Field calibration of POCIS for atrazine sampling in small headwater streams

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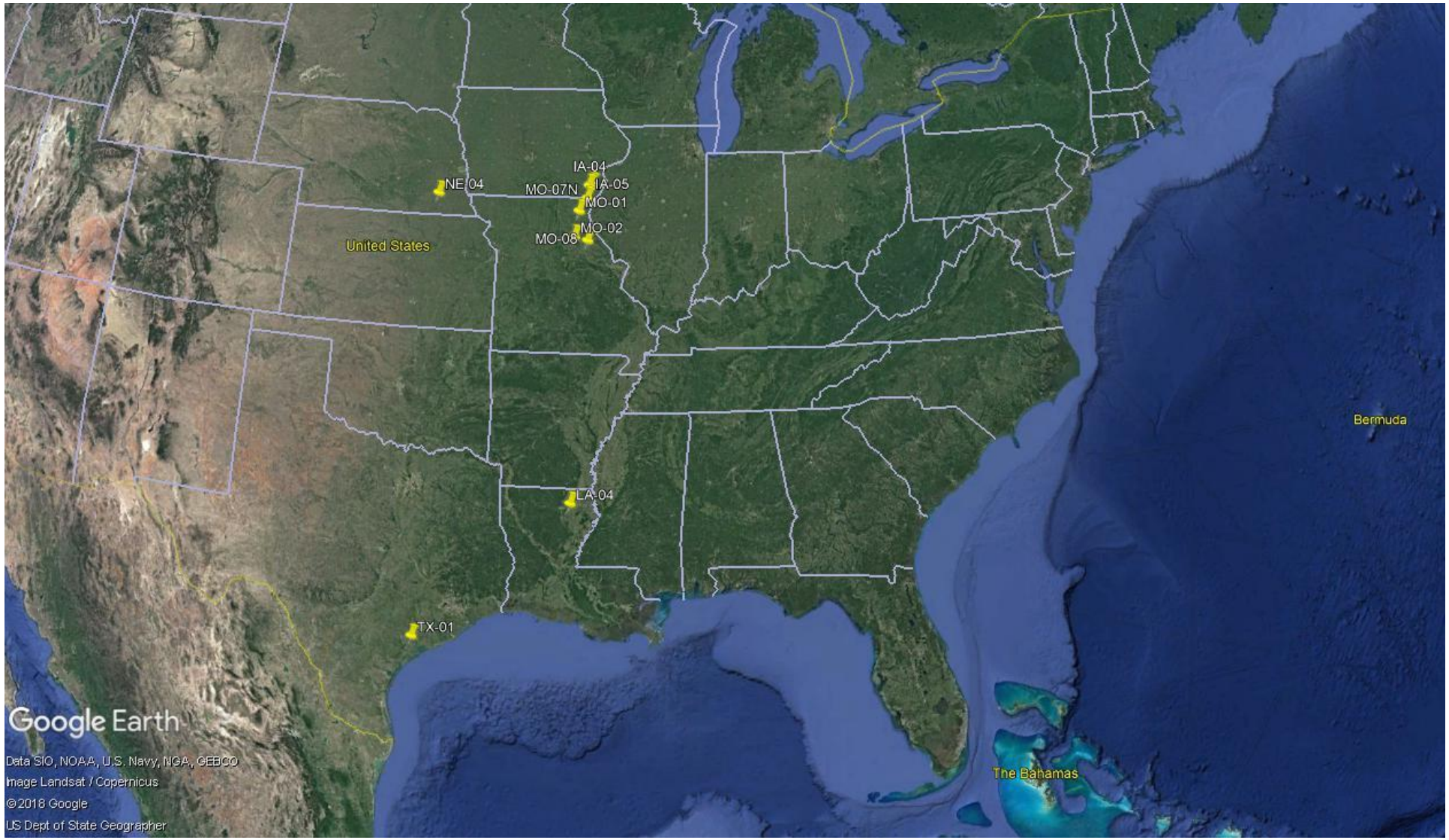
Content

- study design
- effects of flow and temperature
- relationship between k_w inside canister to flow outside canister
- mass transfer model for atrazine uptake
- conclusions

Study Design

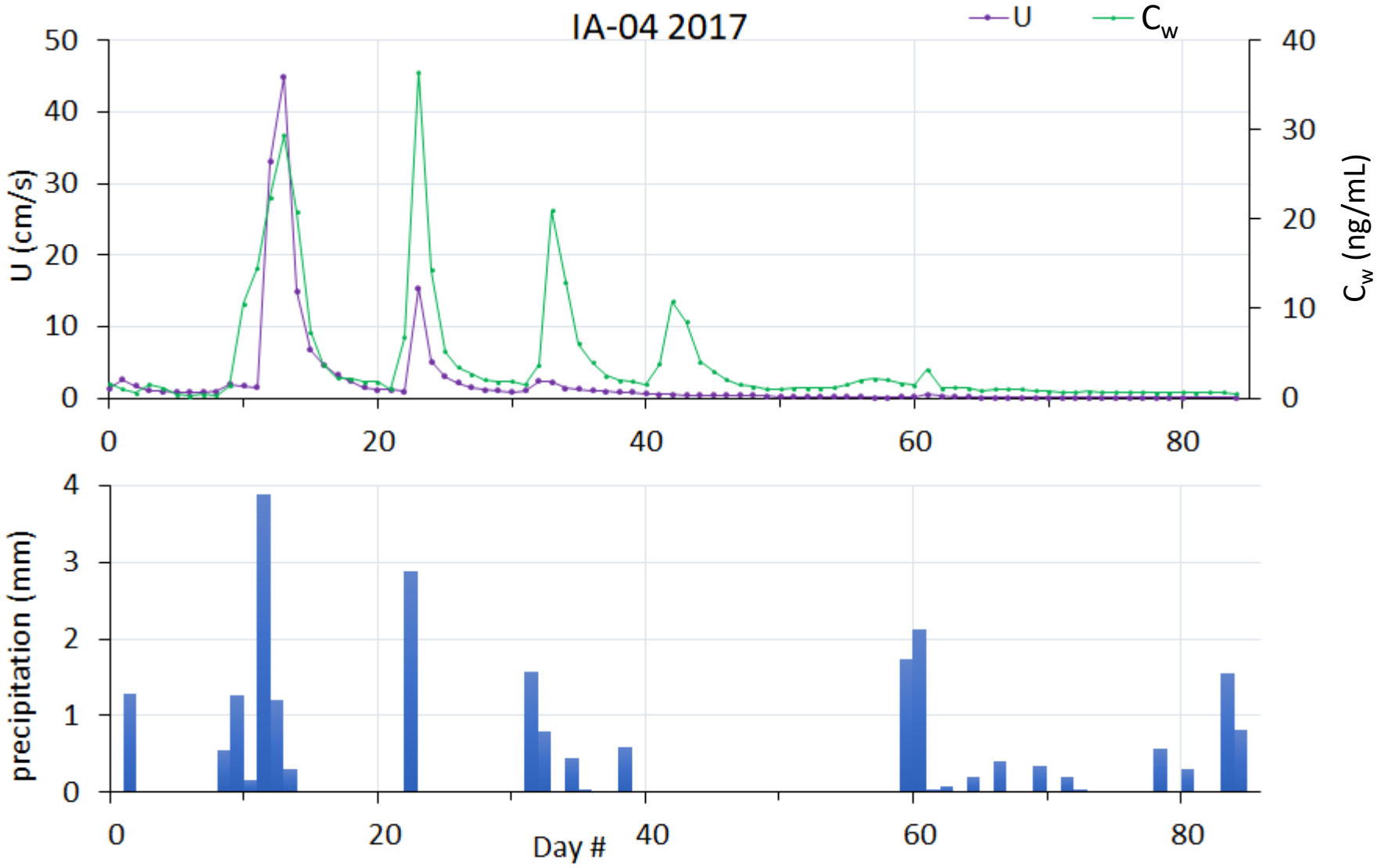
- 3 years (2016, 2107, 2018), 9 agricultural sites, 4 to 6 exposure periods of 2 to 3 weeks, 149 sampling rate data
- continuous water sampling with ISCO samplers
- measurement of flow velocities and temperatures
- pictures of sorbent distributions before and after exposure (2018)
- measurement of flow attenuation by POCIS canisters

Study Locations

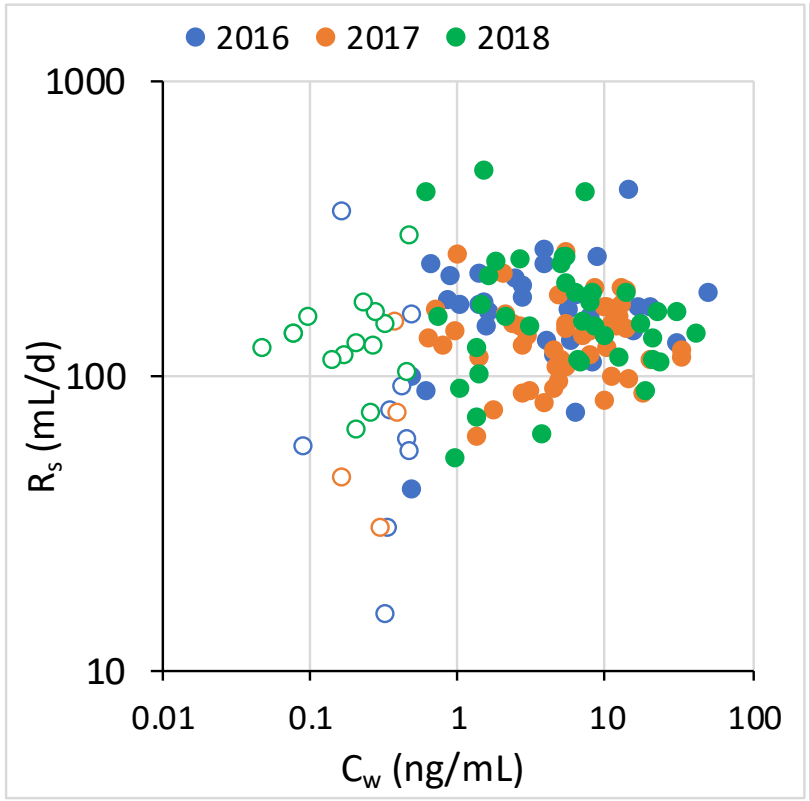


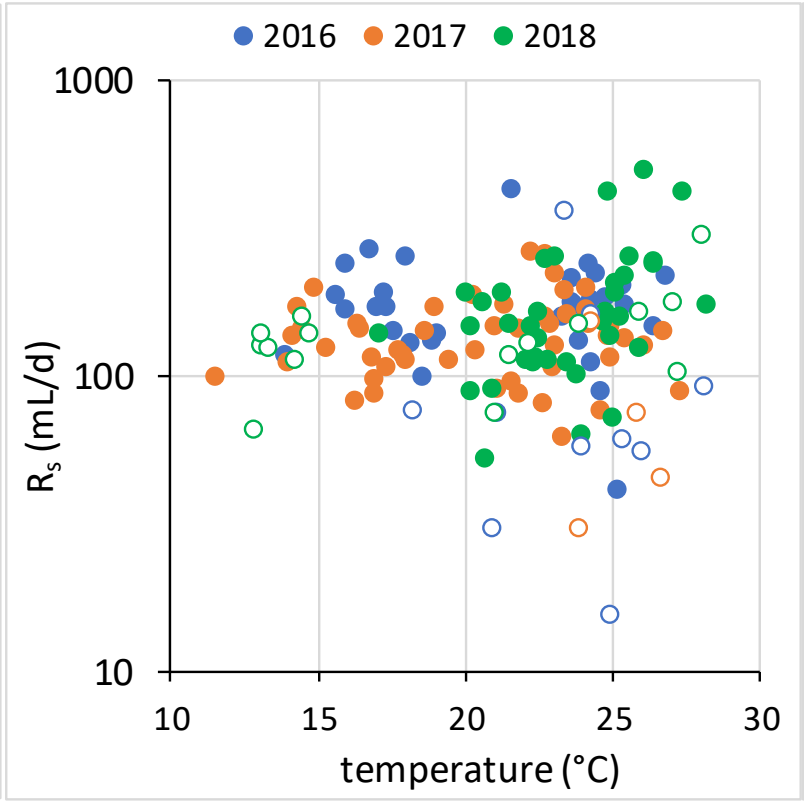
A Representative Monitoring Site

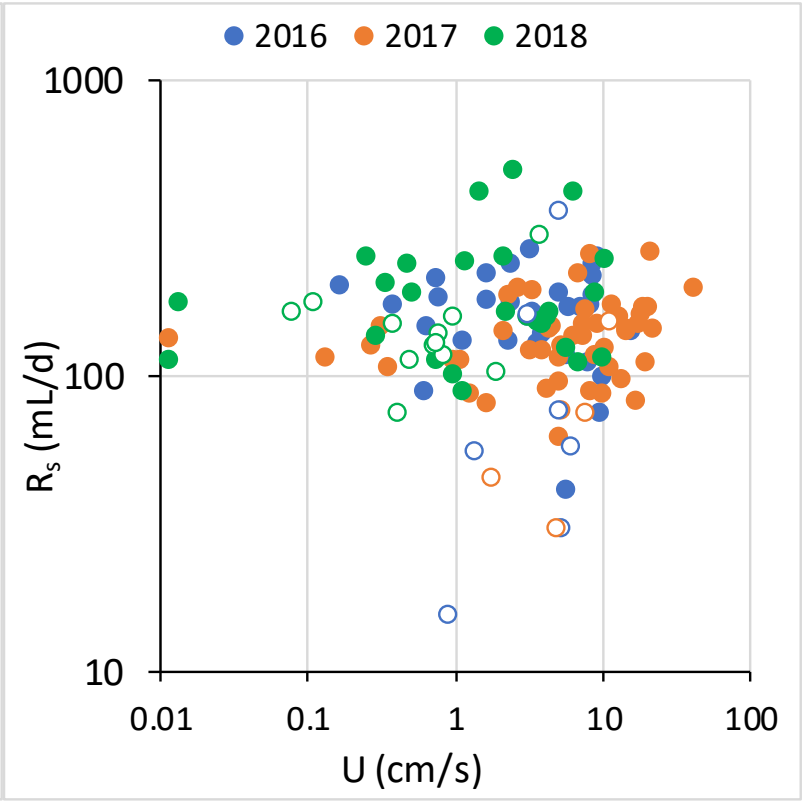
Highly variable concentrations, related to flow and precipitation



No flow and temperature effects on R_s visible
95% of the R_s between 64 and 334 mL/d

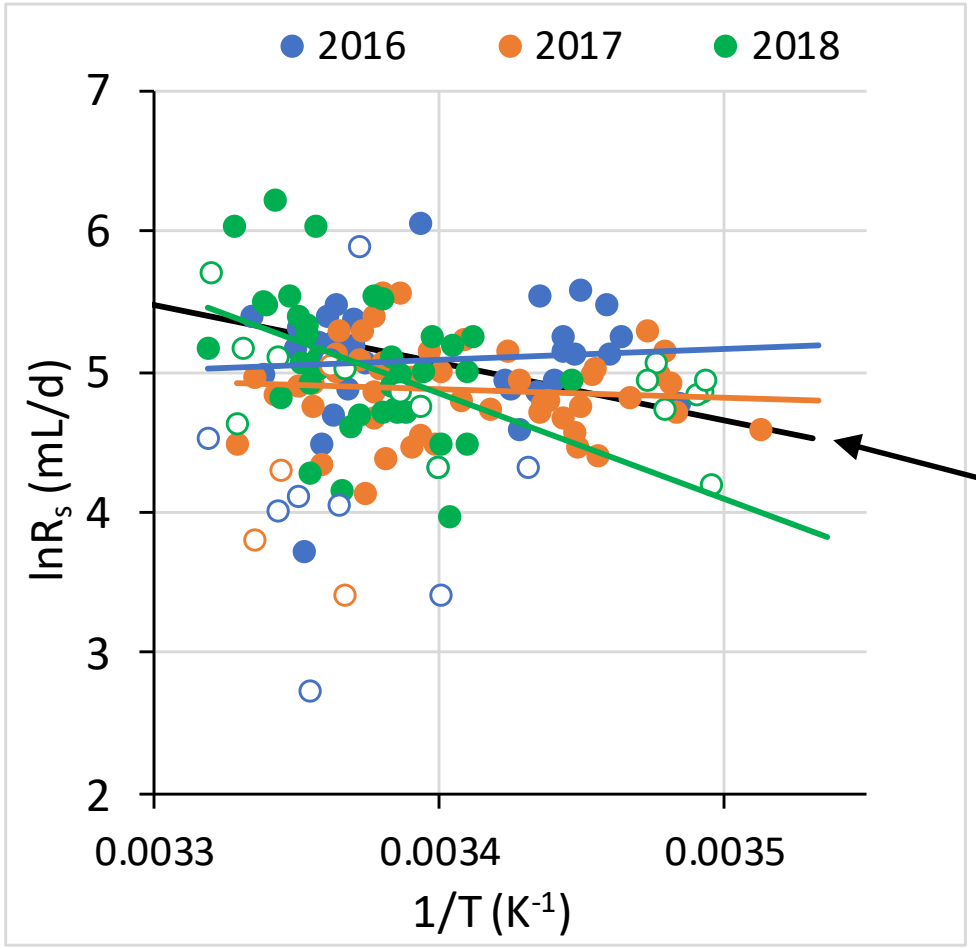






open symbols: C_w < 0.5 ng/mL

R_s-Temperature relationship (Arrhenius plot)



Literature (Toteu-Djomte et al. 2018)

Expected temperature effect (factor 2.6) is obscured by other factors

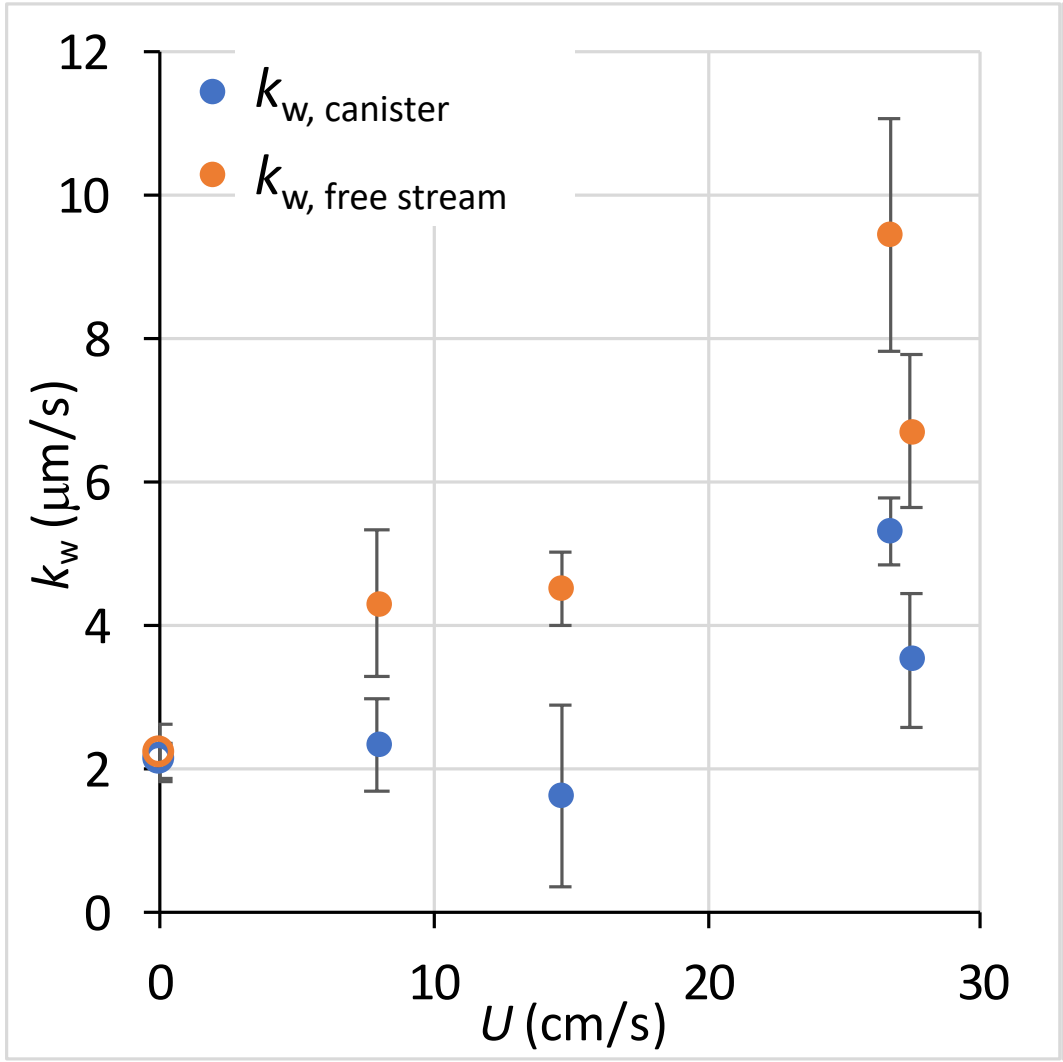
Does the canister flatten out flow effects on R_s?

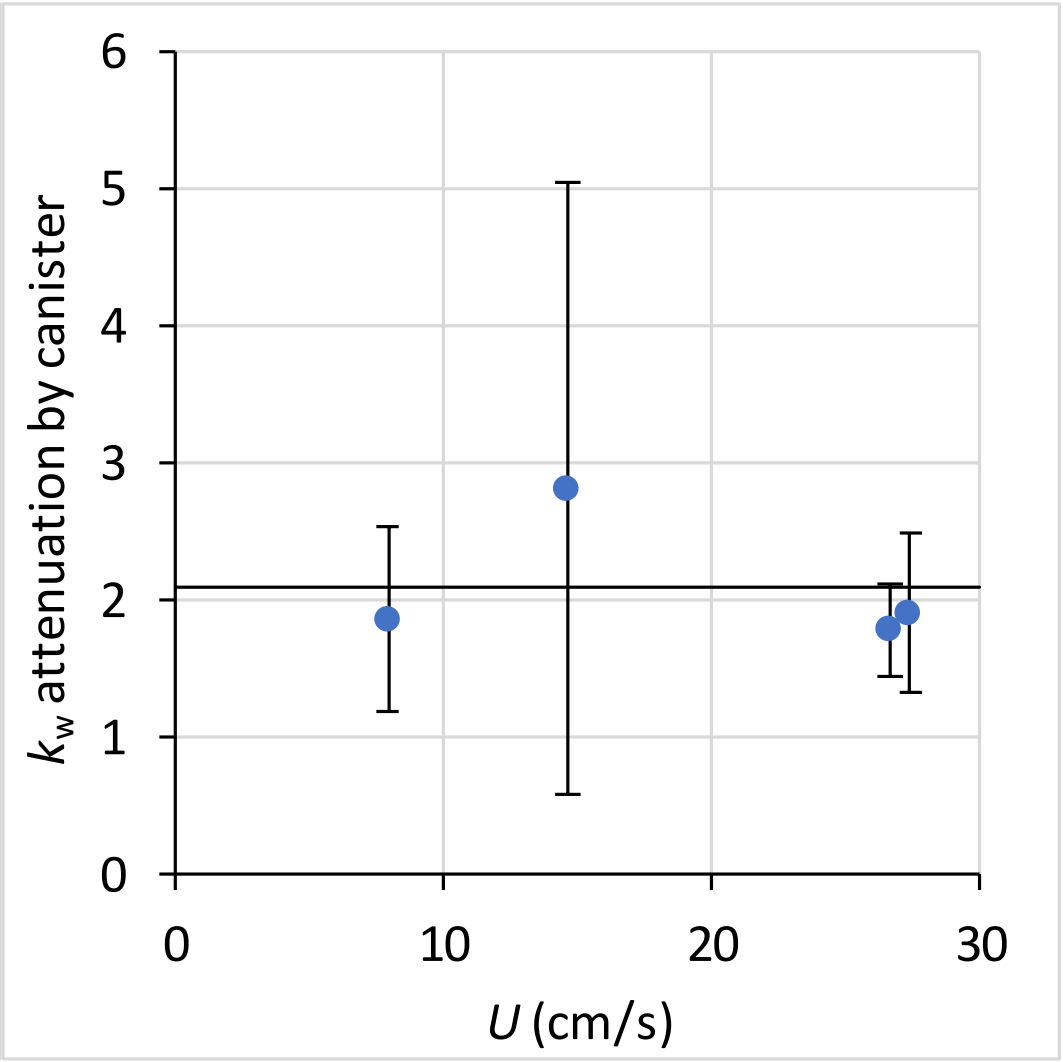
alabaster plate outside canister

alabaster plate inside canister

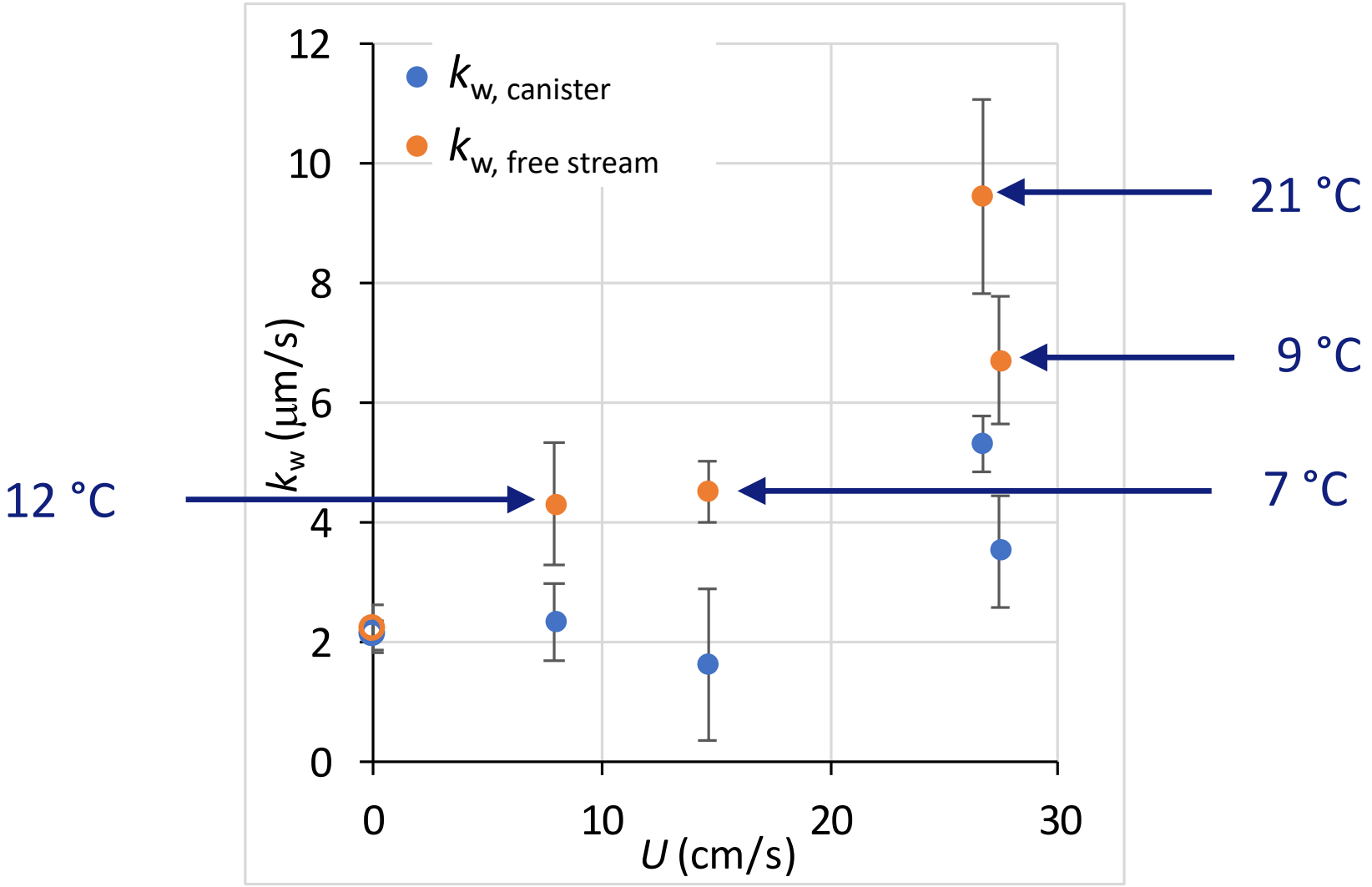
pictures by Waterborne Environmental Inc

The canister effects on k_w at all U



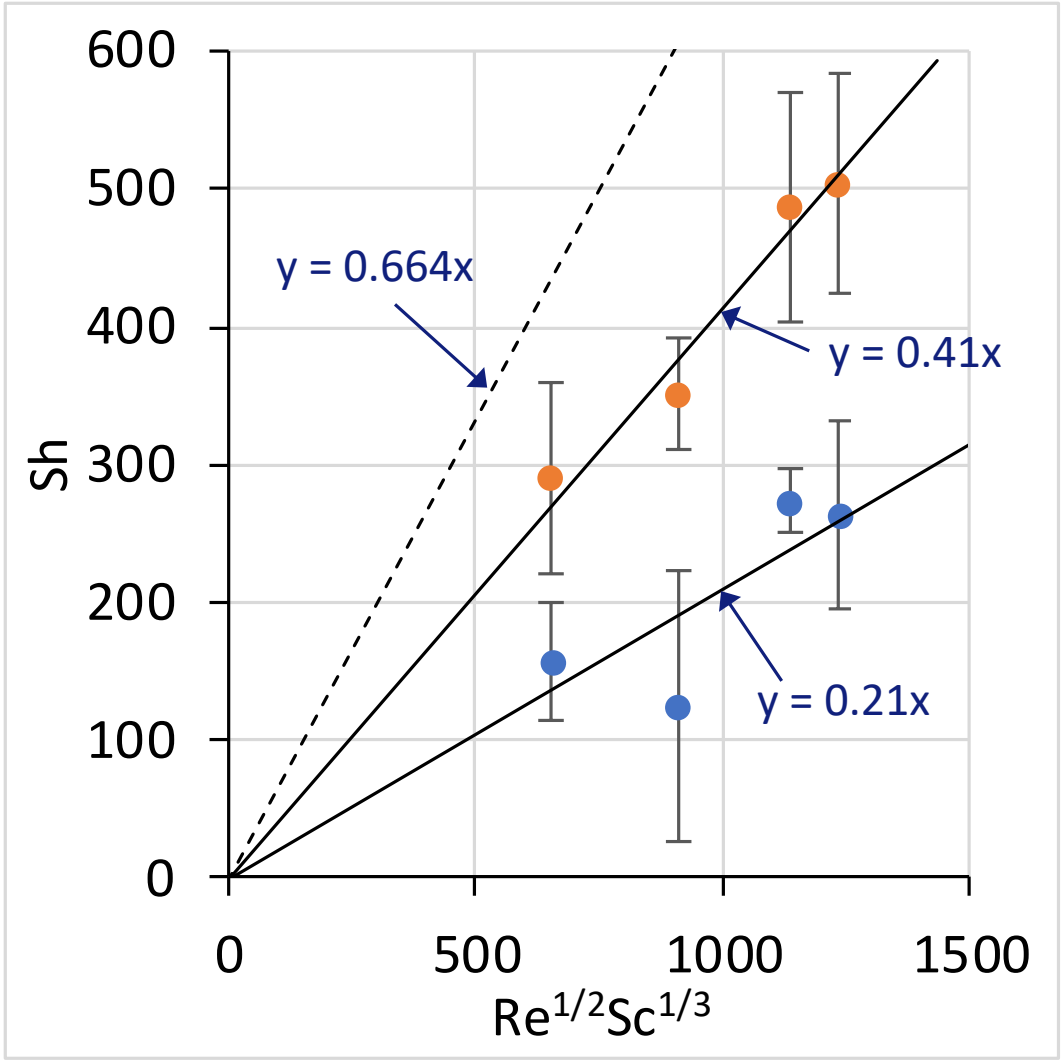


k_w is not a simple function of U



.... but Sh is a simple function of $Re^{1/2}Sc^{1/3}$

k_w inside canister can be linked to U outside canister



$$Sh = \frac{k_w L}{D_w}$$

$$Re = \frac{UL}{\nu}$$

$$Sc = \frac{\nu}{D_w}$$

laminar flow, parallel with flat plate

$Sh = 0.664\ Re^{1/2}Sc^{1/3}$ (dashed line)

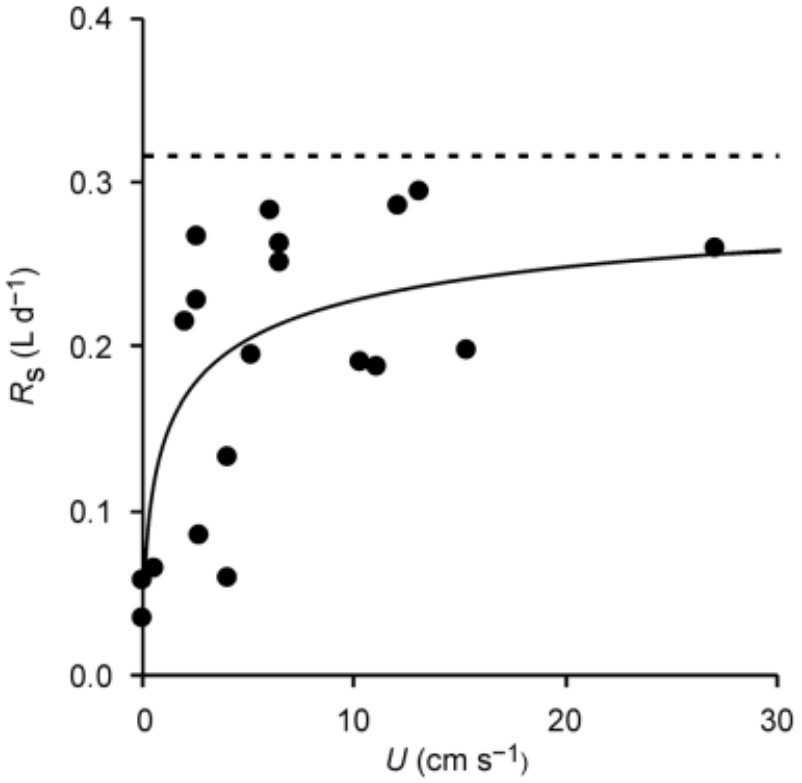
POCIS outside canister (orange)

$Sh = 0.41\ \ Re^{1/2}Sc^{1/3}$

POCIS inside canister (blue)

$Sh = 0.21\ \ Re^{1/2}Sc^{1/3}$

Mixed WBL-membrane control model



literature review data
(Booij & Chen, 2018)

Assume:

- diffusion through pore space only
- sorbent acts as infinite sink

$$\frac{1}{R_s} = \frac{1}{k_w A} + \frac{1}{R_{s,max}} \qquad R_{s,max} = \frac{\phi D_w}{\tau_w^2 d} A$$

cast in dimensionless form:

$$\frac{1}{\left(\frac{R_s\ L}{A\ D_w}\right)} = \frac{1}{0.21\ \mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}} + \frac{1}{\left(\frac{\phi\ L}{\tau_w^2 d}\right)}$$

Overall WBL membrane

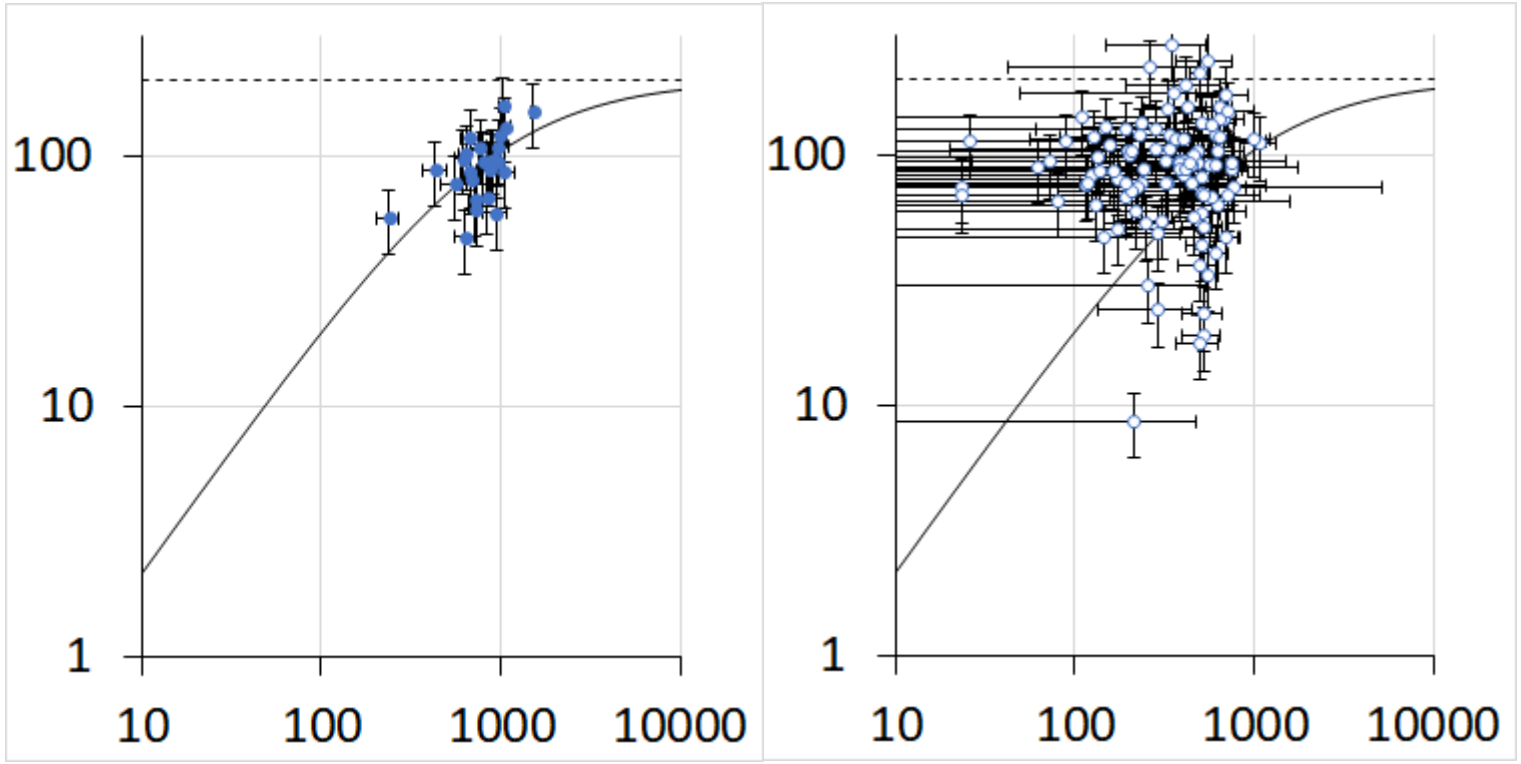
$$\mathrm{Sh} = \frac{k_w L}{D_w} \qquad \mathrm{Re} = \frac{UL}{\nu} \qquad \mathrm{Sc} = \frac{\nu}{D_w}$$

Model could only be tested for a small (17%) part of the data due to large uncertainty in *U*

$$\frac{1}{\left(\frac{R_s\ L}{A\ D_w}\right)} = \frac{1}{0.21\ Re^{1/2}Sc^{1/3}} + \frac{1}{\left(\frac{\phi\ L}{\tau_w^2 d}\right)}$$

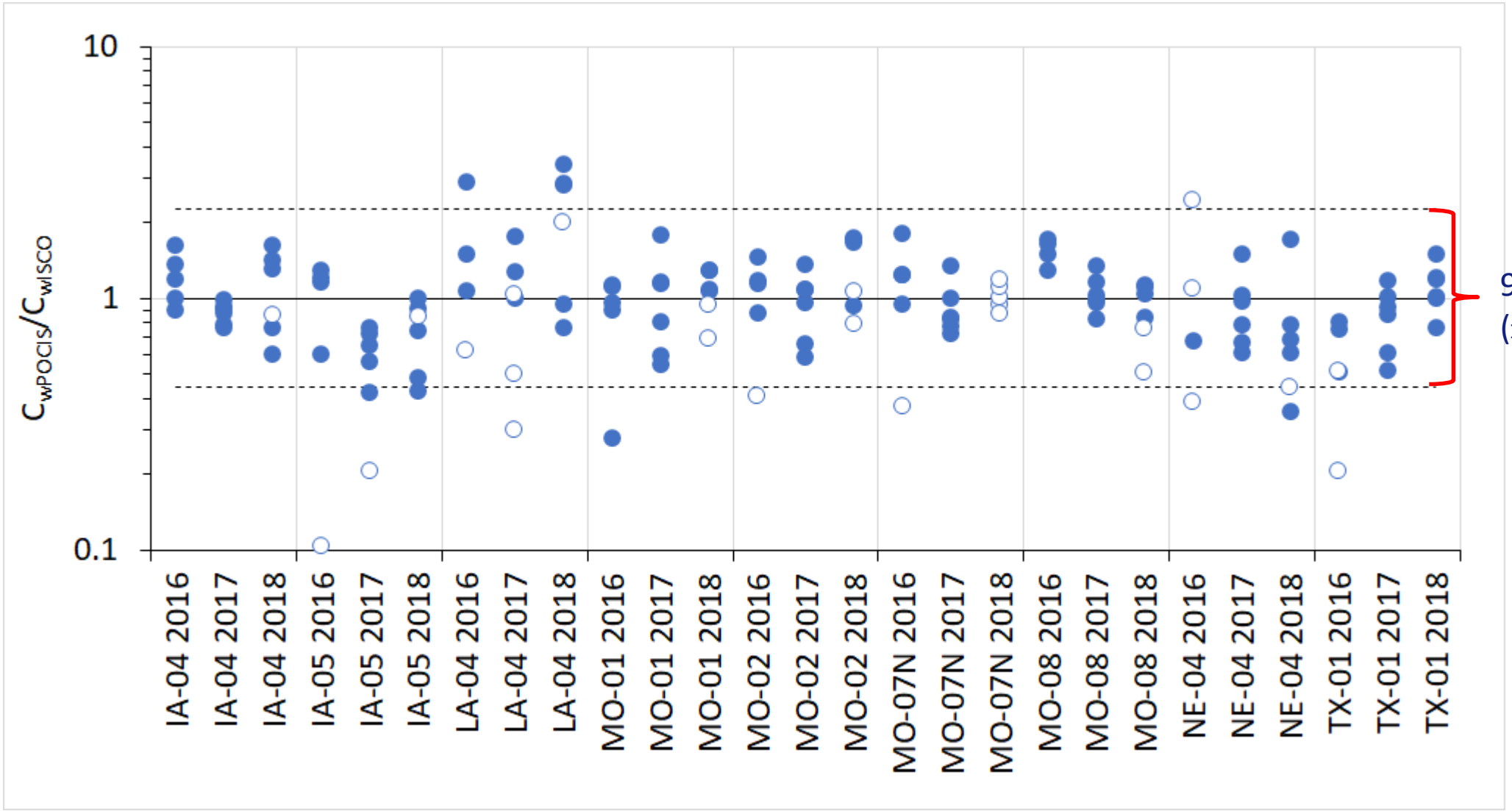
U values with small uncertainty

U values with large uncertainty

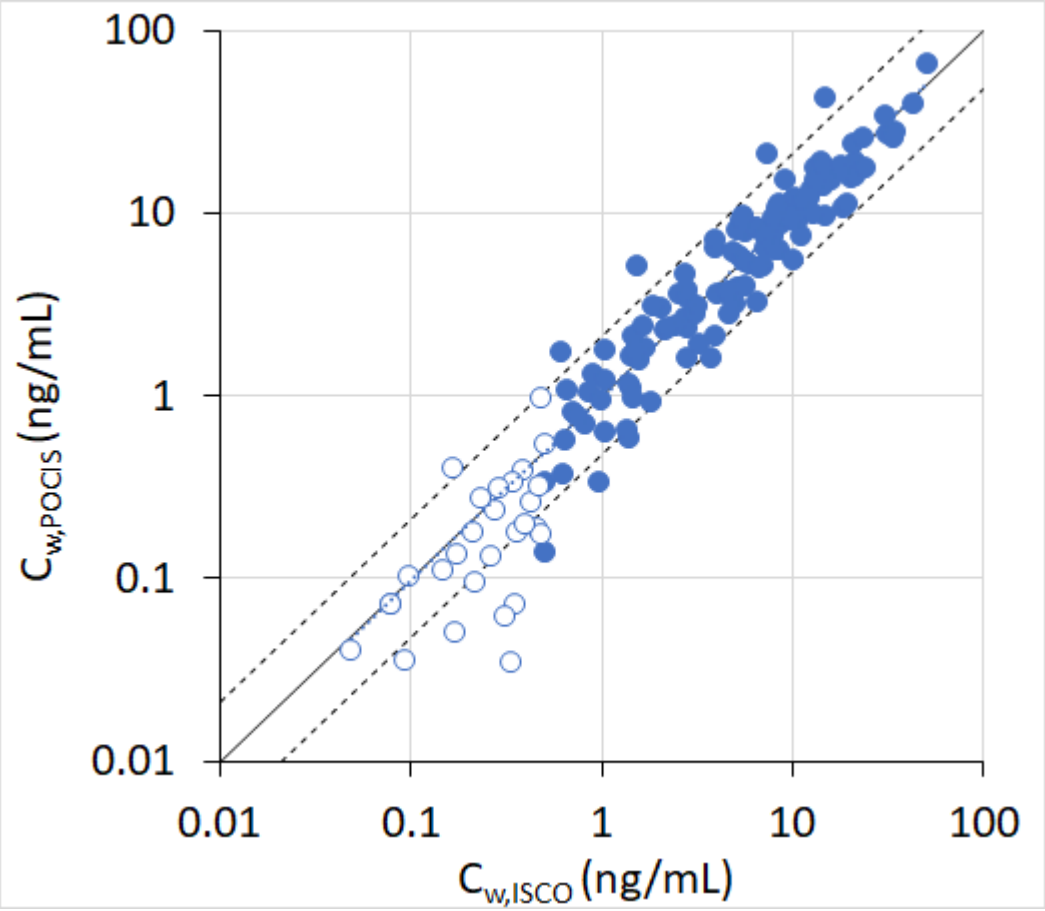


Exchange surface area
11 cm^2
Exposed membrane area
46 cm^2

So far, R_s = 147 mL/d is the best available model applicable to all sites and years



1:1 correspondence of $C_{w,POCIS}$ and $C_{w,ISCO}$



Drawn line = 1:1 relationship

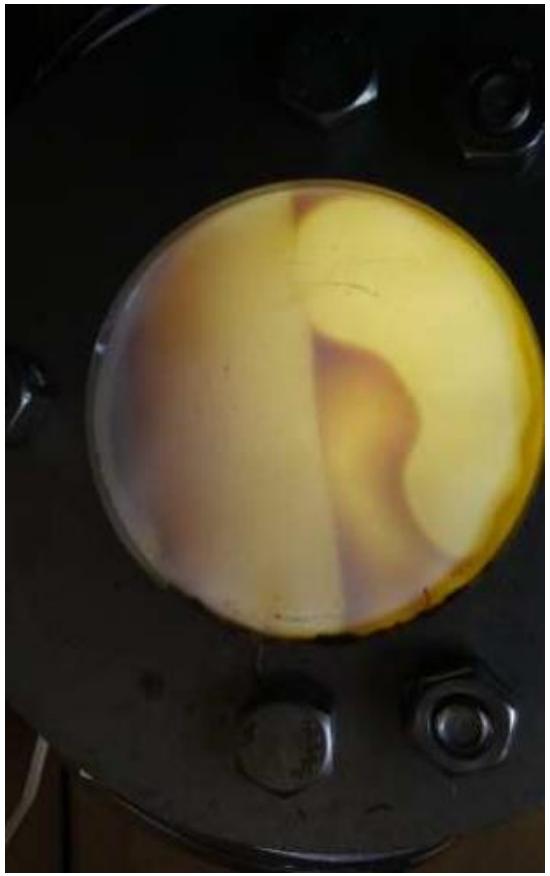
Dashed lines span the 95% confidence range

Open symbols: $C_{w,ISCO}$ < 0.5 ng/mL

Exchange surface area is time variable (Sorbent moving around in the membrane envelope)

before deployment

at mid-term check



after deployment

Conclusions

- Presently best available method for modeling atrazine sampling rates is to adopt a temperature and flow independent sampling rate of 147 mL/d.
- POCIS based concentrations showed a 1:1 relationship with ISCO with a precision factor of 1.5 (standard deviation) or 2.3 (95% confidence level).
- Flow effects are not reduced by the POCIS canisters
- An engineering approach in modeling could be useful (dimensionless numbers)
- Variability of factor 1.5 may be related to
  - sorbent coverage of the membrane
  - fouling (the usual suspect)
- POCIS offers potential as an alternative to conventional sampling method

Acknowledgments

- The field work was carried out by Waterborne Environmental Inc. on behalf of Syngenta
- Kees Booij acknowledges financial support by Syngenta