



**Passive sampler calibrations:
what do you need?**



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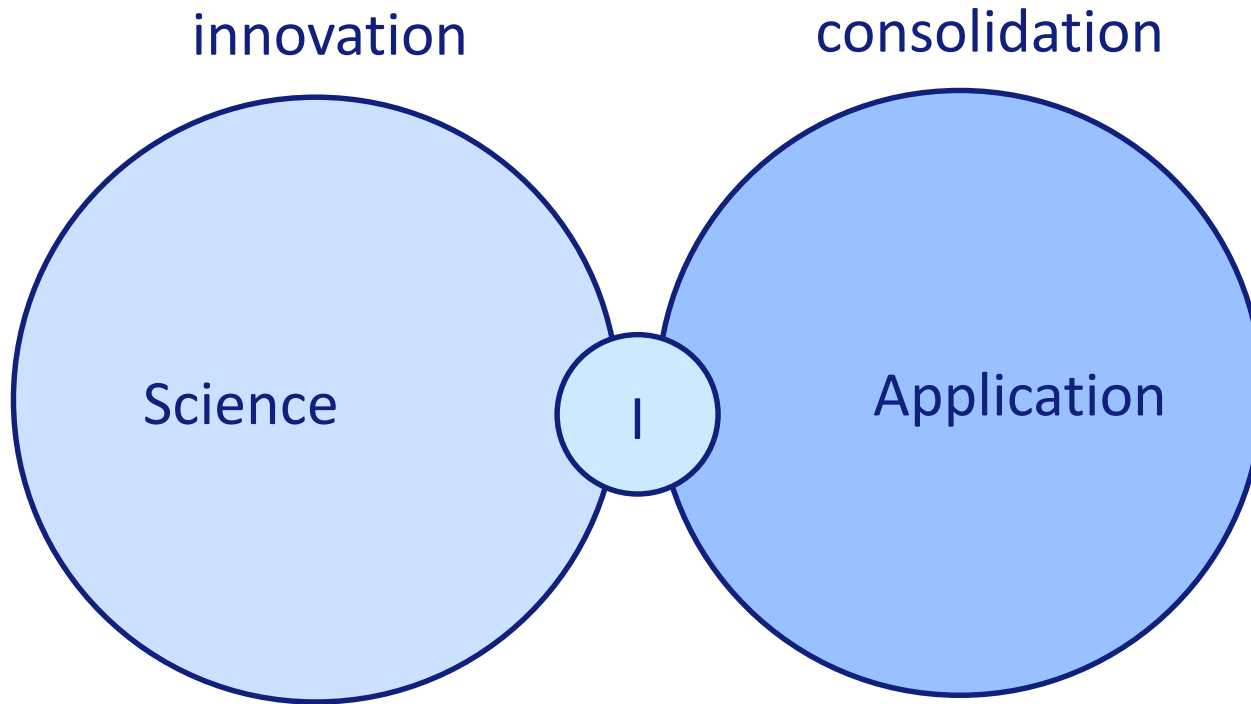
Summary

- My background
- Challenges with chemical analysis
- Challenges with calibration parameters
- Developments in uptake modeling
- (Focus on Chemcatchers with SDB-RPS sorbent)





Where I stand....





Challenges with the chemical analysis

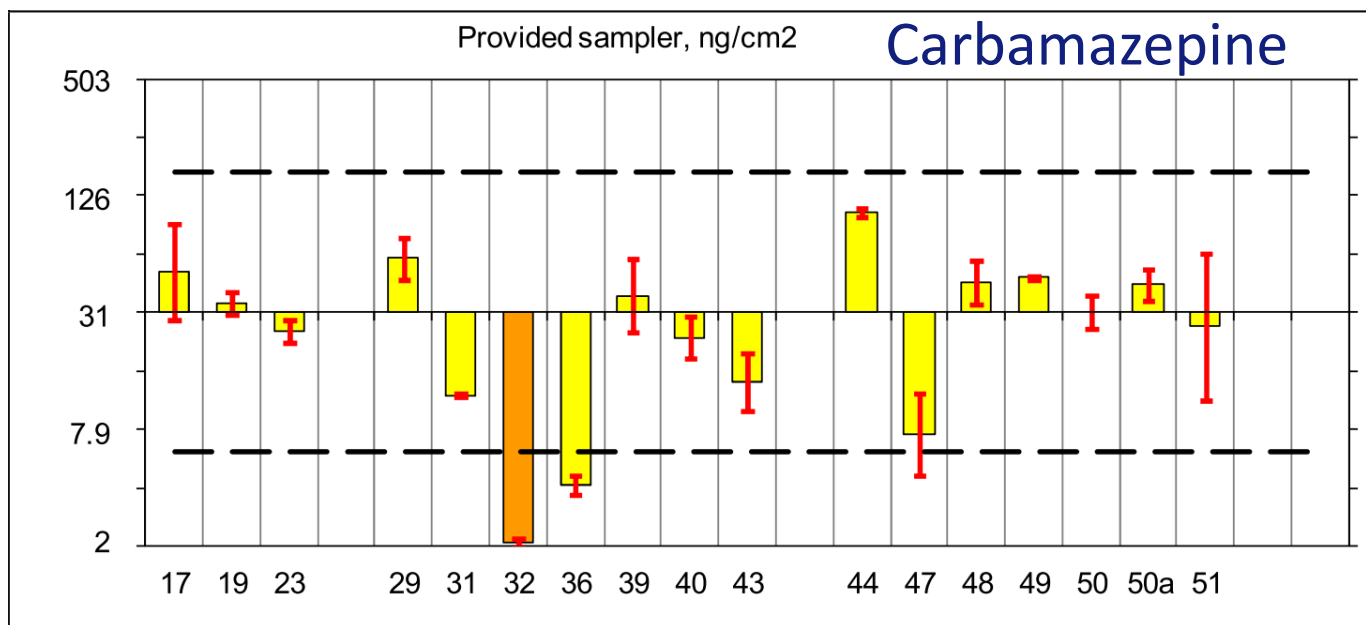
- exist for grab sampling
- exist for passive sampling
- exist for calibration parameters (R_s and K_{sw}) as both are derived from chemical analysis of water and sampler





Variability due to chemical analysis can be substantial

NORMAN Interlaboratory study



} factor 28

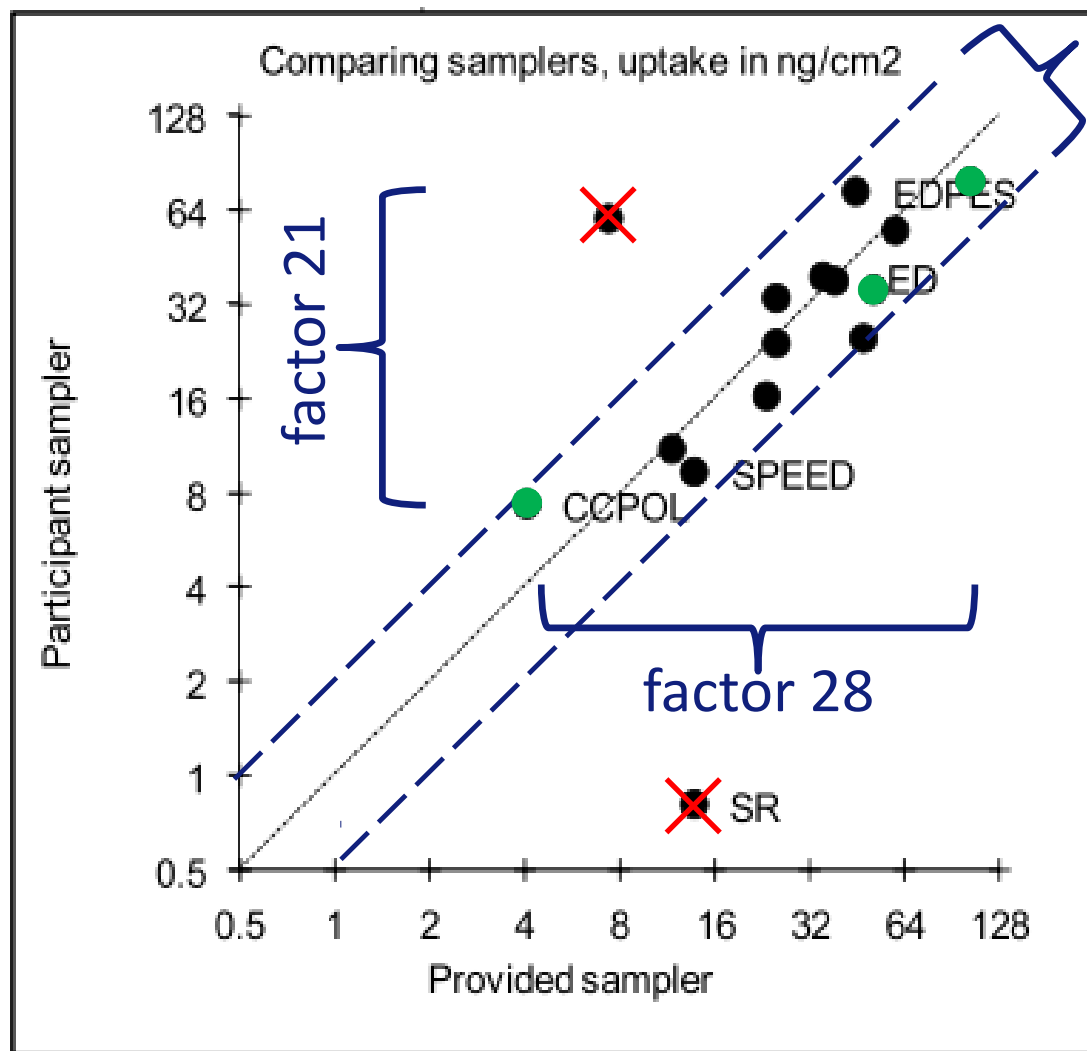
———— median
- - - - ± 2 standard deviations

standard solution: CV = 13%





Different samplers: similar chemical analysis errors



- Chemcatcher SDB-RPS + PES membrane
- SPEED = Speedisk sampler
- SR = silicone
- unlabeled ● = POCIS





Errors ($k = 2$) in the chemical analysis of passive samplers

Error in the amount : factor 5

Error in the amount ratio : factor 2

(for NORMAN Interlaboratory study)

R_s and K_{sw} are derived from absorbed amounts and C_w

Those are ratios.

Possibly a factor 2 error can be expected from chemical analysis

Possibly more (different matrices, different concentration levels)





Grab sample analysis can also be a source of error

166 74 32 31 20

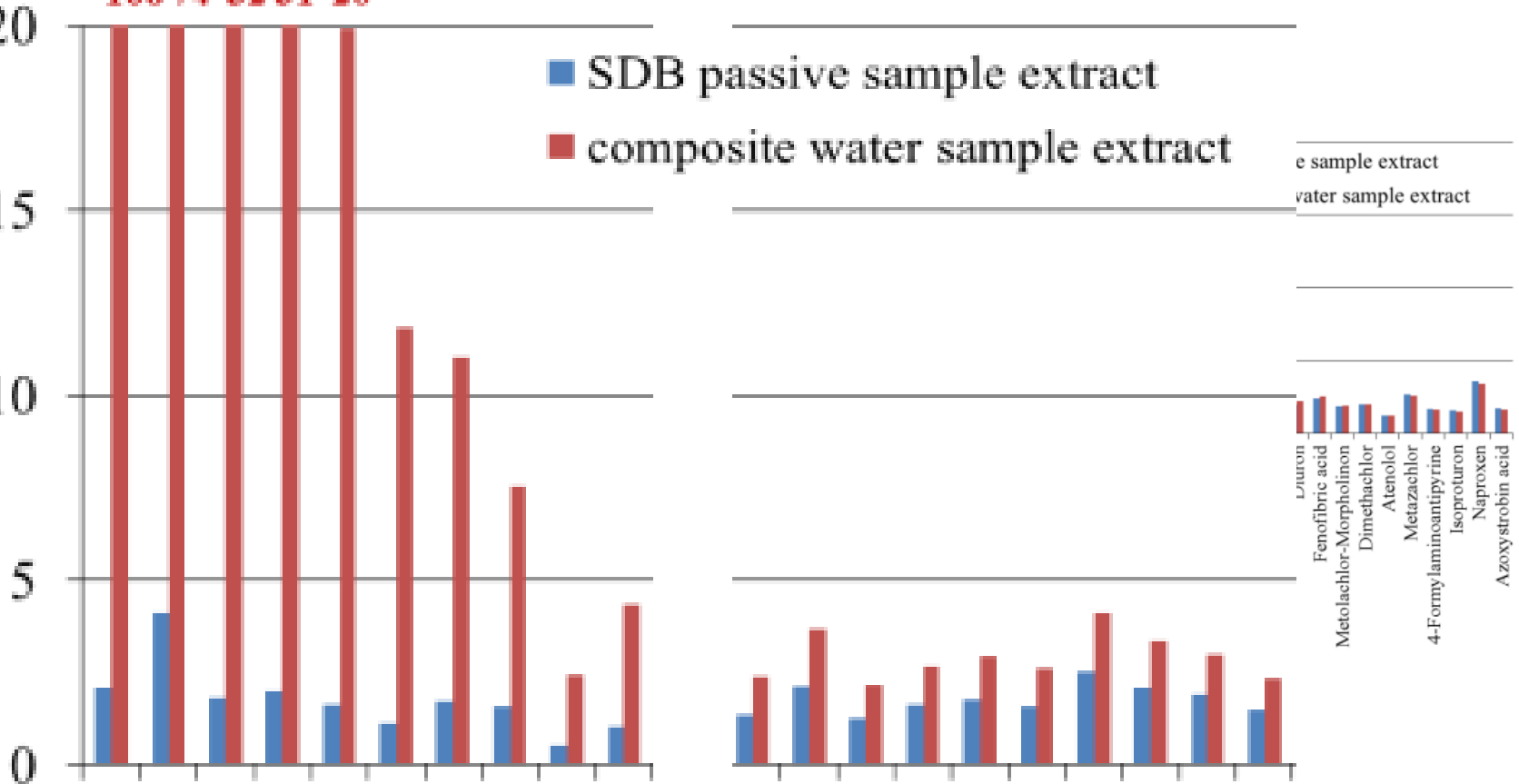
SLK

Matrix Factor

Matrix Factor

■ SDB passive sample extract
 ■ composite water sample extract

■ e sample extract
 ■ water sample extract





Wrap up: Errors in chemical analysis

- Passive sampler calibrations: C_w and N_{sampler} (ratio of the two)
 - Both can have appreciable errors in the chemical analysis
- Field validations: $C_{w,\text{grab}}$ and $C_{w,\text{sampler}}$
 - Both can have appreciable errors in the chemical analysis
 - $C_{w,\text{sampler}}$ can have appreciable errors in the calibration parameters
 - In addition: $C_{w,\text{grab}}$ can be subject to sampling variability (peak events)
- (EU requirement that error $< 50\%$ at $k = 2$ may not be realistic, neither for grab sampling nor for passive sampling)





Error summary

Error source	Grab sampling	Passive sampling
Chemical analysis	large	large (maybe less large)
Modeling/Calibration	none ($C_w = N/V$)	appreciable
Sampling variability	large	small





Challenges with selecting calibration data

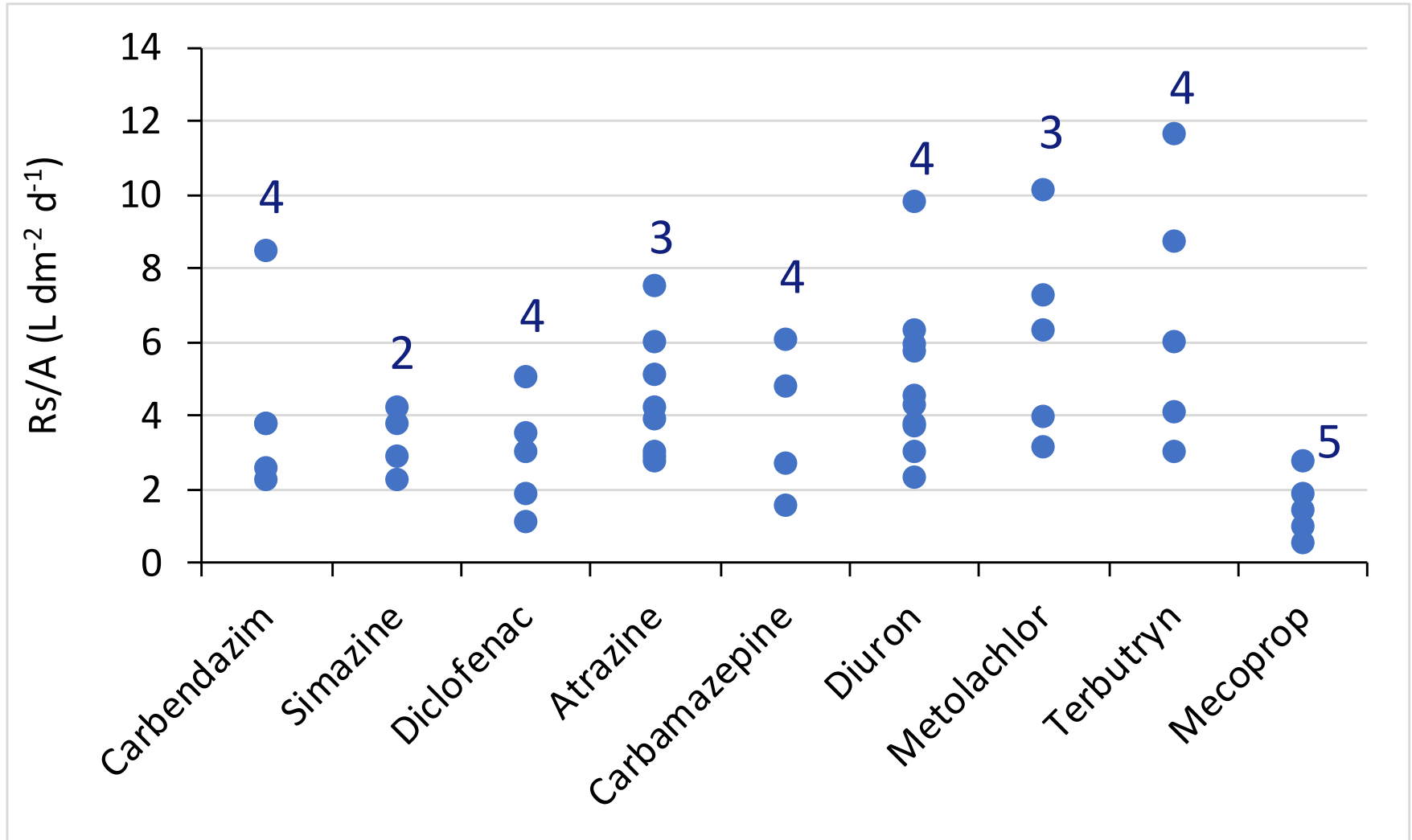
Example for Chemcatchers

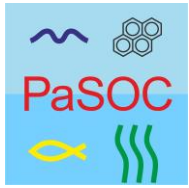
- Chemcatchers with SDB-RPS sorbent
- with and without membrane: $n > 10$
- R_s/A (areas 0.126, 0.159, 0.35 dm²)
- basically from two labs
- years 2005 - 2019



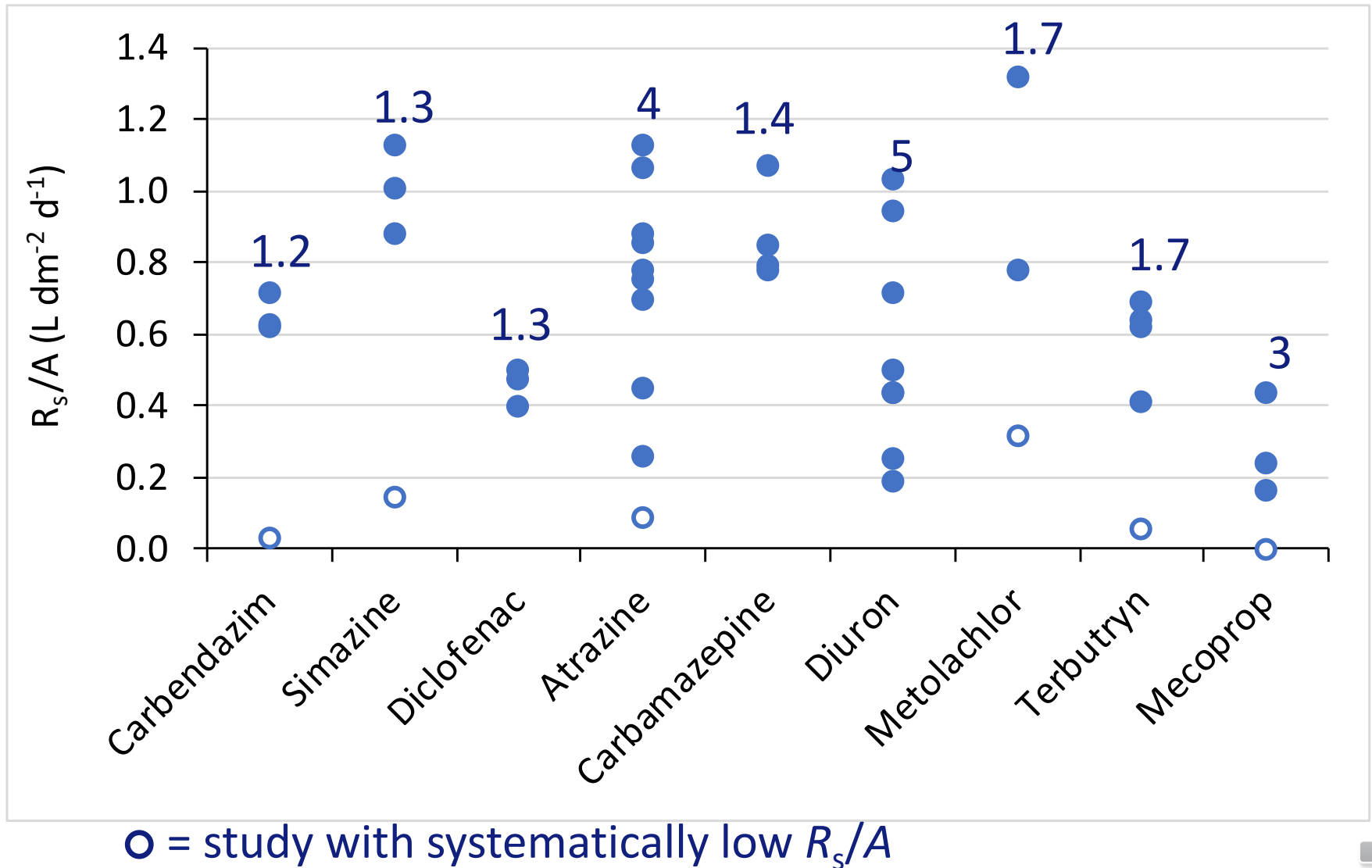


Chemcatchers without membrane (numbers: max/min)





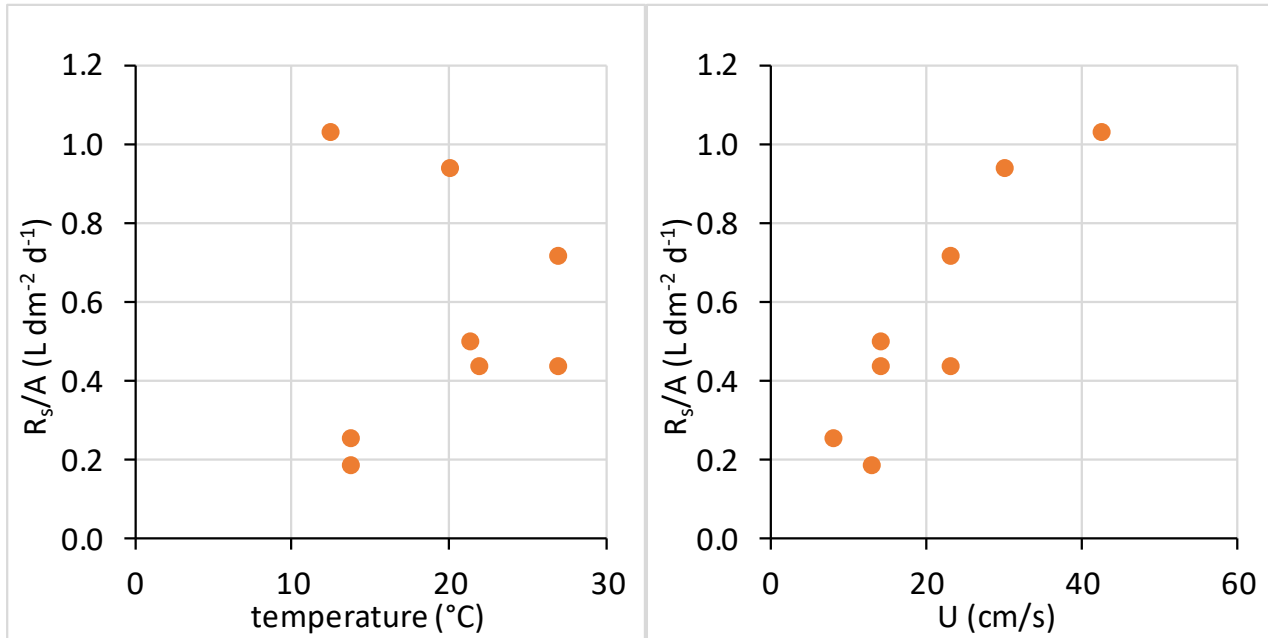
Chemcatchers with PES membrane (numbers = max/min)





Scatter maybe related to temperature and flow?

Diuron (Chemcatcher with PES membrane)



Take R_s from regression equation?

Take the median?

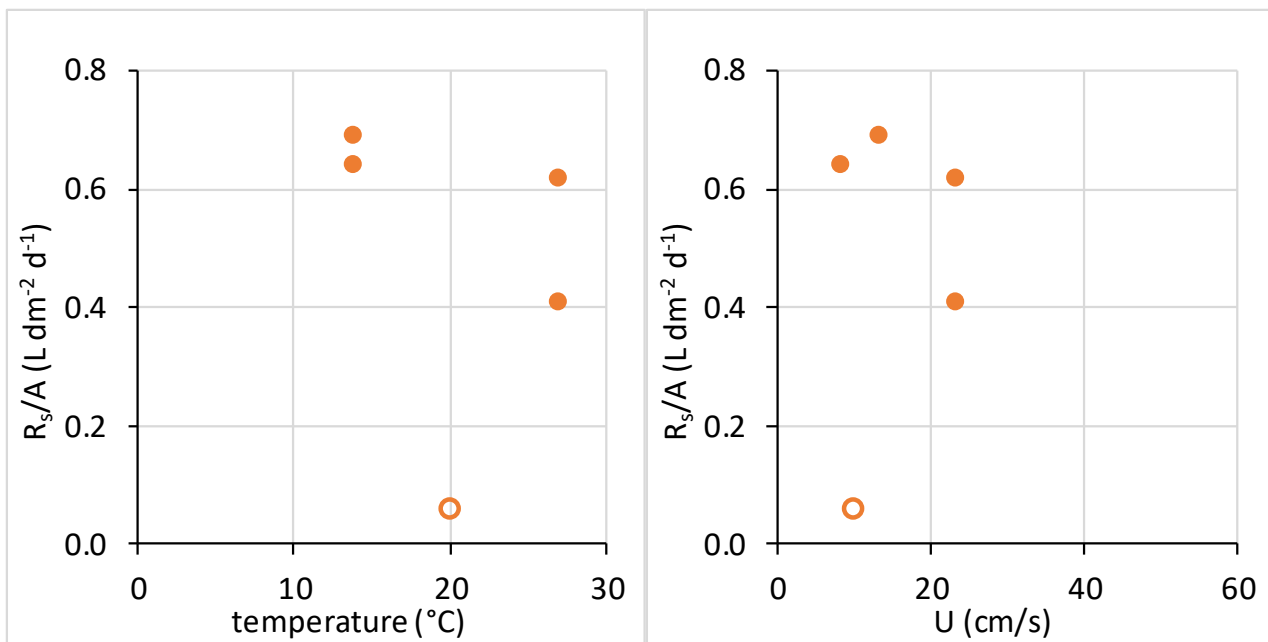
Hard to decide based on statistical considerations





Scatter maybe related to temperature and flow?

Terbutryn (Chemcatcher with PES membrane)



Hard to decide based on statistical considerations
And for most compounds you have less values (1 or 2)





Temperature effects observed within one study for SDB-RPS without membrane

SDB-RPS without membrane

$U = 10$ cm/s, temperature 13 °C

$U = 12$ cm/s, temperature 26 °C

$$R_{s,26^{\circ}\text{C}}/R_{s,13^{\circ}\text{C}} = 1.7 \pm 0.5$$

22 compounds





Within-study flow effects for SDB-RPS with PES membrane

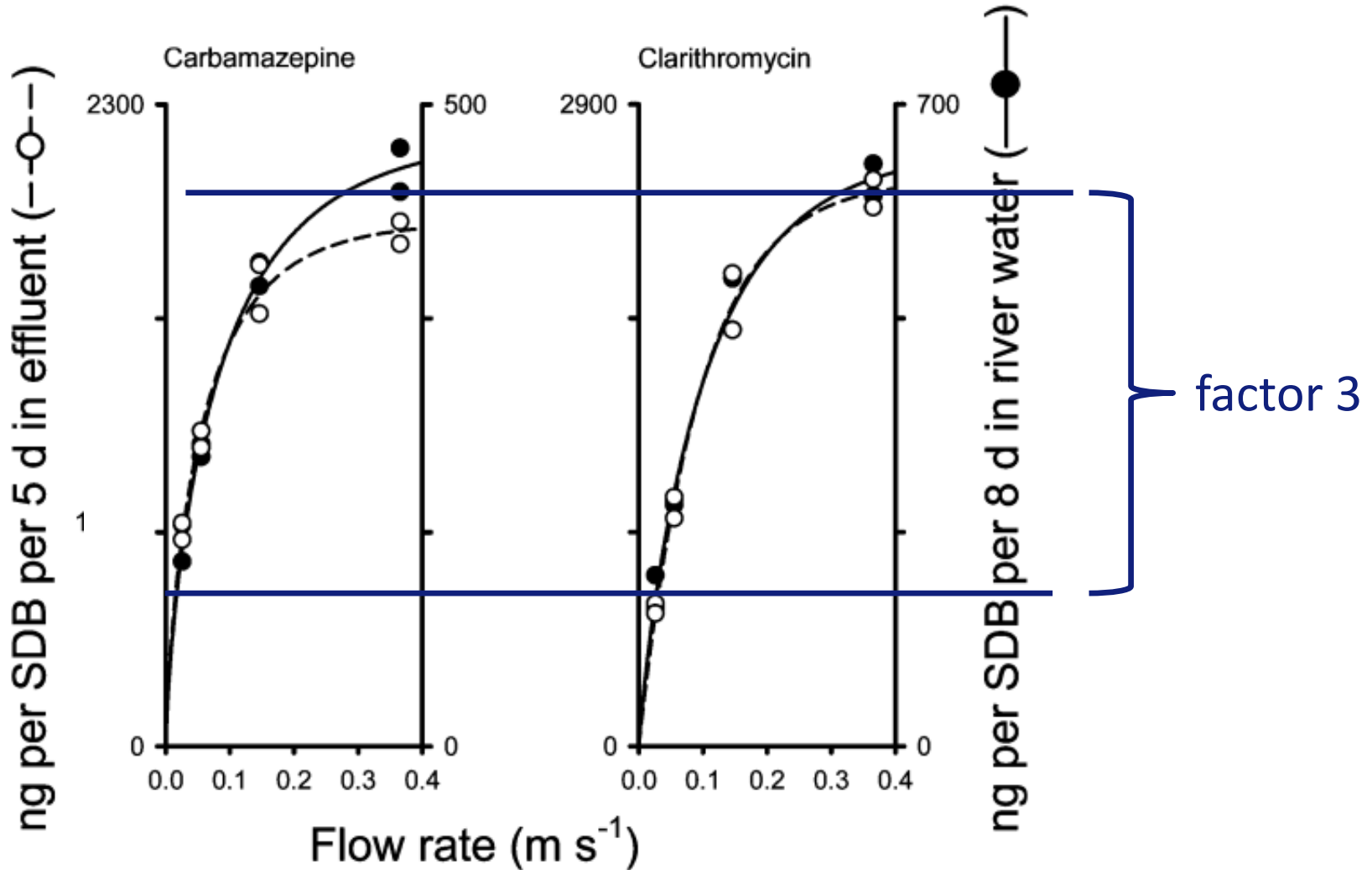
t (°C)	U (cm/s)	Promethryn R_s (L/d)	Atrazine R_s (L/d)
16	0	0.01	0.01
17	3	0.03	0.04
19	8	0.06	0.07
19	16	0.11	0.12
22	24	0.13	0.14

But Gunold et al. (2008) did not find a flow effect between 13(?) and 40 (?) cm/s for SDB-XC without membrane (R_s ratio 0.94 ± 0.15)





Within-study flow effects for SDB-RPS without membrane





Conclusions for temperature and flow effects so far

- Substantial scatter in R_s data between studies
(max/min ~factor 1.3 to 5)
- Within-study temperature effects are observed (thin ice)
- Within-study flow effects are observed (thin ice)
- Between-study temperature and flow effects are overshadowed by.....
 - maybe analytical variability
 - maybe insufficiently accurate/relevant flow velocities
 - maybe other factors (general handling)





Mechanistic models can help

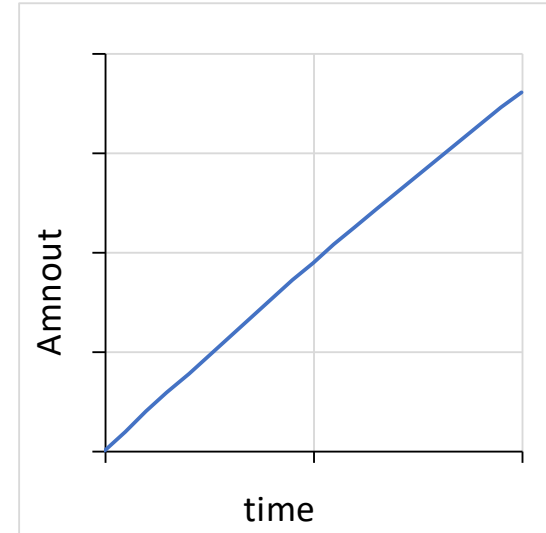
Sampling rate model

linear uptake
(sorbent is infinite sink)

$$N = C_w R_s t$$

accumulation rate
(amount per unit time)

$$\frac{dN}{dt} = C_w R_s$$



flux
(amount per unit surface area per unit time)

$$j = \left(\frac{R_s}{A} \right) C_w = k_o C_w$$

flux
(more general)

$$j = k_o \left(C_w - \frac{C_s}{K_{sw}} \right)$$

flux →

↑ mass transfer coefficient

← concentration difference





flux
↓
 j
current

mass transfer coefficient
↓
 k_o
conductivity

concentration difference
↓
 $\left(C_w - \frac{C_s}{K_{sw}} \right)$
driving force

=

i = $\frac{1}{R}$ V Ohm's law: $V = i R$

j = $\left(\frac{R_s}{A} \right) \left(C_w - \frac{C_s}{K_{sw}} \right)$



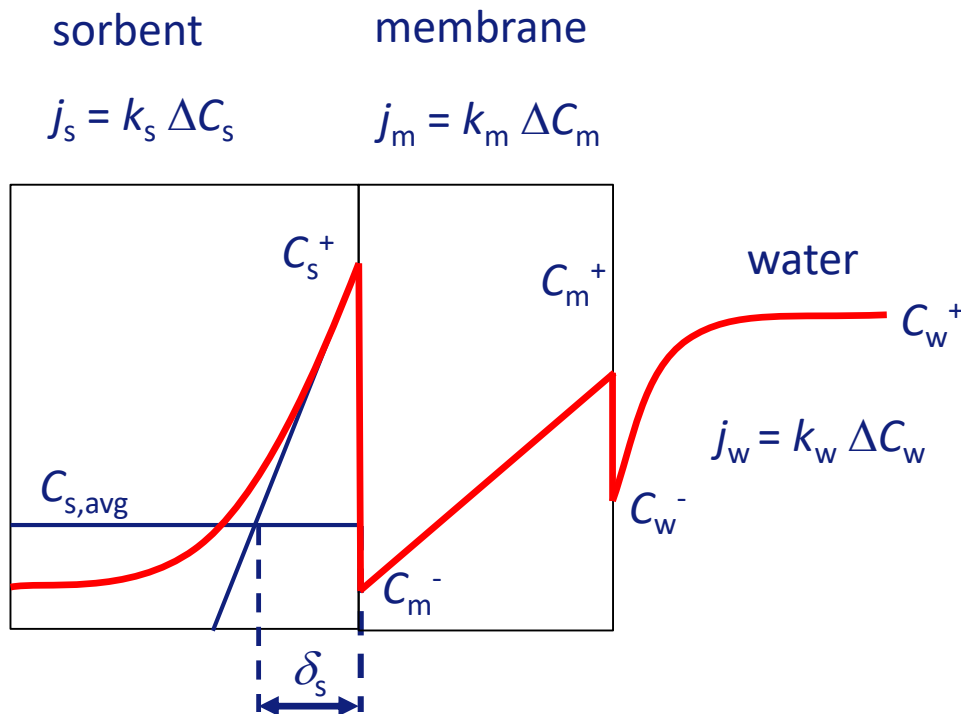


Series resistance model

Evaluate the respective transport steps:
Water, membrane, sorbent

assumptions:

- steady state flux: $j_w = j_m = j_s$
- equilibrium at the interfaces
 - $C_m^+ = K_{mw} C_w^+$
 - $C_s^+ = K_{sm} C_m^-$





Series resistance model: transport resistances are additive

$$\frac{1}{k_o} = \frac{1}{k_w} + \frac{1}{\frac{D_m}{d_m} K'_{mw}} + \frac{1}{\frac{D_s}{\delta_s} K'_{sw}}$$

overall resistance = WBL resistance + membrane resistance + sorbent resistance

$$\frac{1}{R_s} = \frac{1}{R_{s,w}} + \frac{1}{R_{s,m}} + \frac{1}{R_{s,s}}$$

The terms $\frac{1}{R_{s,m}}$ and $\frac{1}{R_{s,s}}$ are circled in red, with an arrow pointing to $\frac{1}{R_{s,max}}$.

Experimentally approach to rate control steps:

- WBL: higher/lower flow
- membrane: thicker/thinner (0, 1, 2, 3,... membranes)
- sorbent: thicker/thinner (0.5, 1, 2, 3,....extraction disks)





We have some crude guesses on WBL control and membrane control already

Full WBL control:

$$\frac{k_w L}{D_w} = 0.664 \text{Re}^{1/2} \text{Sc}^{1/3} \quad \text{Re} = \frac{UL}{\nu} \quad \text{Sc} = \frac{\nu}{D_w}$$

Full membrane control
(transport through pore water only)

$$\frac{R_{s,m}}{A} = \frac{\phi D_w}{\tau_{w,m}^2 d_m}$$

Stephens et al., 2005. ES&T 39:8891-8897

Alvarez et al., 2004. Environ.Toxicol.Chem 23:1640-1648

$$\left(\frac{R_s}{A} \right) = \frac{1}{k_w} + \frac{1}{\frac{\phi D_w}{\tau_{w,m}^2 d_m}} + \dots$$

Series resistance model.....

$$\left(\frac{R_s L}{A D_w} \right) = \left(\frac{k_w L}{D_w} \right) + \left(\frac{\phi L}{\tau_{w,m}^2 d_m} \right) + \dots$$

... put in dimensionless form.

(temperature effects are accounted for through D_w and ν)





Some guesses regarding PES membranes

porosity : $\phi = 0.7$

tortuosity : $\tau = 1.2$

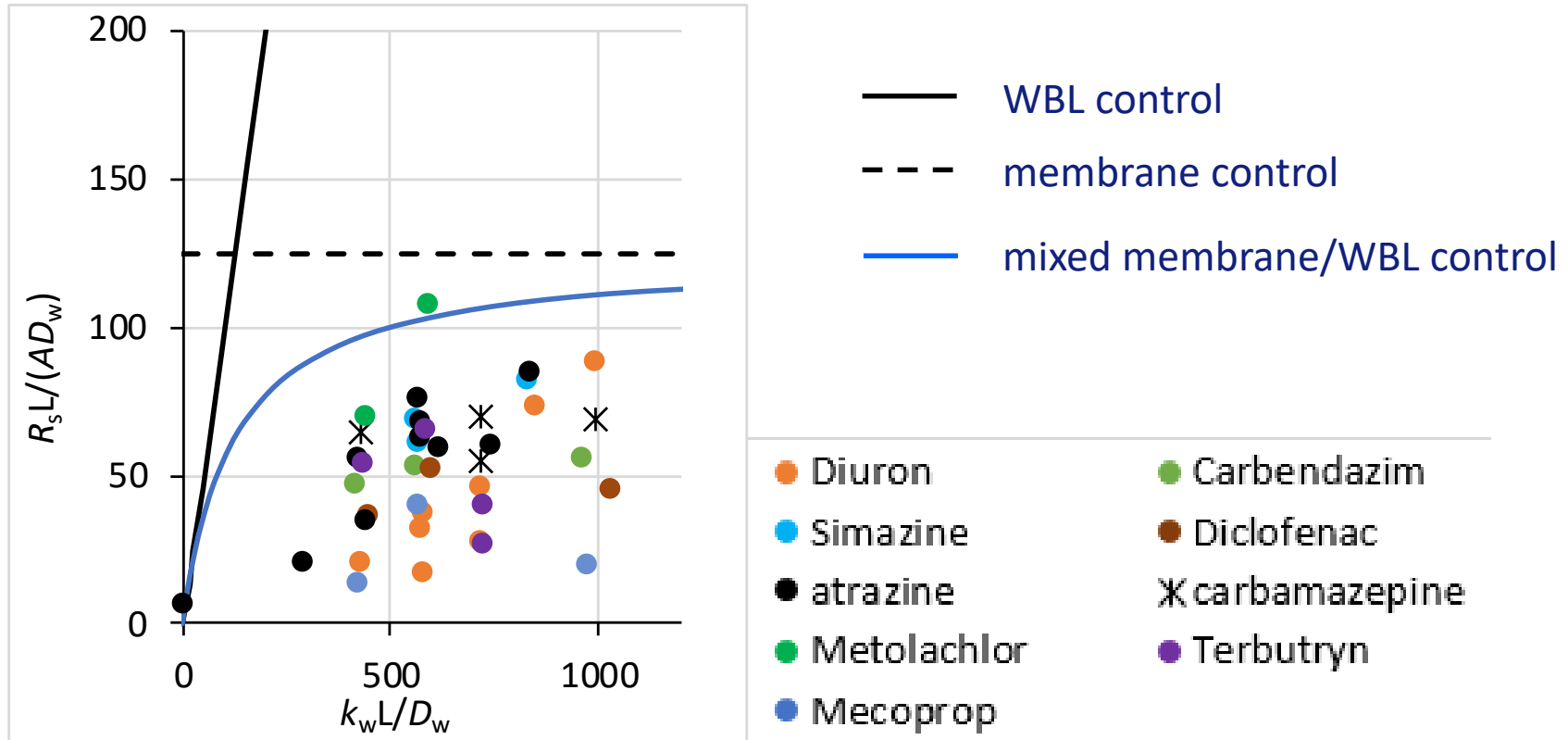
thickness : $d_m = 130 \mu\text{m}$





Calculating R_s from scratch

Chemcatchers with PES membrane



Crude R_s estimates: too large, but right order of magnitude

$R_s L / (A D_w) = 50$ could be a fair default value

Factor 2 uncertainty could be caused by analytical error.

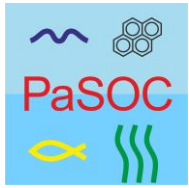




Summary

- Large between-study variability in R_s
(Analytical variability? Experimental variability? Speciation?)
- Better understanding of WBL-membrane-sorbent is needed.
(study transport mechanisms experimentally.)
- Experimental:
 - calibrate under controlled k_w conditions, rather than RPM settings and calculated velocities
 - study membrane permeation, vary membrane thickness,....
- A crude model for WBL/membrane gives a fair prediction of R_s





Thank you for listening.
Happy to discuss further.

Also happy to support
(calibrating the transport through WBL/membranes/sorbent,
literature surveys, modeling templates, data analysis)

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