# Sampler-water exchange of polar compounds. A mechanistic approach. (An invitation)

Kees Booij

www.pasoc.eu

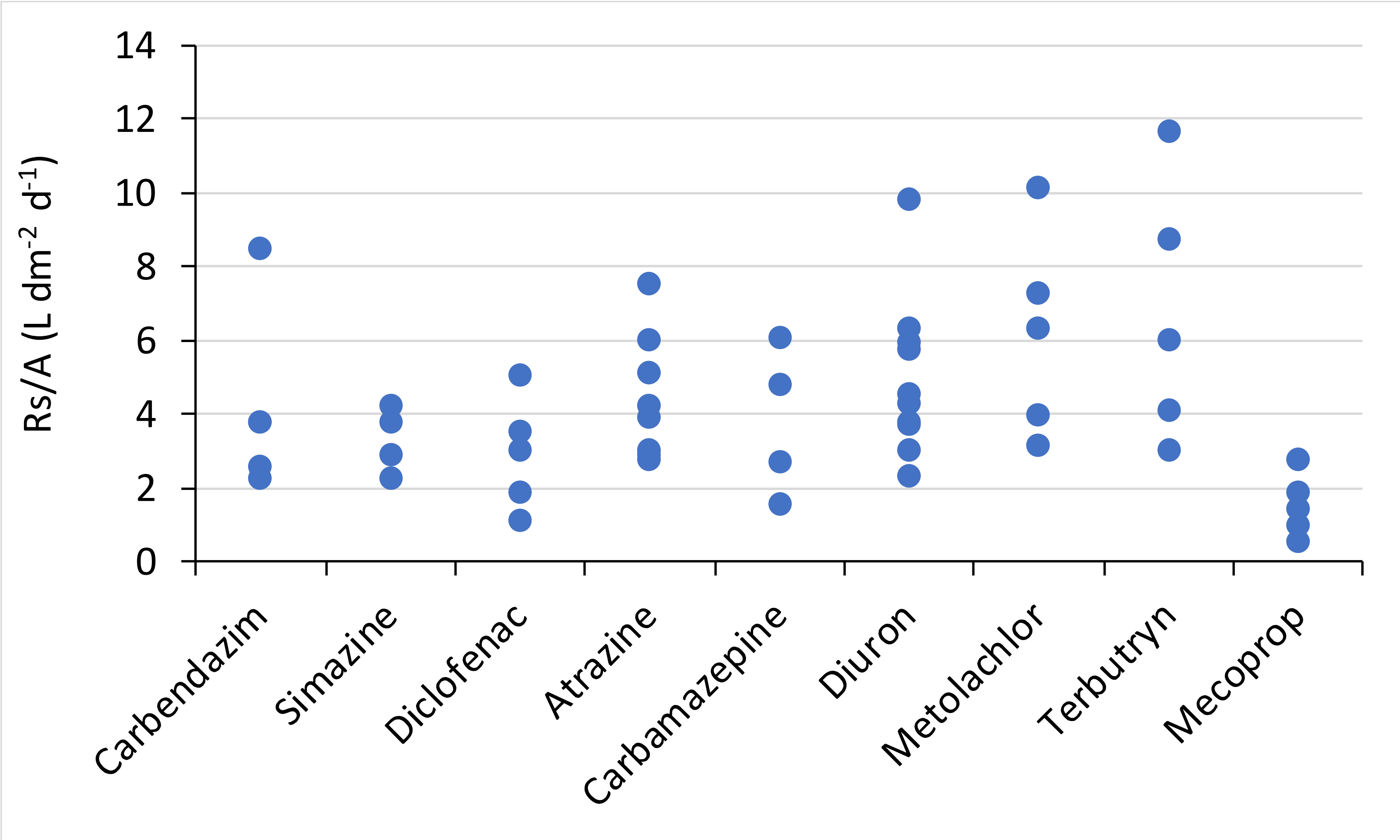
# Summary

- The issue for samplers of polar compounds
  - calibration parameters show a large scatter
    - any number goes
    - validity is assessed by outlier tests and field validation
  - calibrating for all compounds is an insurmountable task
- Strengthening our mechanistic understanding may help
  - Design calibration experiments within a mechanistic framework
  - Play around with sampler design
  - Interpret $R_s$ in terms of rate limiting steps

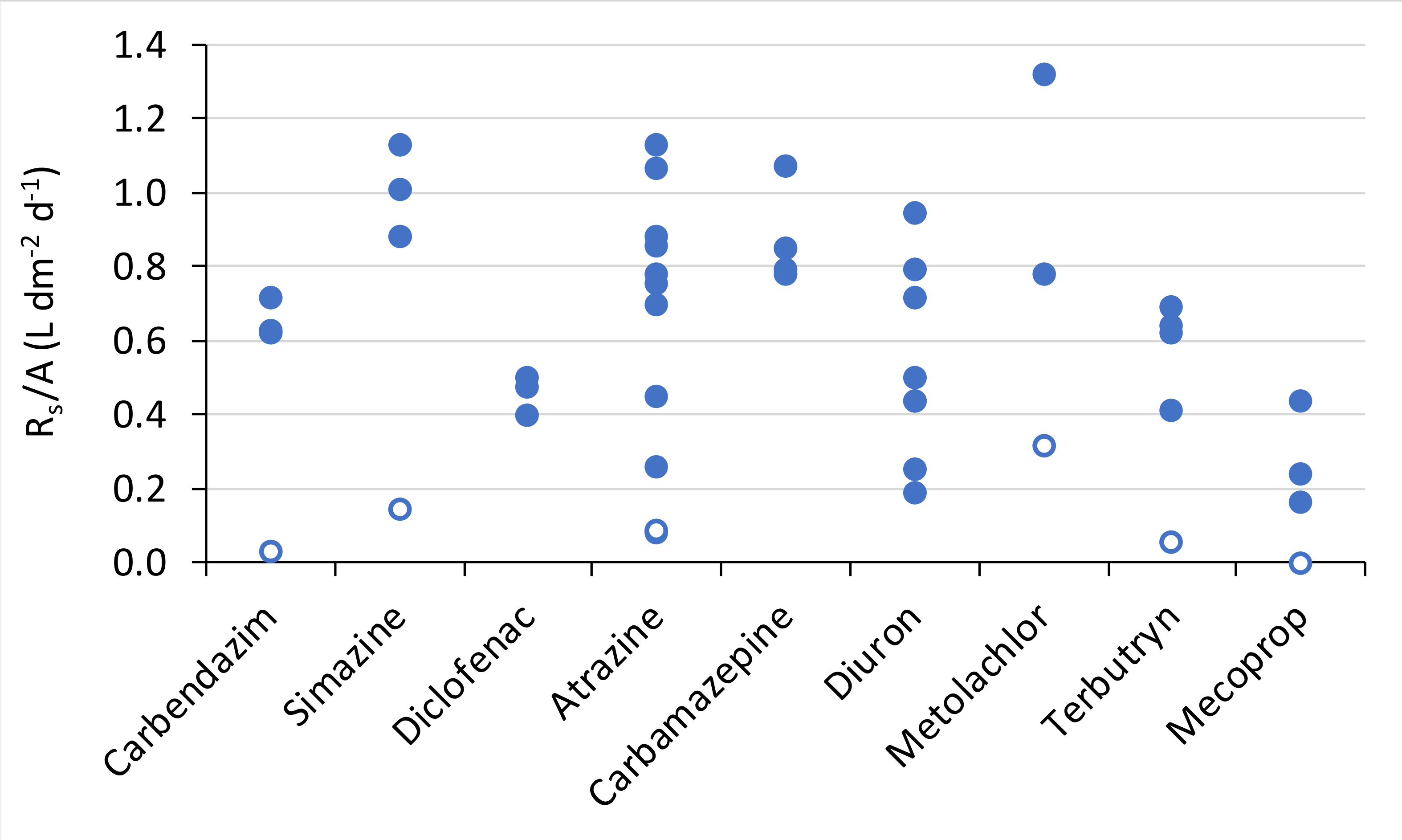
# Scatter in calibration data. Example for Chemcatchers

- Chemcatchers with SDB-RPS sorbent
- with and without membrane: $n > 10$
- $R_s/A$ (areas 0.126, 0.159, 0.35 $dm^2$)
- basically from two labs
- years 2005 - 2019

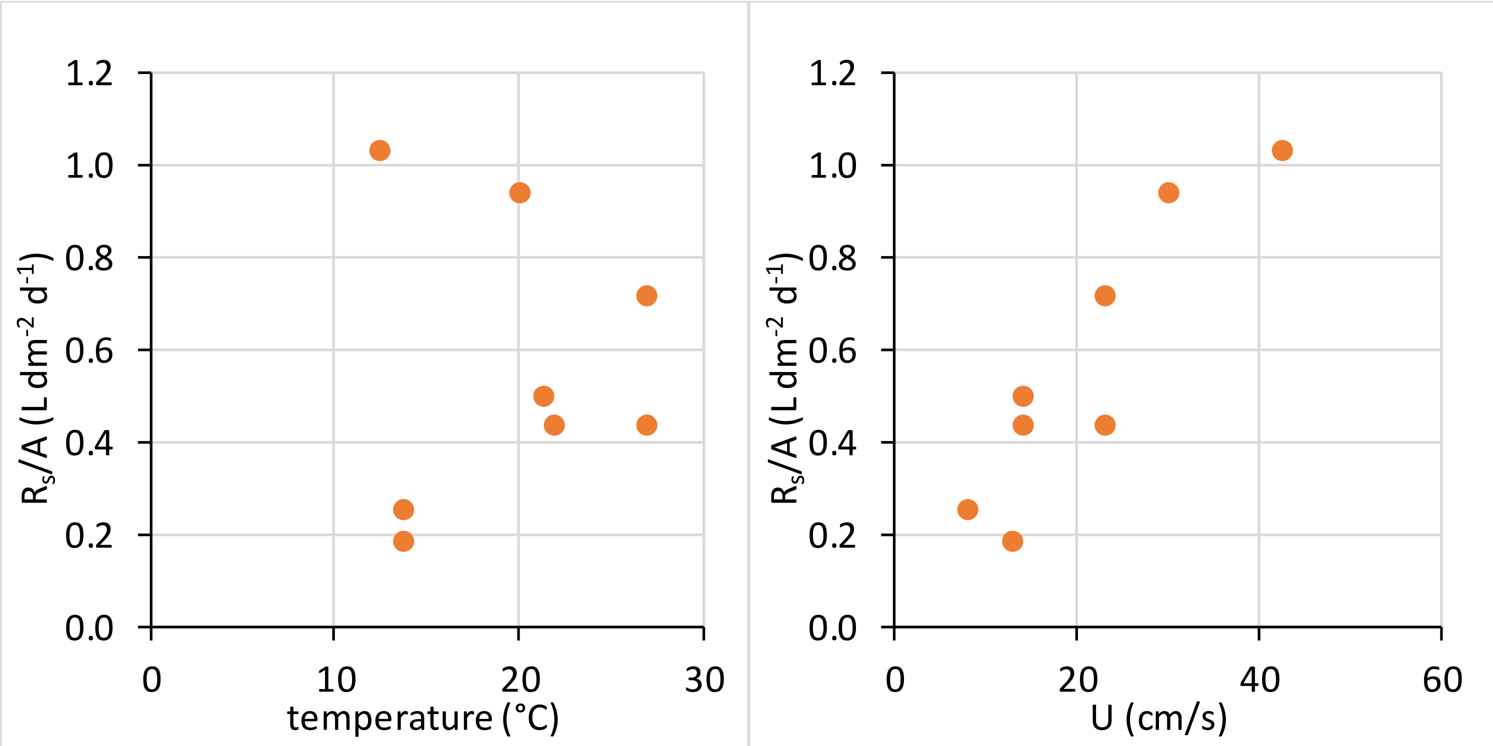
# Chemcatchers without membrane



# Chemcatchers with PES membrane



# Scatter maybe related to temperature and flow?
# Diuron (Chemcatcher with membrane)

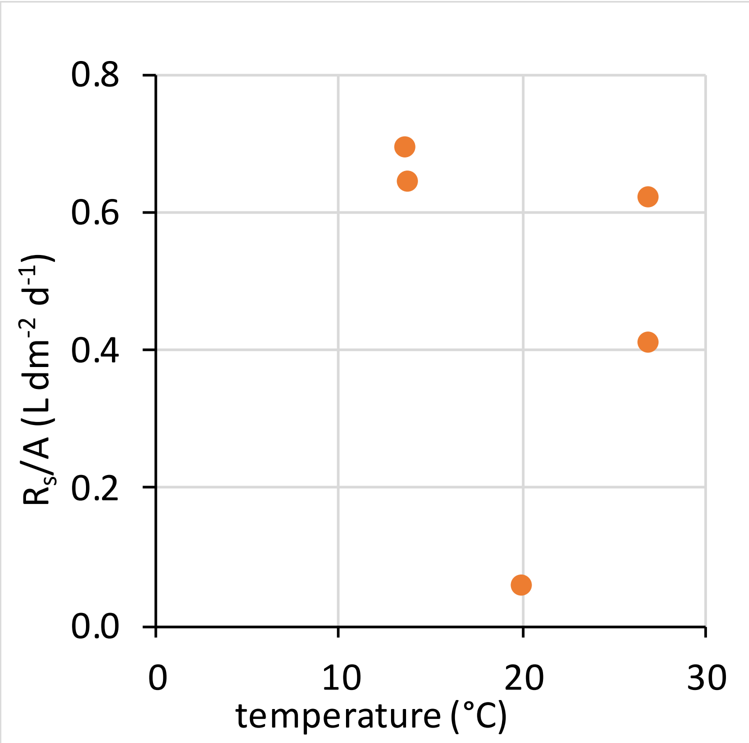


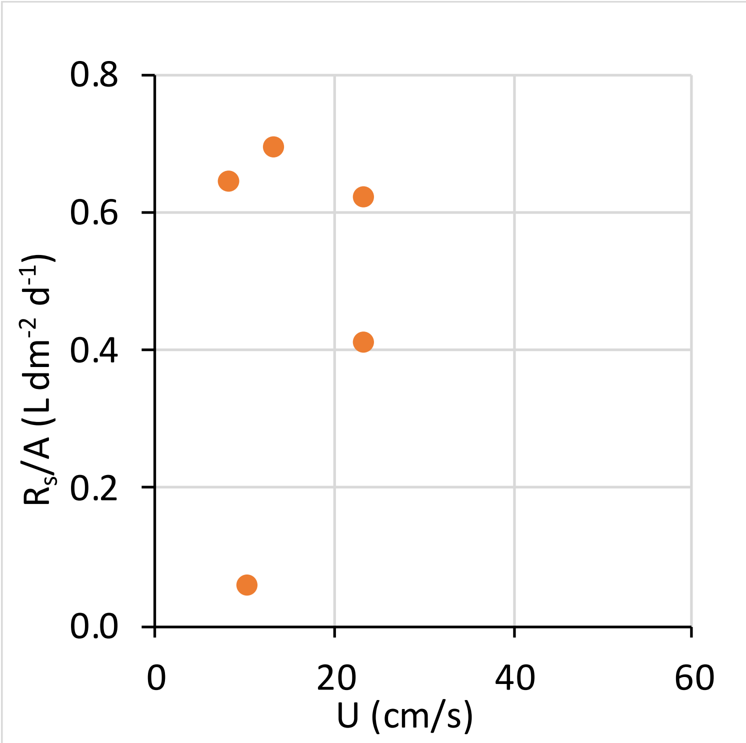

Take $R_s$ from regression equation?

Take the median?

Hard to decide based on statistical considerations

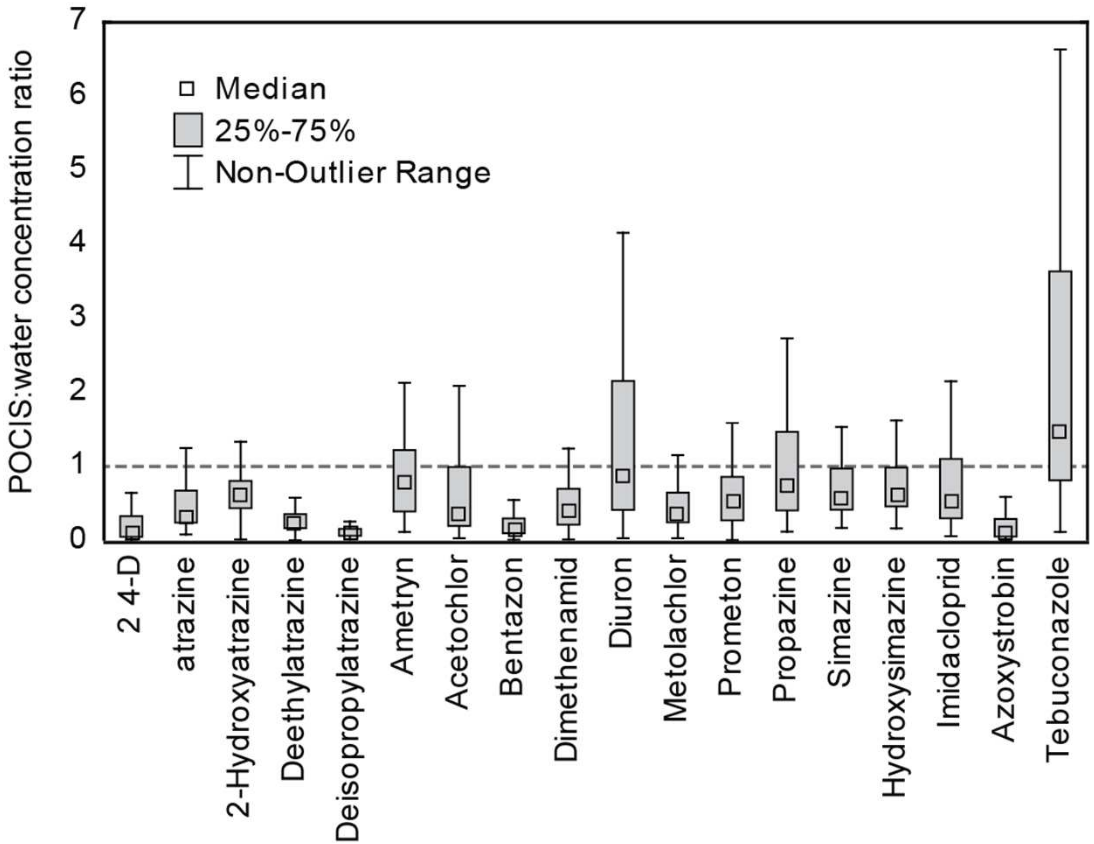
# Scatter maybe related to temperature and flow?
# Terbutryn (Chemcatcher with PES membrane)




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

# Passive vs. active sampling

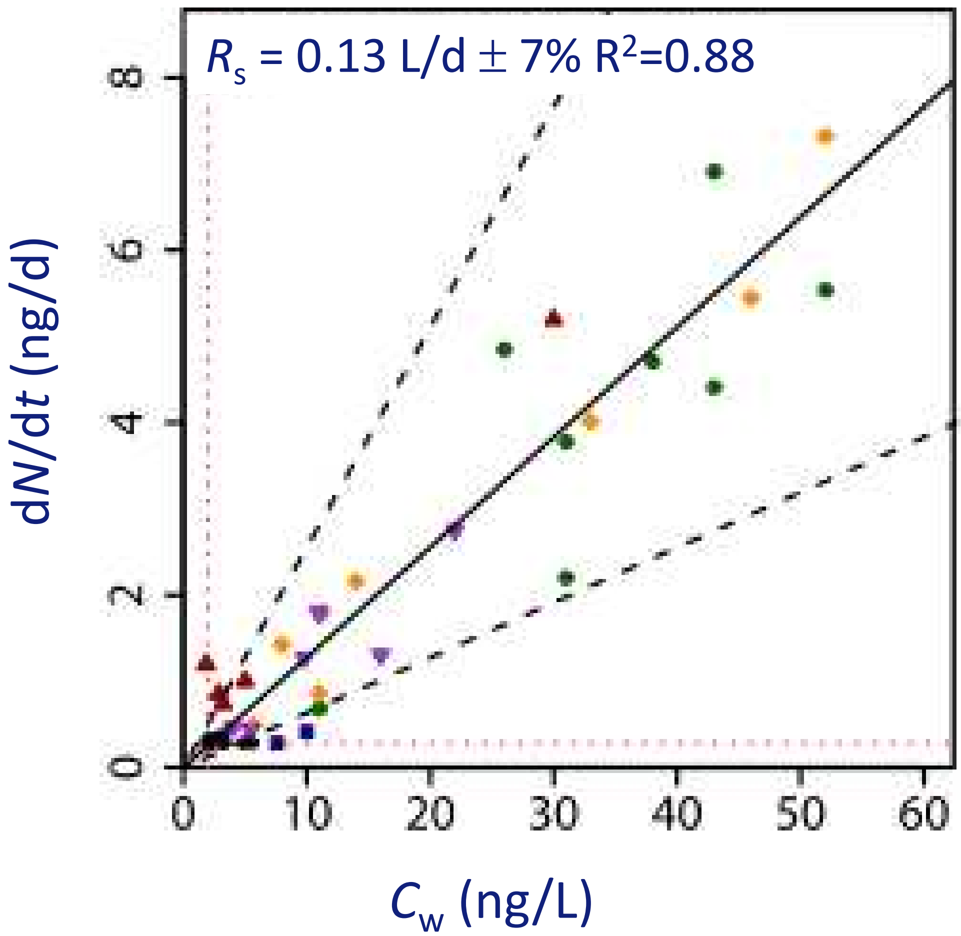



Median passive/active: 0.1 to 1.5

that is an order of magnitude

Van Metre et al. 2017, EnvPoll 220A:431-440

# Do field calibration?




diuron $R_s/A$

| | | |
|---|---|---|
| Five Swiss rivers | : 1.0 | L/(dm$^2$ d) |
| Seven lab calibrations | : 0.2 to 0.9 L/(dm$^2$ d) | |

Moschet et al. 2015 Water Res. 71:306-317

# Series resistance model

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

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

$$\frac{1}{R_{s,max}}$$

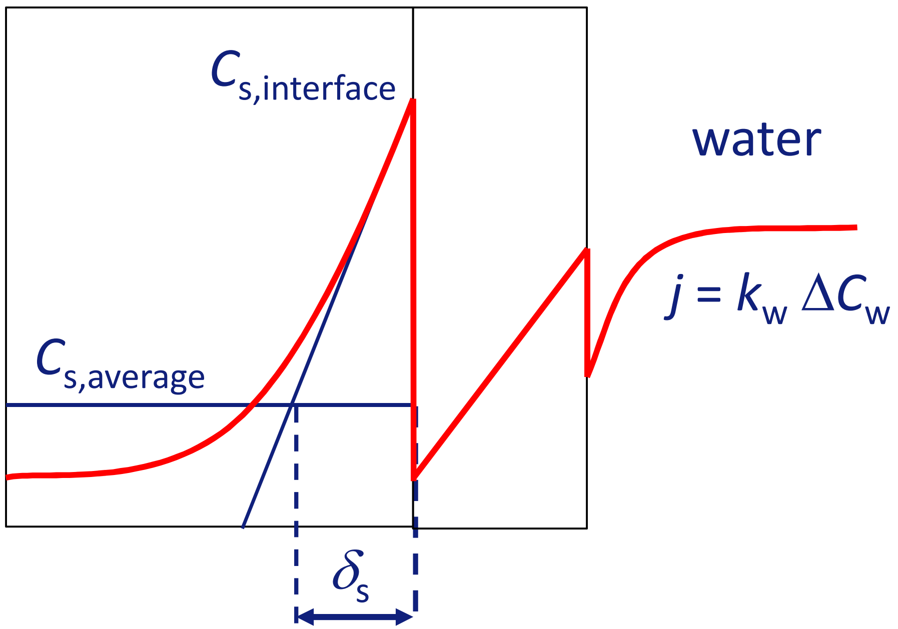
$R_s = k_o A$

sorbent

$j = k_s \Delta C_s$

membrane

$j = k_m \Delta C_m$




$\delta_s$ = SomeConstant $\times$ $d_s$

# Limiting $R_s/A$ for WBL control and membrane control

Full WBL control:

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

$$\frac{R_{s,w} L}{A D_w} = 0.664\ \mathrm{Re}^{1/2}\ \mathrm{Sc}^{1/3}$$

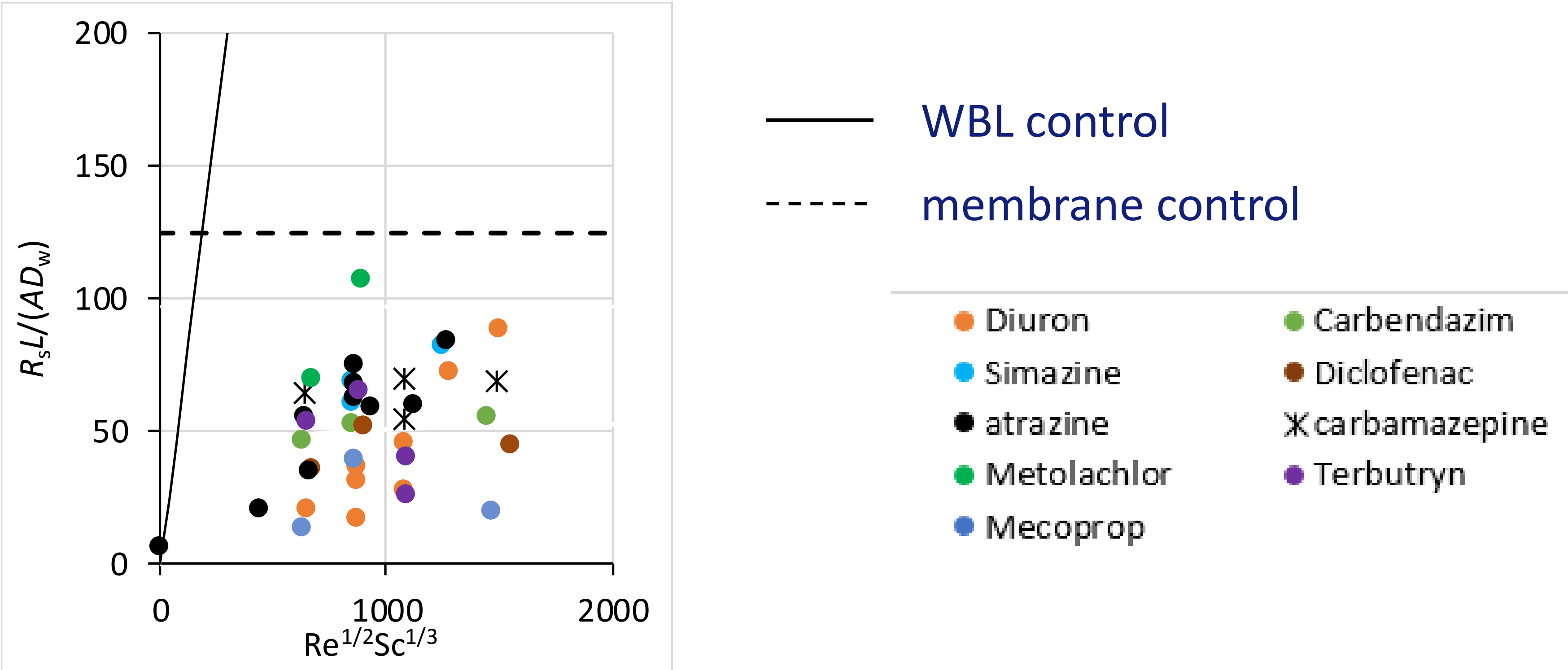
Full membrane control
(transport through pore water only)

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

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

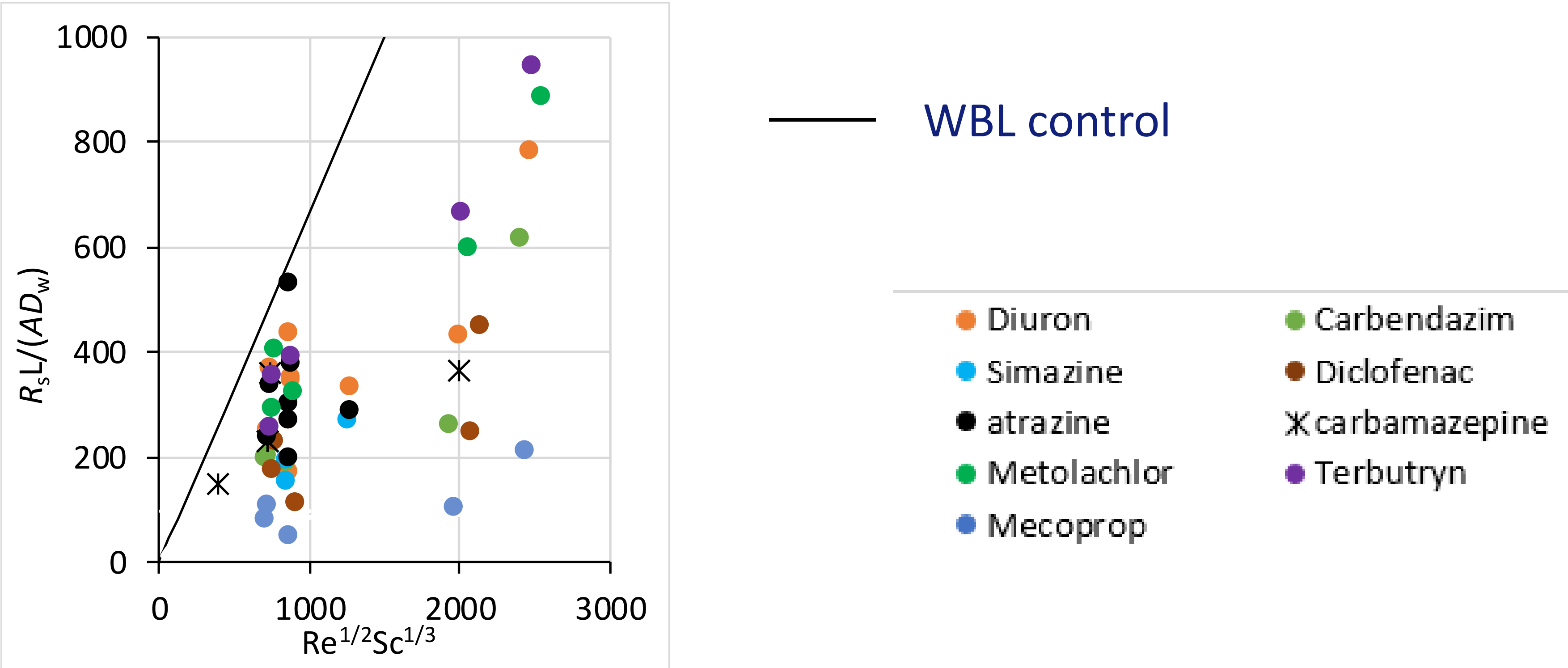
Alvarez et al., 2004. EnvironToxicolChem 23:1640-1648

# Chemcatchers with membrane: some degree of sorbent control:




WBL and membrane allow faster kinetics

# Chemcatchers without membrane: Appreciable degree of sorbent control




WBL allows faster kinetics

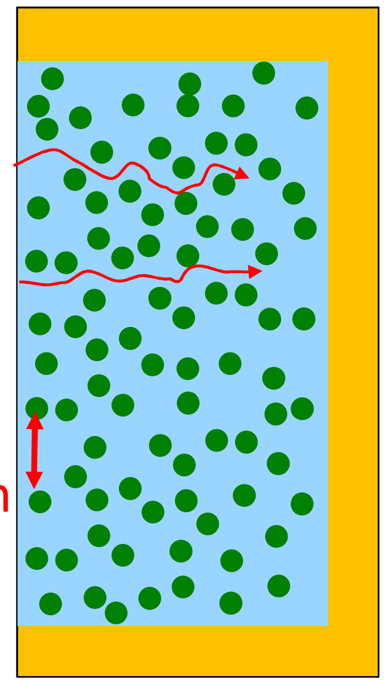
# Intermezzo: Sorbent resistance models are nasty
# Processes not always well understood

Solutions exist if sorbent - pore water equilibrium can be assumed

- From polymers-water exchange, partial sorbent/WBL control
  - Crank, 1975. The Mathematics of Diffusion.
  - Tcaciuc et al., 2015. EnvironToxicolChem 34(12): 2739-2749
- Numerical
  - Endo, Matsuura, Vermeirssen, 2019. EnvironSciTechnol 53: 1482-1489

$$D_s = \frac{\phi \, D_w}{\tau_{w,s}^2 \left[ \phi + \left(1 - \phi\right) \rho_s K_{sw} \right]}$$

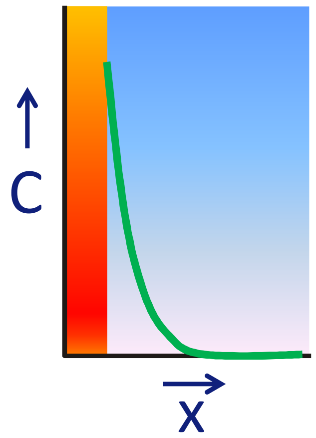
- Sorbent resistance is time dependent. $R_s$ concept breaks down.



# Back to WBL and membrane

- $k_{\mathrm{w}}A$ sets an upper limit to $R_{\mathrm{s}}$ (WBL controlled kinetics)
- $\dfrac{\phi\, D_{\mathrm{w}}}{\tau_{\mathrm{w,m}}^{2} d_{\mathrm{m}}} A$ sets an upper limit to $R_{\mathrm{s}}$ (membrane controlled kinetics)
- Both can be measured with mass transfer sensors (alabaster or otherwise)
  - with membrane : $\dfrac{1}{k_{\mathrm{o,1}}A} = \dfrac{1}{k_{\mathrm{w}}A} + \dfrac{\tau_{\mathrm{w,s}}^{2} d_{\mathrm{m}}}{\phi\, D_{\mathrm{w}} A}$
  - without membrane : $\dfrac{1}{k_{\mathrm{o,2}}A} = \dfrac{1}{k_{\mathrm{w}}A}$

# Experimental: calibrate under controlled $k_w$ conditions




$$\frac{dN}{dt} = k_w A \left( C_w^* - C_w \right)$$

Measure $k_w$ with

- alabaster dissolution rates
- benzoic acid dissolution rates
- PRC dissipation in LDPE or silicone
- limiting currents (electrochemical)

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

| | | |
|---|---|---|
| experi-mental | flow dependent | compound/sampler dependent |

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

$k_w A \approx R_s$ ? $\Rightarrow$ full WBL control

$k_w A >> R_s$ ? $\Rightarrow$ no flow effects

# Experimental: manipulate membrane thickness

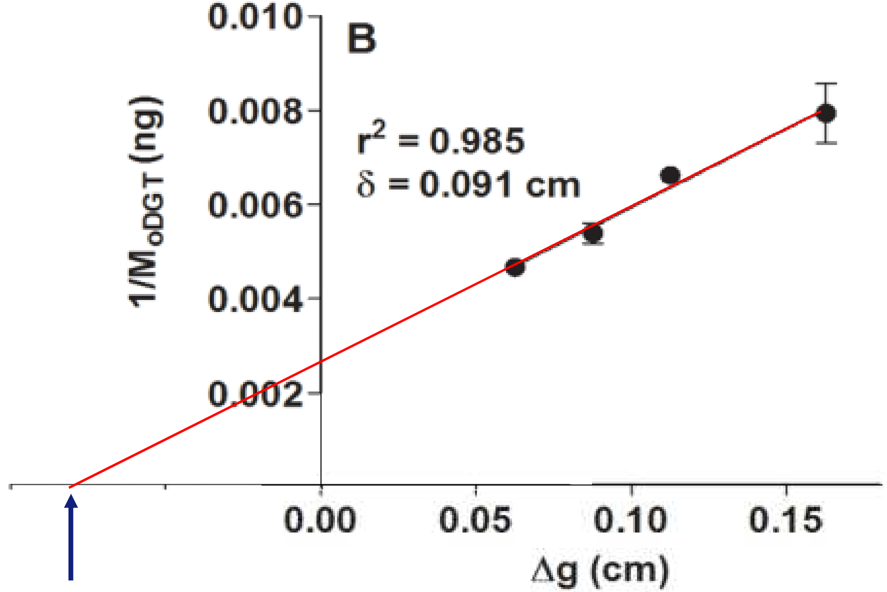
$1/R_s$ vs. number of membranes ($n$ = 0, 1, 2,...)

$$\frac{1}{R_s / A} = \frac{1}{k_w} + \frac{\delta_s}{D_s K'_{sw}} + n \frac{d_m}{D_m K'_{mw}}$$

experi-mental | intercept | slope

$M_{oDGT} = C_w R_s t$

$M_{oDGT} \sim R_s$

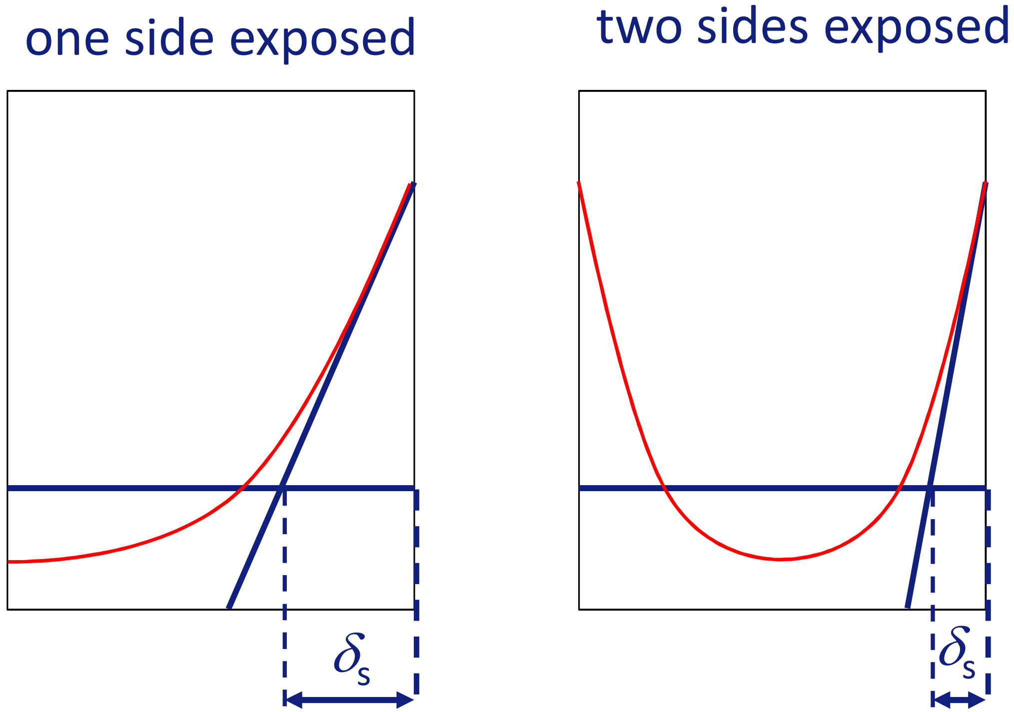



0.075 cm = 750 μm

Challis et al. 2016, AnalChem 88(21): 10583-10591

# Experimental: manipulate sorbent thickness

| sides exposed | one | two |
|---|---|---|
| compound | $R_s$ (L/d) | $R_s$ (L/d) |
| tebuthiuron | 0.48 | 1.53 |
| hexazinone | 0.48 | 1.57 |
| simazine | 0.46 | 1.48 |
| atrazine | 0.68 | 1.78 |
| diuron | 0.59 | 1.58 |
| amethryn | 0.75 | 1.38 |




Shaw & Mueller 2009, EnvironSciTechnol 43:1443-1448

# Invitation

- Put experimental $R_s$ into perspective
  - Report $R_s$ together with measured $k_w$
  - Characterise the membrane with measured $\frac{\tau_{w,s}^2 d_m}{\phi}$
- Establish relationship between $k_w$, $U$, temperature for your sampler in the field

$$\text{POCIS inside canister}: \frac{k_w L}{D_w} = 0.21\ \mathrm{Re}^{1/2}\ \mathrm{Sc}^{1/3}\ ?$$

$$\text{POCIS outside canister}: \frac{k_w L}{D_w} = 0.41\ \mathrm{Re}^{1/2}\ \mathrm{Sc}^{1/3}\ ?$$

# Summary

- Large between-study variability in $R_s$
  - Analytical variability (experimental variability?) may be an issue
- Framework for interpreting measured $R_s$ is needed (rate control by WBL/membrane/sorbent)
  - Easily done for WBL and membrane controlled kinetics
  - More challenging for sorbent controlled kinetics
  - $R_s$ measurement under varying $k_w$, membrane thickness, sorbent thickness may yield very valuable insights.
- I am happy to support

Thank you for listening.
Happy to discuss further.