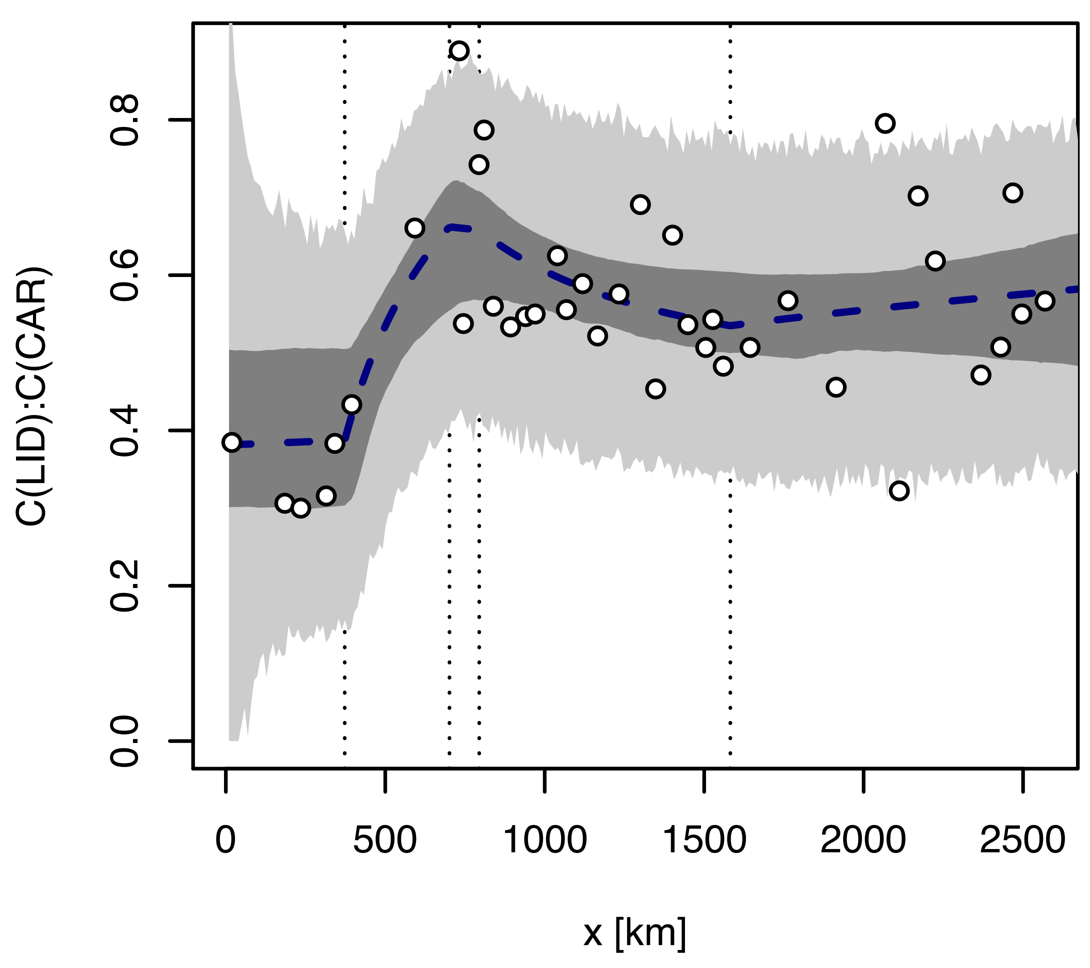
AMI:CAR (JDS3)



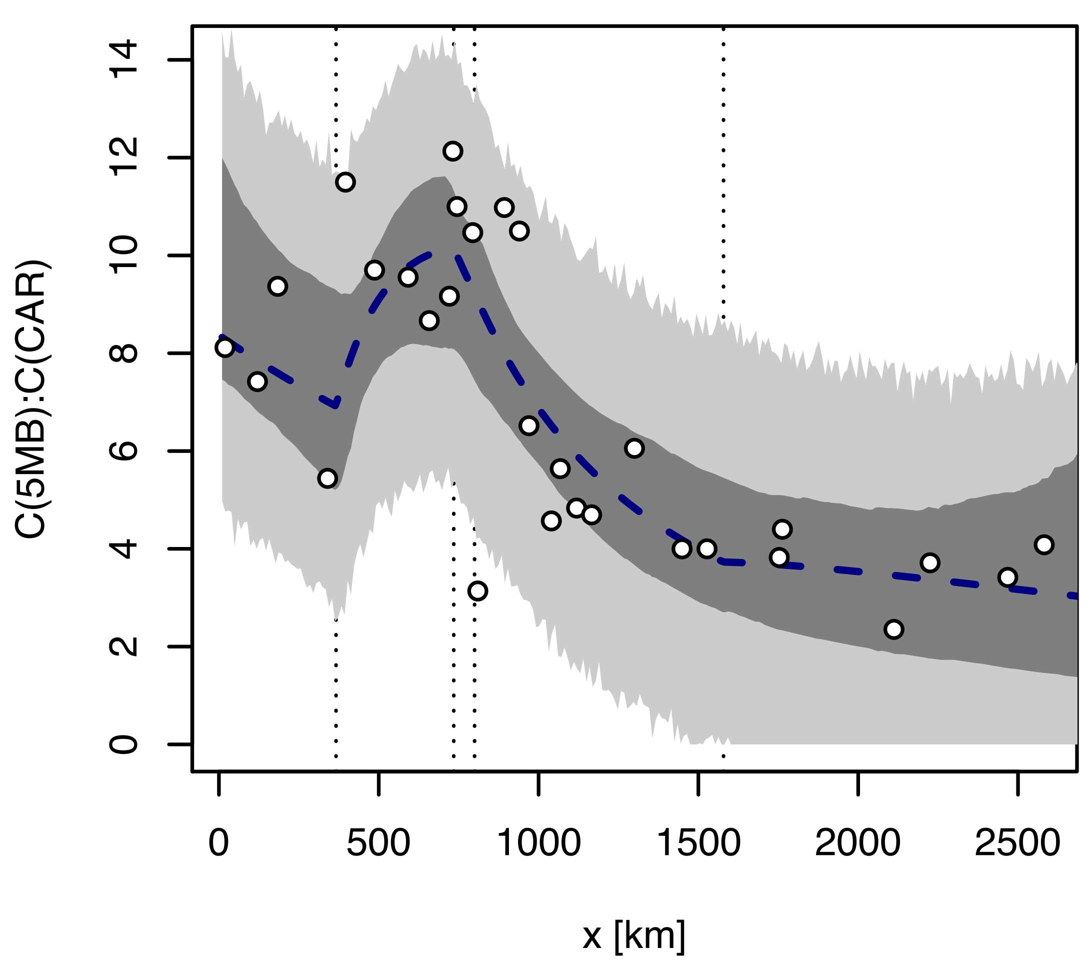
DIC:CAR (JDS3)



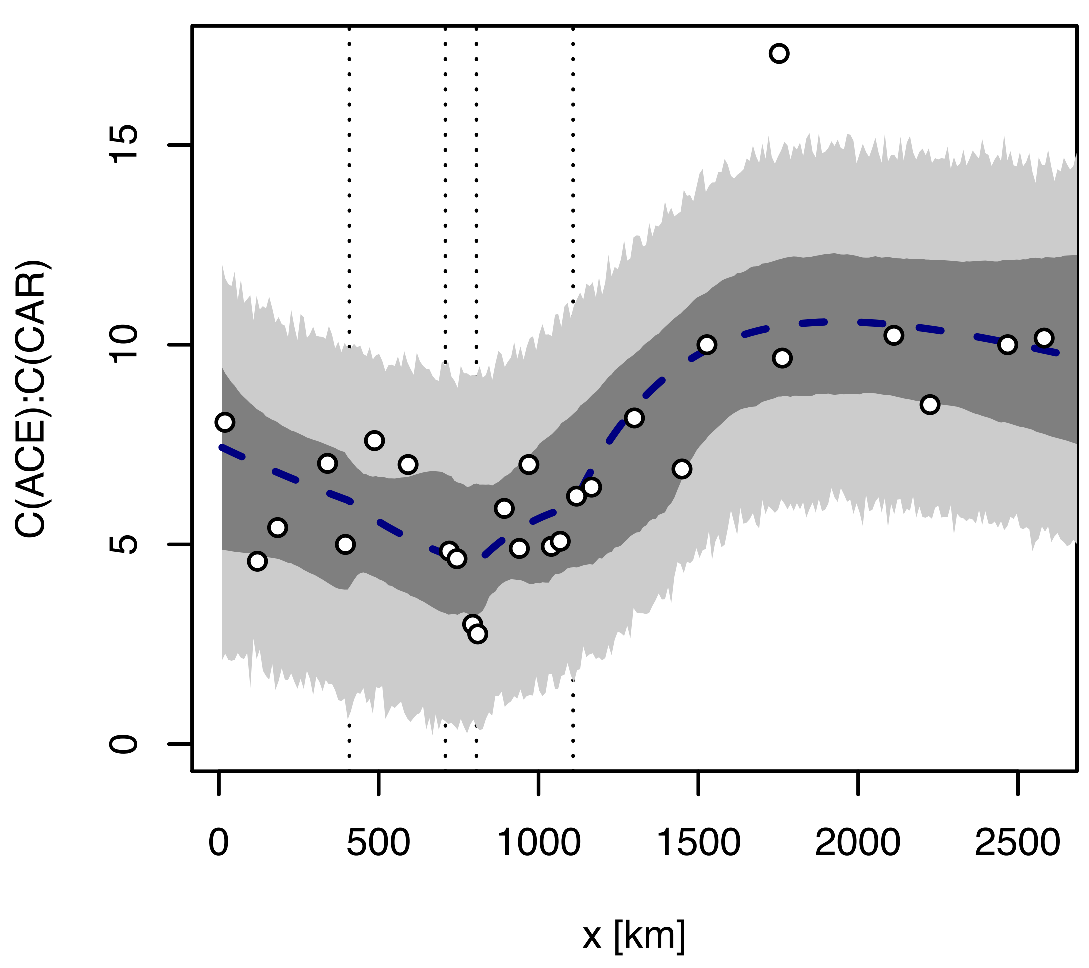
LID:CAR (JDS3)



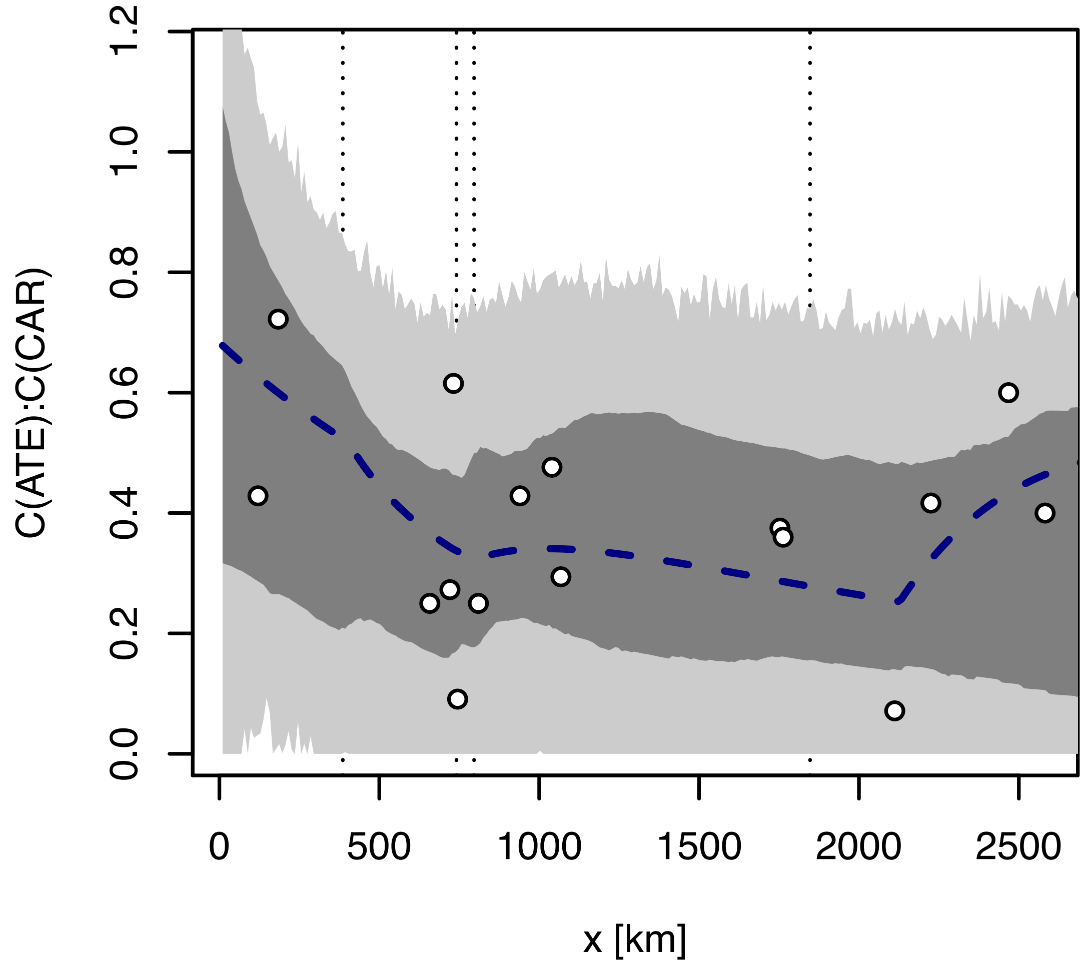
5MB:CAR (JDS4)



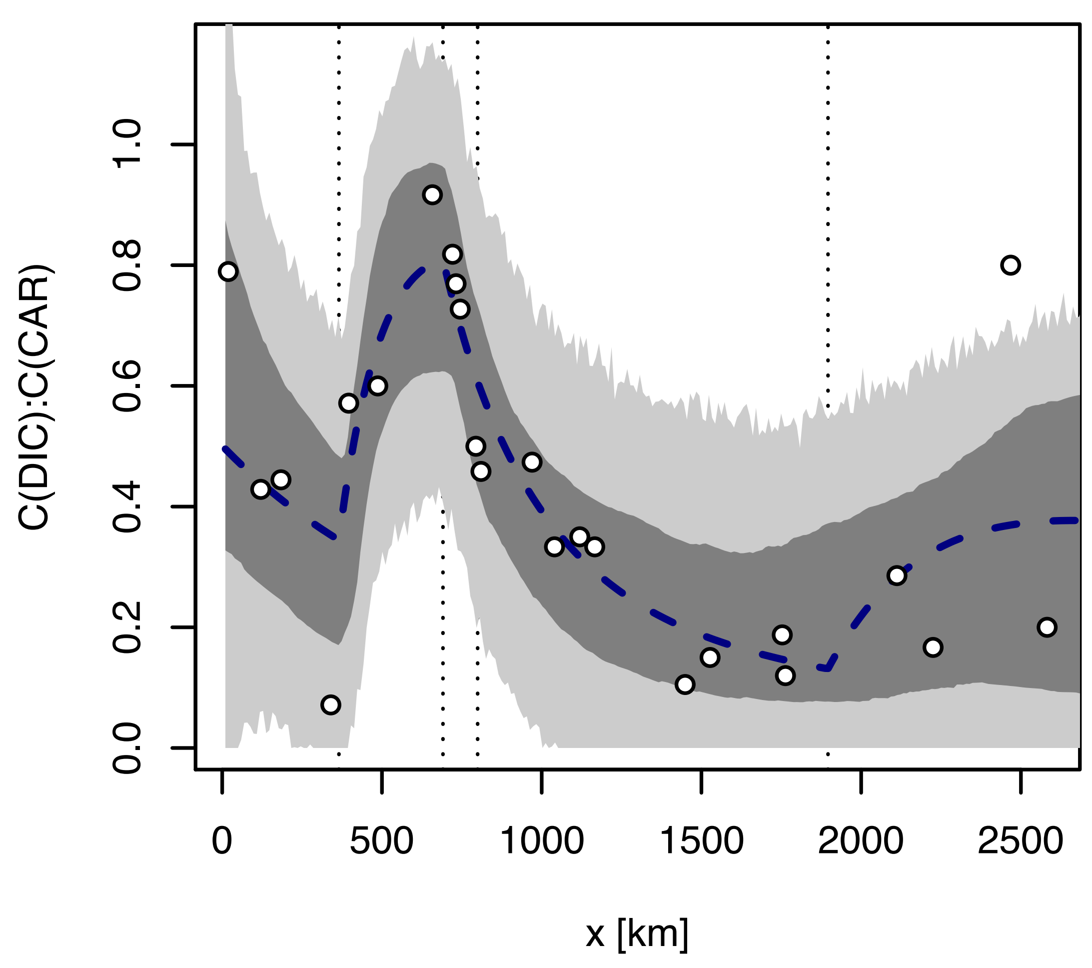
ACE:CAR (JDS4)



ATE:CAR (JDS4)



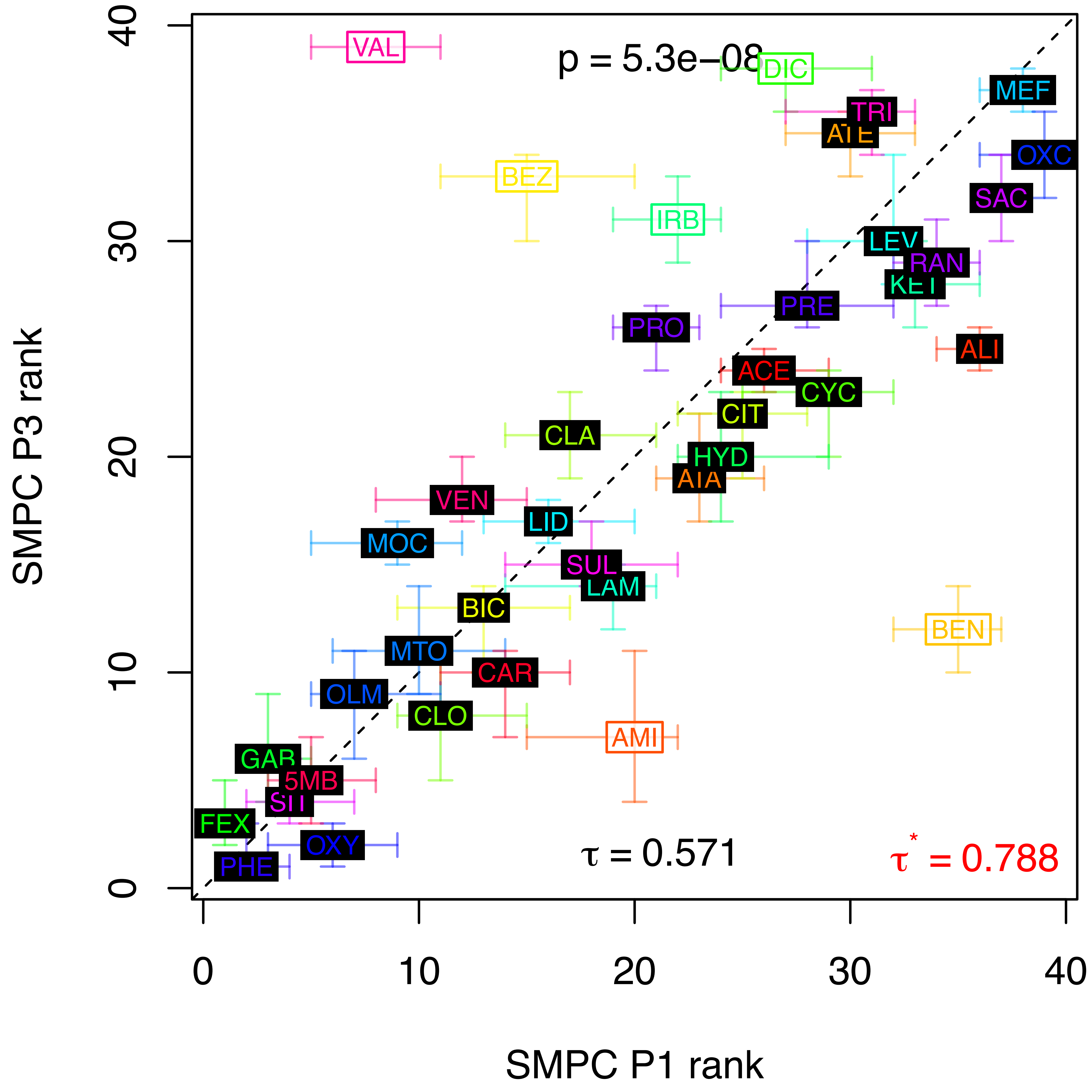
DIC:CAR (JDS4)

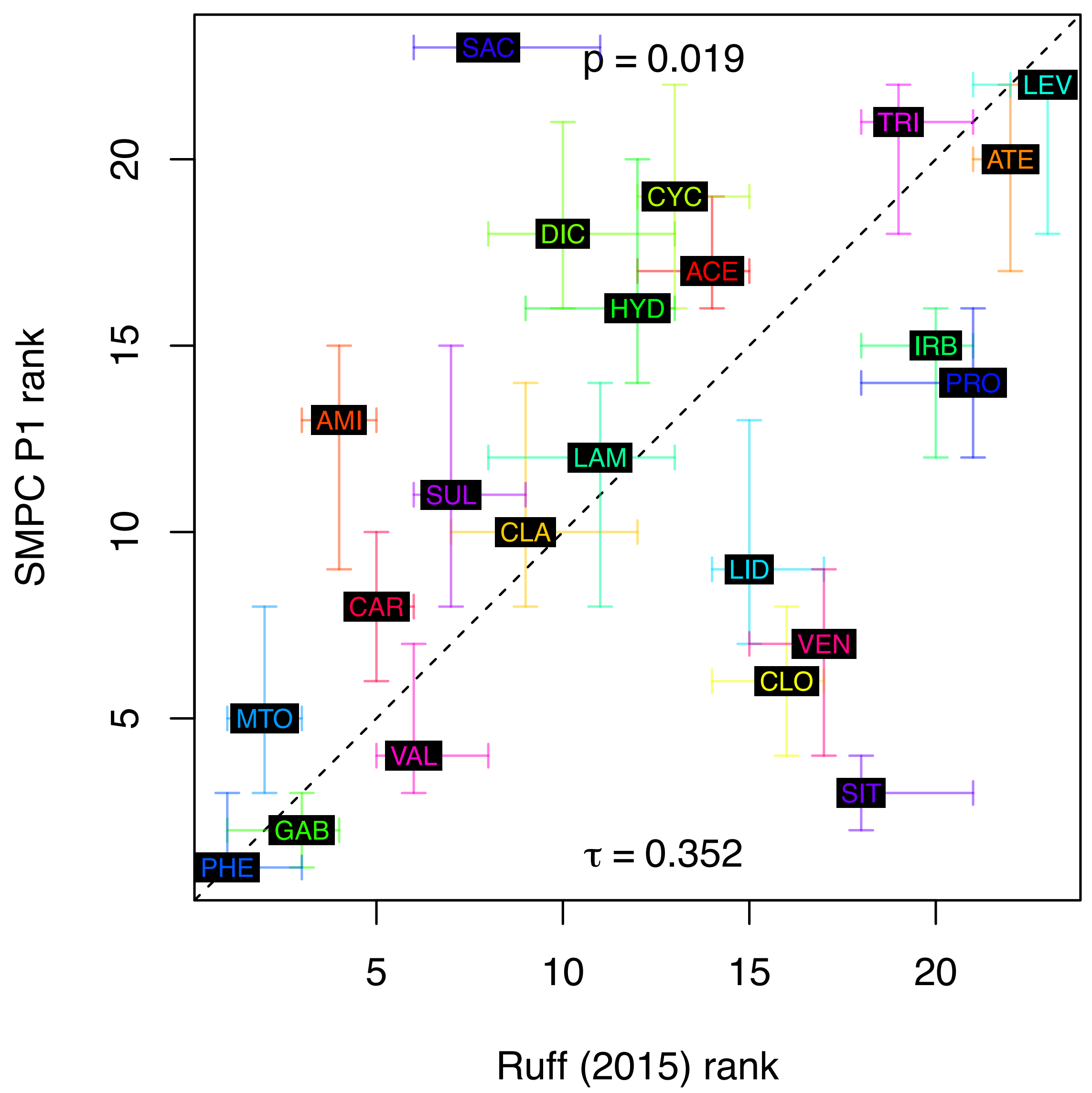


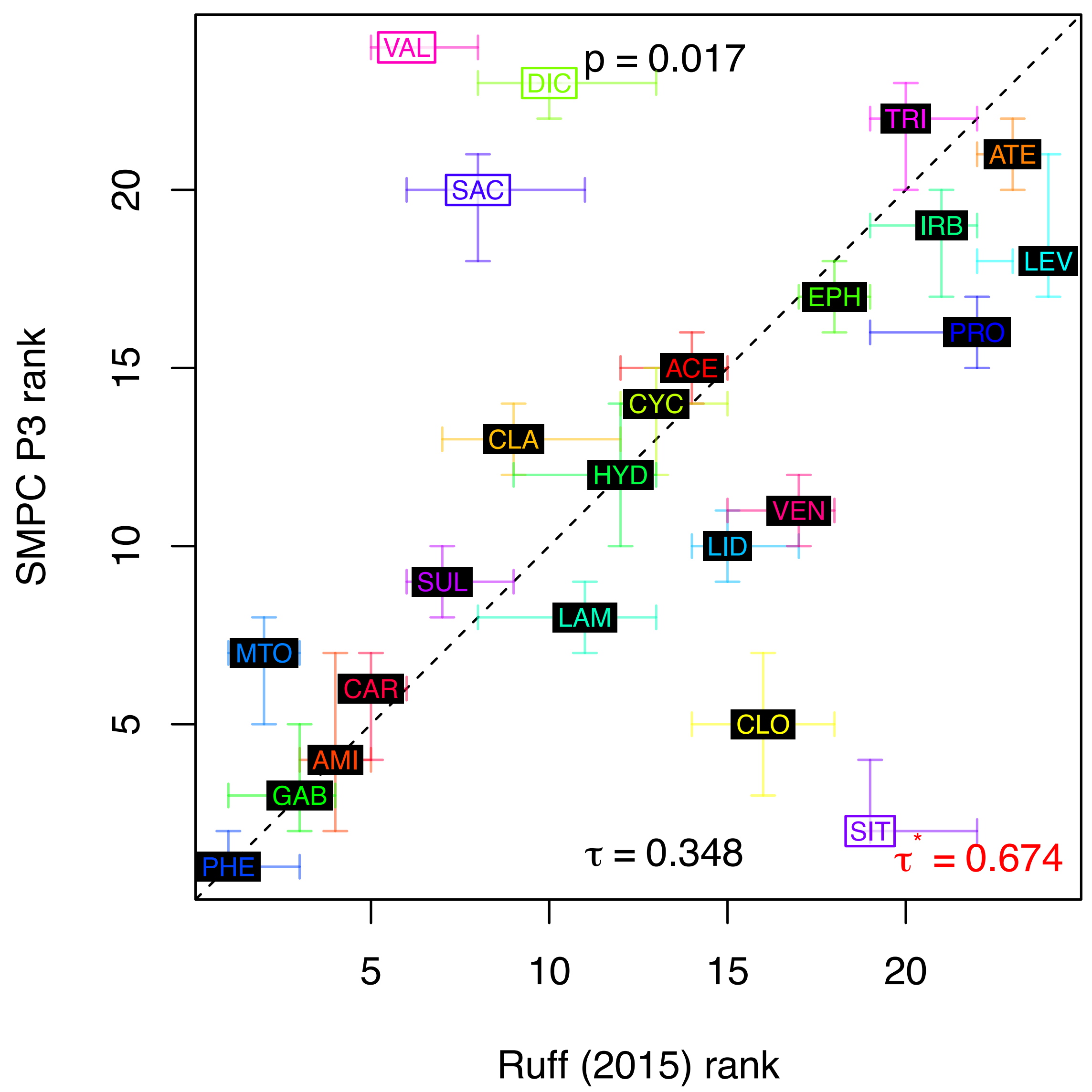
Estimated persistence (Rhine & Danube)

APIs and artificial sweeteners

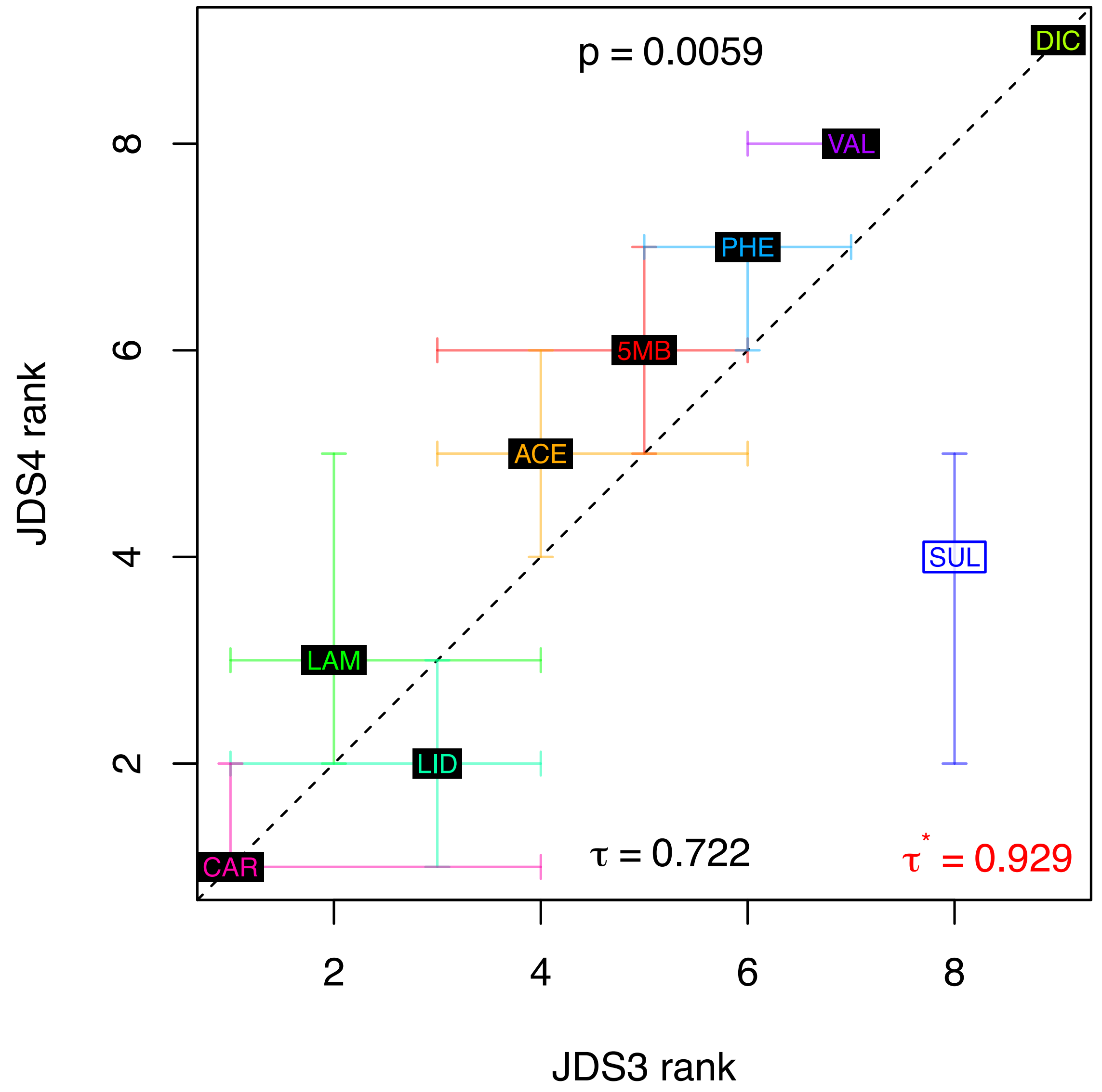
Estimated persistence (Rhine & Danube)







APIs and artificial sweeteners



Outliers mostly explained by

- environmental conditions,
- chemical properties or
- adaptation of degraders

Conclusions

- Benchmarking is a viable presistence-assessment procedure for large rivers
  - given that (precise) concentration data are available along several days of travel time
  - can distinguish between degrading and persistent compounds
  - does not need a complete catchment-model
  - BUT does not work across rivers (yet). Why?