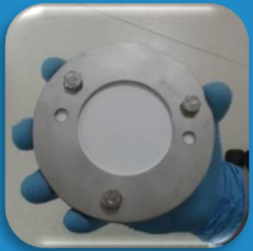
Measuring POCIS sampling rates (Rs) of 44 pharmaceuticals in lab-scale artificial river with various flow conditions

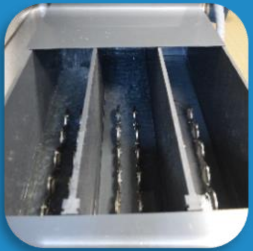
Proposition of mathematical equation to estimate pharmaceuticals Rs

Guibal Robin, Lissalde Sophie*, Guibaud Gilles

Research Group on Water, Soil and Environment (Peirene – EA 7500 – URA IRSTEA), University of Limoges, 123 Avenue Albert Thomas, 87060 Limoges Cedex, FRANCE

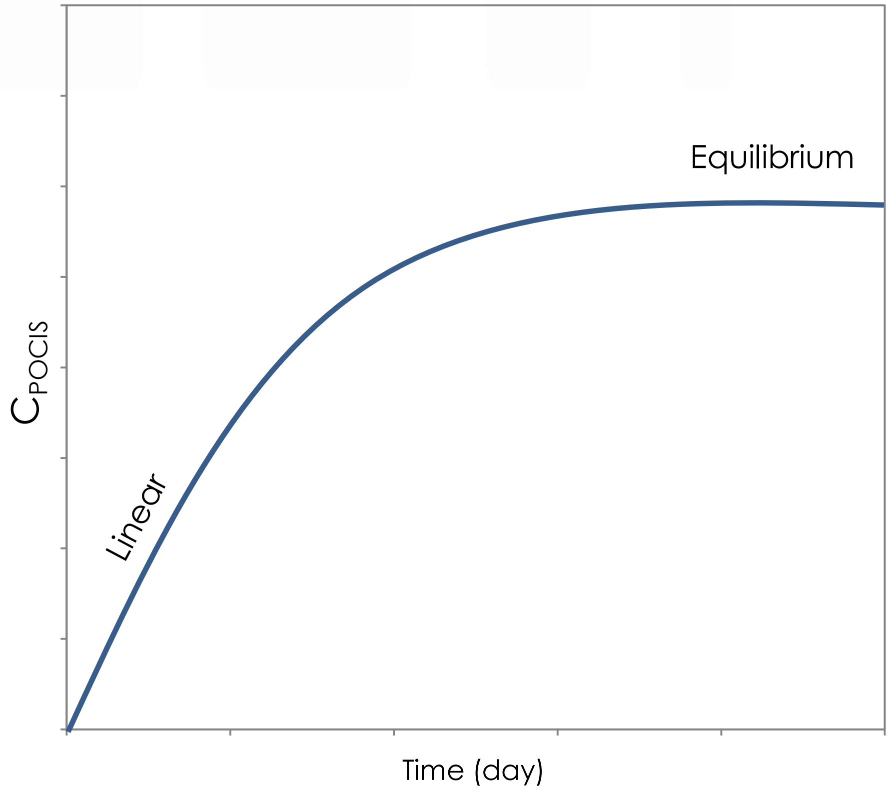
*sophie.lissalde@unilim.fr





Context

- Evaluate water quality regarding micropollutants: passive sampler is a complementary method to grab sampling
- Time-weighted average concentration (TWAC = C_w)
- POCIS especially used for neutral pesticides and pharmaceuticals



- POCIS theory
  - $C_{POCIS} = C_w \times k_u \times t$
  - $Rs = k_u \times m_{sorbent}$

- Rs = sampling rate: compound dependent

→ **Sampling rates calibration**

Context

POCIS calibration in literature: numerous protocols using different volumes and materials

Beaker

- 1L: Alvarez *et al.*, 2004, Arditsoglou *et al.*, 2008 ; Thomatou *et al.*, 2011 and Charlestra *et al.*, 2012
- 2L: Bartelt-Hunt *et al.*, 2011 and Martinez-Bueno *et al.*, 2009

Tank

- 2L: Togola and Budzinski 2007
- 3L: Li *et al.*, 2010; MacLeod *et al.*, 2007 and Metcalfe *et al.*, 2014
- 7L: Di Carro *et al.*, 2014
- 20L: Bailly *et al.*, 2013
- 27L: Belles *et al.*, 2014
- 30L: Zhang *et al.*, 2008
- 80L: Mazzella *et al.*, 2007; Lissalde *et al.*, 2011; Fauvelle *et al.*, 2012 and Poulier *et al.*, 2014
- 95L: Ahrens *et al.*, 2015

Artificial channel

- Lotufo *et al.*, 2018

In situ

- Channels: Harman *et al.*, 2011; Ibrahim *et al.*, 2013

Context

POCIS calibration in literature: numerous protocols using different volumes and materials

Beaker

Tank

Artificial channel

Different agitation modes and water quality parameters

Quiescent

Stirred

pH ; DOC ; temperature…

- Aim of the study:
  - Estimate Rs of pharmaceuticals in laboratory conditions close to environmental conditions
  - Mathematical equation to estimate Rs

Material and method

- 44 pharmaceuticals
- Polar Organic Chemical Integrative Sampler (POCIS)
  - Duplicate
  - Blank POCIS
- Lab deployment: **1, 3, 5, 7, 10, 15 and 21 days**
- Temperature measured by Tinytag

- **Tap water** spiked at **0.5 µg/L** by each pharmaceutical
- Water sampling (evry 2 or 3 days)
- **4 flow velocities** investigated for Rs determination:

- V0 = 0 cm/s → **Tank filled with 200 L of tap water**

- V1 = 2-3 cm/s
- V2 = 6-7 cm/s
- V3 = 20 cm/s

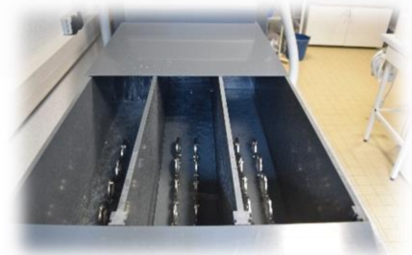
→ **Lab-scale artificial River filled with 500 L of tap water**

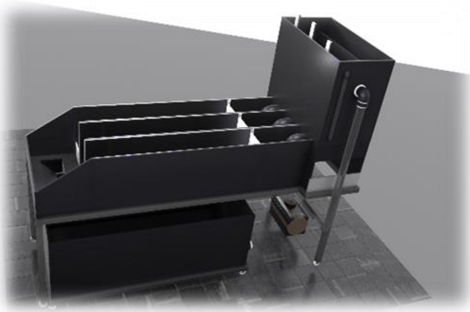
Material and method – Calibration experiment

Tank

- Volume: 200 L
- Flow velocity: 0 cm/s

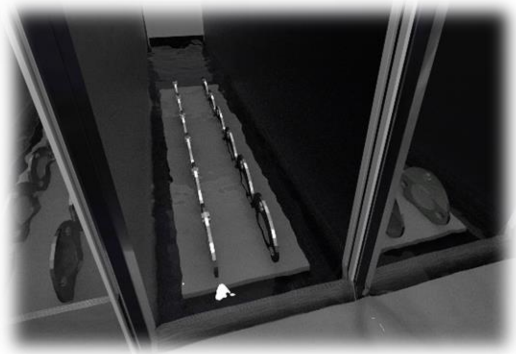
Material and method – Calibration experiment

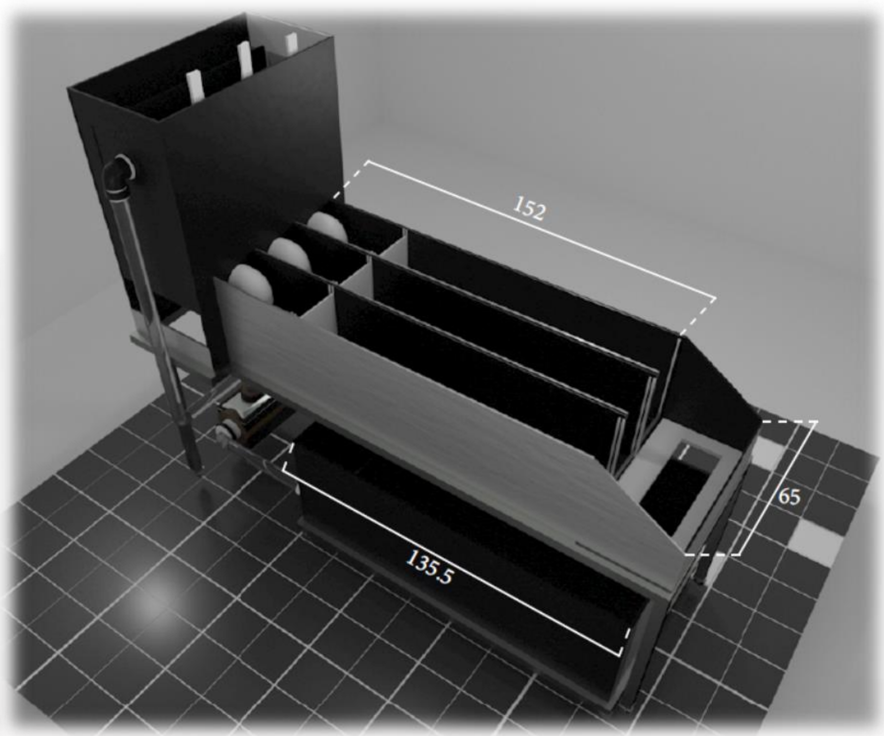


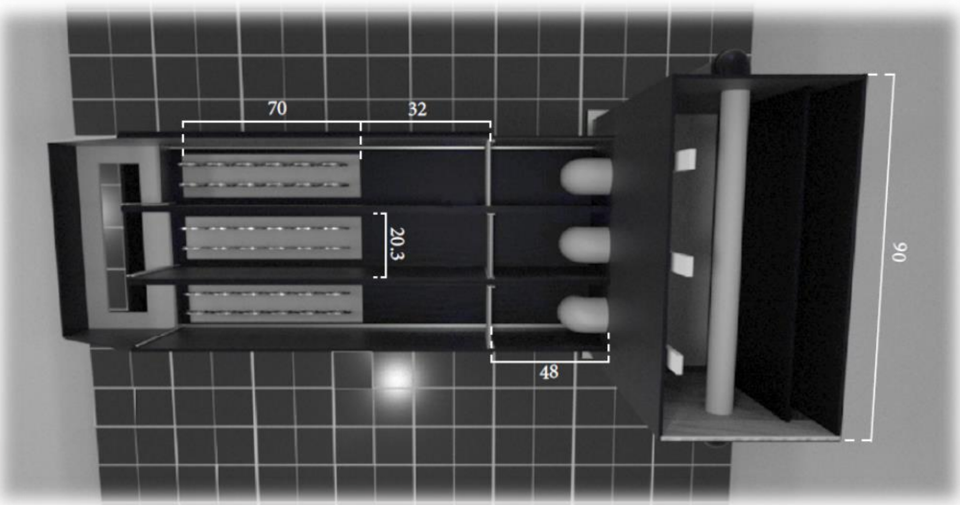


Lab-scale artificial River

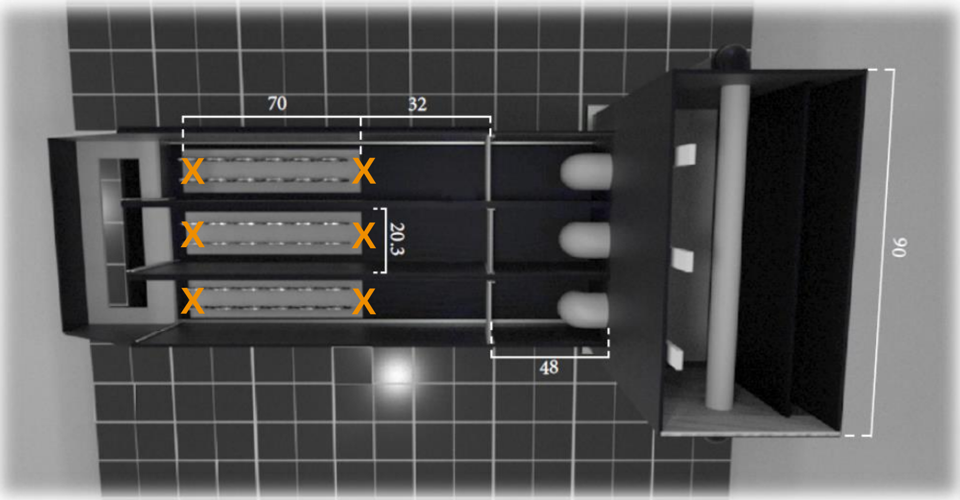
- Volume: 500 L
- Pump flow rate: 13 m^3/h
- HRT : 139s
- Flow velocities: 3 channels:
    - 2-3 cm/s
    - 6-7 cm/s
    - 20 cm/s
- 12 POCIS / channel



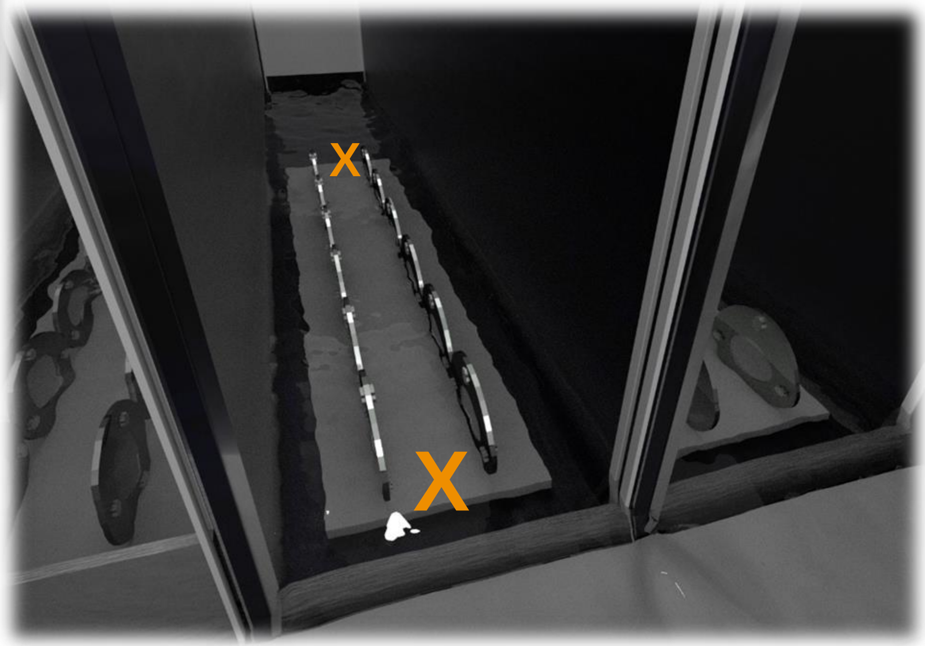




Material and method – Calibration experiment

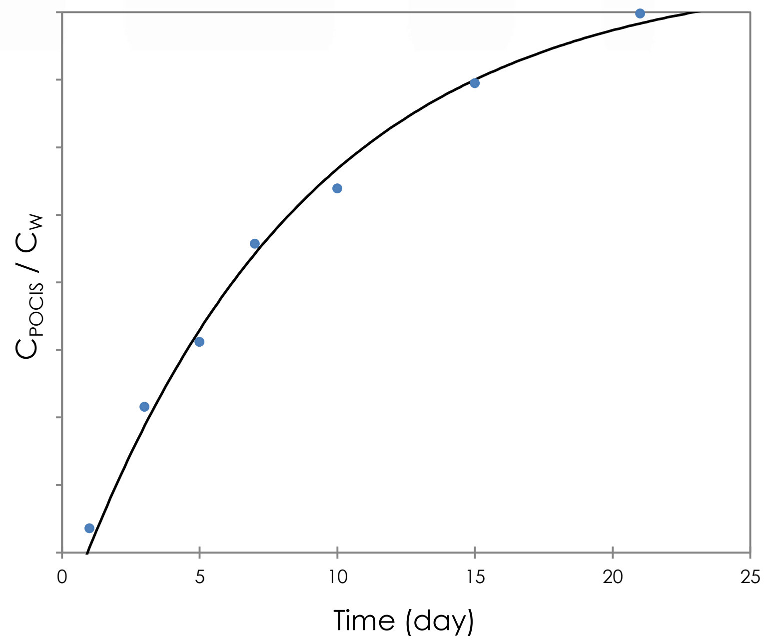


Location of flow velocities measurement



Material and method – Theory

- POCIS theory
  - $C_{POCIS} = C_w \times k_u \times t$
  - $\frac{C_{POCIS}}{C_w} = K_{HLBw} \times (1 - e^{-ke \times t})$



- Determination of sampling rates:
  - $y = pr1 \times (1 - e^{-pr2 \times X})$

Where y = $\frac{C_{POCIS}}{C_w}$; pr1 = K_{HLBw} ; $pr2 = ke$ and X = t

With K_{HLBw} = $\frac{k_u}{k_e}$ → Rs = $\mathrm{pr1} \times pr2 \times 0.2$

→ performed by XLStat software

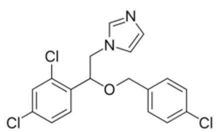
- Determination of difference between experimental and theoretical sampling rates:
  - $\%_{diff} = \frac{Rs_{th} - Rsexp}{Rs_{th}} \times 100$

Results and discussion – Sampling rates determination

- Estimation of 38 sampling rates out of 44 parmaceuticals tested ($r^2 > 0.90$ for 32, 33, 30 and 35 compounds for V0, V1, V2 and V3, respectively).
- 12 new Rs (not available in literature):
  - ✓ Dexamethasone, flunixin, griseofulvin, indomethacin, metronidazole, paraxanthine, perindopril, praziquantel, pyrantel, salbutamol, sulfadiazine and sulfamethoxypyridazine.
- No estimation of Rs for 6 pharmaceuticals:

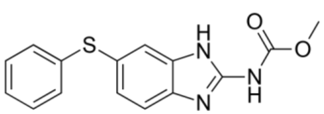
X Econazole

$\text{LogK}_{ow} = 5.35$



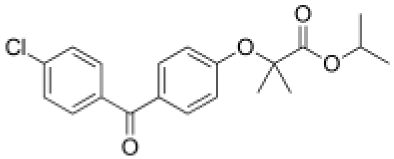
X Fenbendazole

$\text{LogK}_{ow} = 3.41$



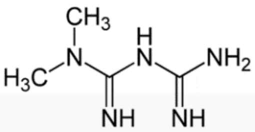
X Fenofibrate

$\text{LogK}_{ow} = 5.28$



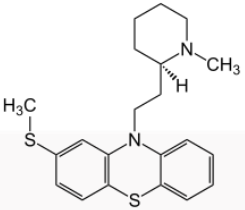
X Metformin

$\text{LogK}_{ow} = -0.92$



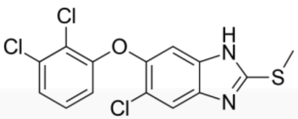
X Thioridazine

$\text{LogK}_{ow} = 5.47$



X Triclabendazole

$\text{LogK}_{ow} = 5.88$



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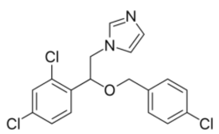
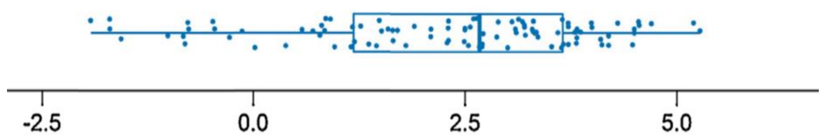


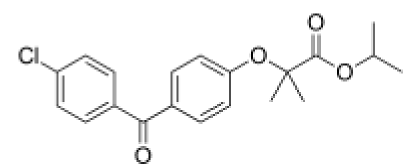
POCIS sampling range



$0 \leq LogK_{ow} \leq 5$

X Fenofibrate

$LogK_{ow} = 5.28$



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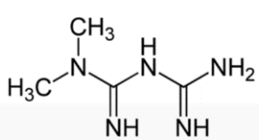

X Thioridazine

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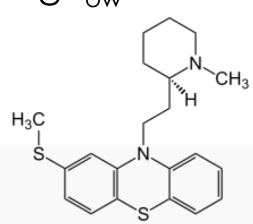

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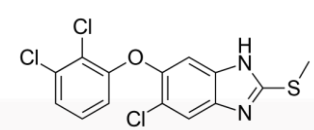

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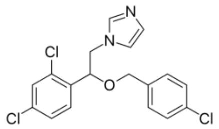

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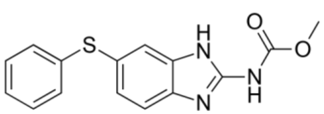

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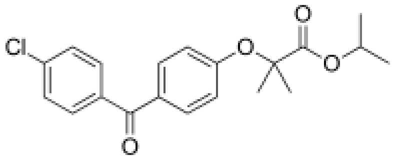

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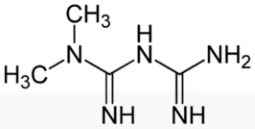

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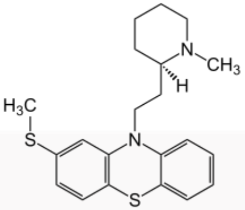

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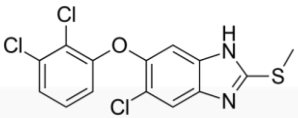
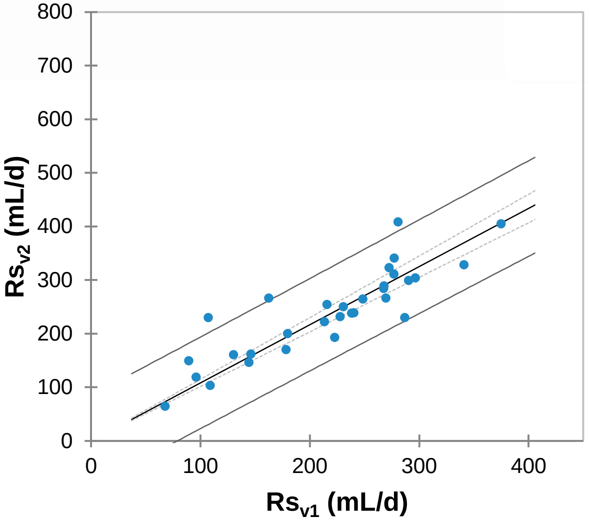
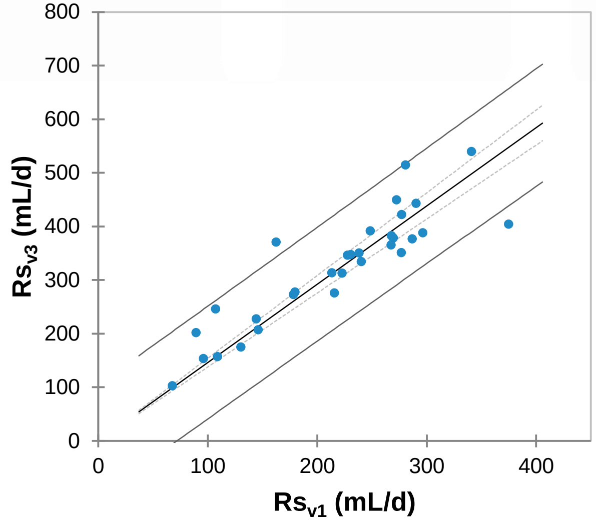
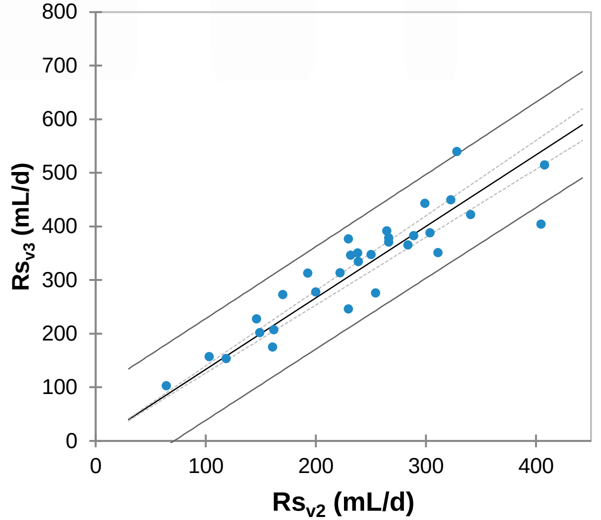


Results and discussion – Effect of flow velocity







$Rs_{v2} = 1.08 * Rs_{v1}$

$r^2 = 0.768$

$Rs_{v3} = 1.46 * Rs_{v1}$

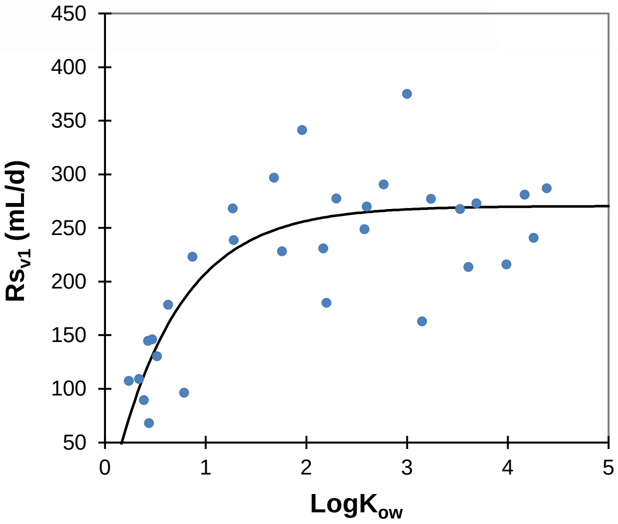
$r^2 = 0.801$

$Rs_{v3} = 1.33 * Rs_{v2}$

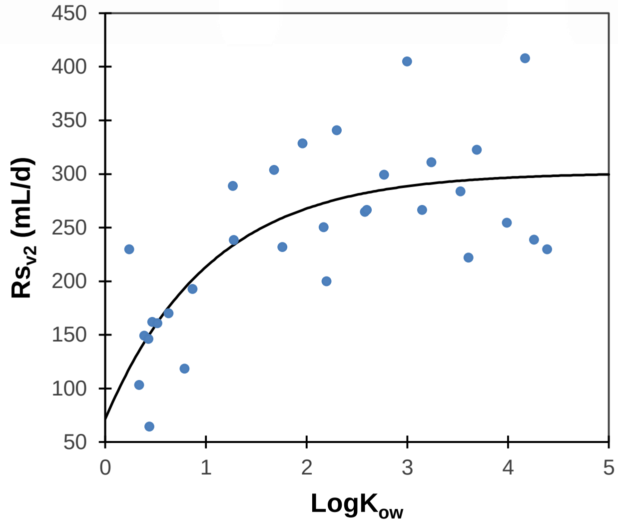
$r^2 = 0.826$

- No correlation between Rs obtained with V0 and other flow velocities (V1, V2 and V3)
- Correlation between Rs obtained with V1, V2 and V3
- $Rs_{v1} < Rs_{v2} < Rs_{v3}$
- With water flow velocity ↗ water boundary layer ↘ → Rs ↗

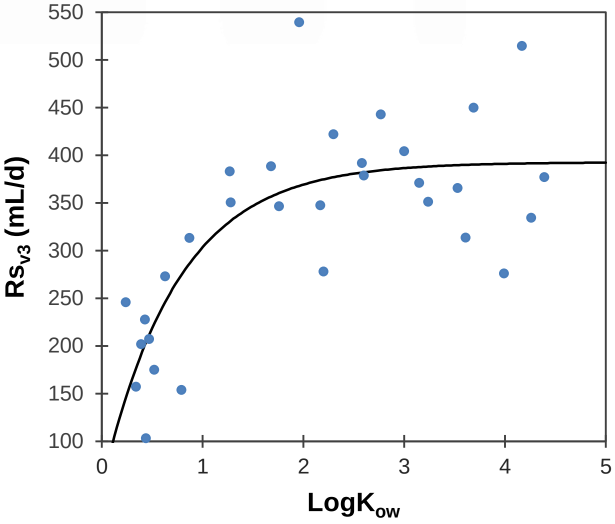
Results and discussion – Non-linear regression with $LogK_{ow}$ to estimate Rs



$$Rs_{v1} = -284 \times e^{-1.51 \times LogK_{ow}} + 270$$
$r^2 = 0.593$



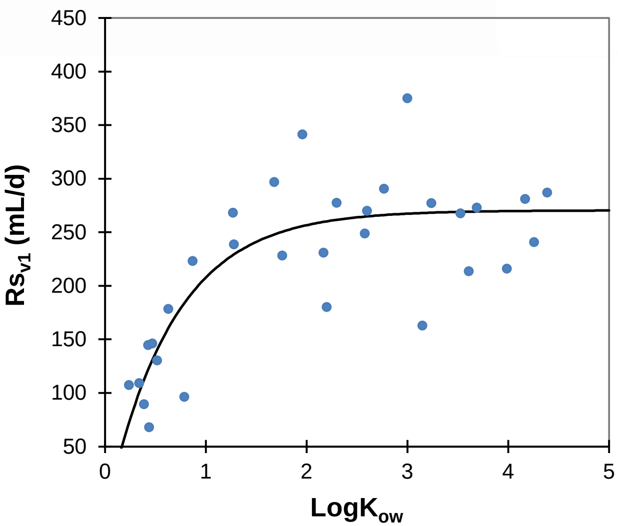
$$Rs_{v2} = -230 \times e^{-0.96 \times LogK_{ow}} + 302$$
$r^2 = 0.554$



$$Rs_{v3} = -340 \times e^{-1.34 \times LogK_{ow}} + 393$$
$r^2 = 0.600$

- 2 parts:
  - $0 < LogK_{ow} < 2$: linear relationship between Rs and $LogK_{ow}$
  - $2 < LogK_{ow} < 5$: constant value for Rs : $Rs_{v1\text{-}max}$: 270 ; $Rs_{v2\text{-}max}$: 300 and $Rs_{v3\text{-}max}$: 380 mL/d
- Differences between experimental and theoretical value of Rs: ± 60%

Results and discussion – Non-linear regression with $LogK_{ow}$ to estimate Rs



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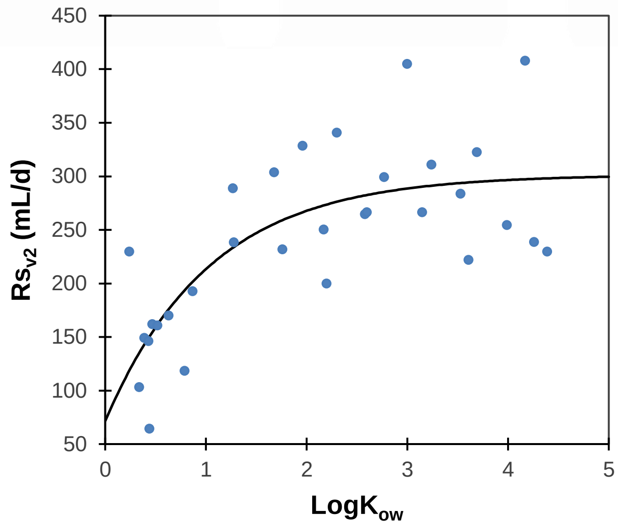

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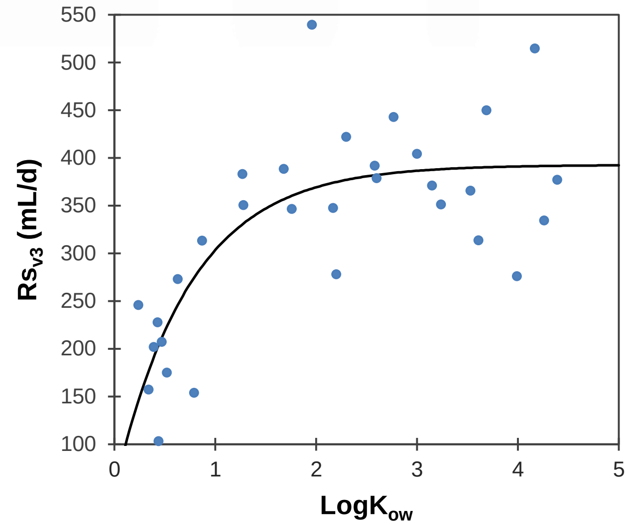
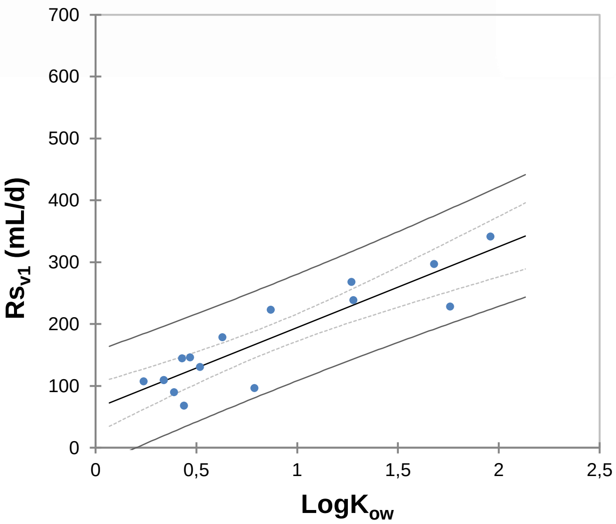


$$Rs_{v3} = -340 \times e^{-1.34 \times LogK_{ow}} + 393$$

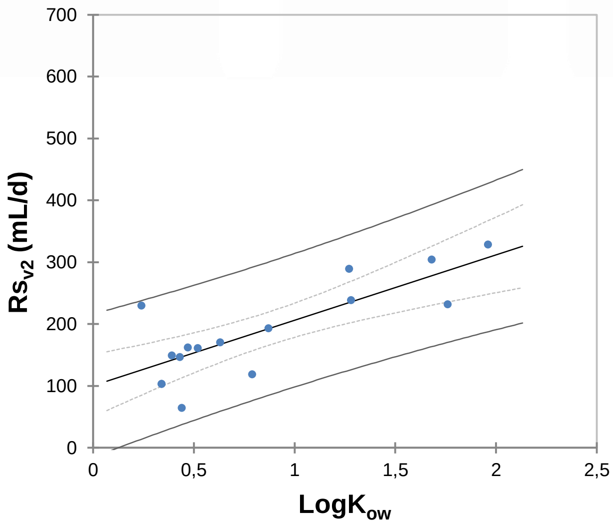
$r^2 = 0.600$

- Comparison with Literature relationship between Rs and $LogK_{ow}$:
  - Linear for $0 < LogK_{ow} < 5$ (Togola *et al.*, 2007) and for $0 < LogK_{ow} < 4$ (Li *et al.*, 2010)
  - Gaussian for $0 < LogK_{ow} < 5$ (Alvarez *et al.*, 2007 and MacLeod *et al.*, 2007)
  - Quadratic for $1.2 < LogK_{ow} < 3$ (Mazzella *et al.*, 2007)
  - Third-order polynomial function for $1.5 < LogK_{ow} < 4.7$ (Thomatou *et al.*, 2011)

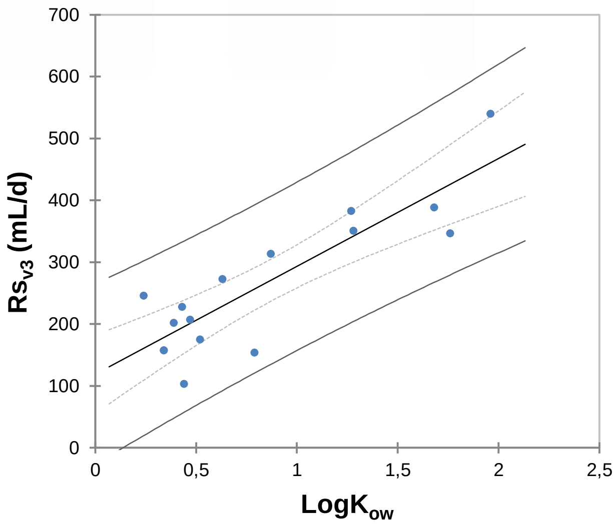
Results and discussion – Linear regression for pharmaceuticals with 0 < $LogK_{ow}$ < 2



$$Rs_{v1} = 131 \times \mathrm{LogK_{ow}} + 64$$
$r^2 = 0.803$



$$Rs_{v2} = 106 \times LogK_{ow} + 101$$
$r^2 = 0.629$

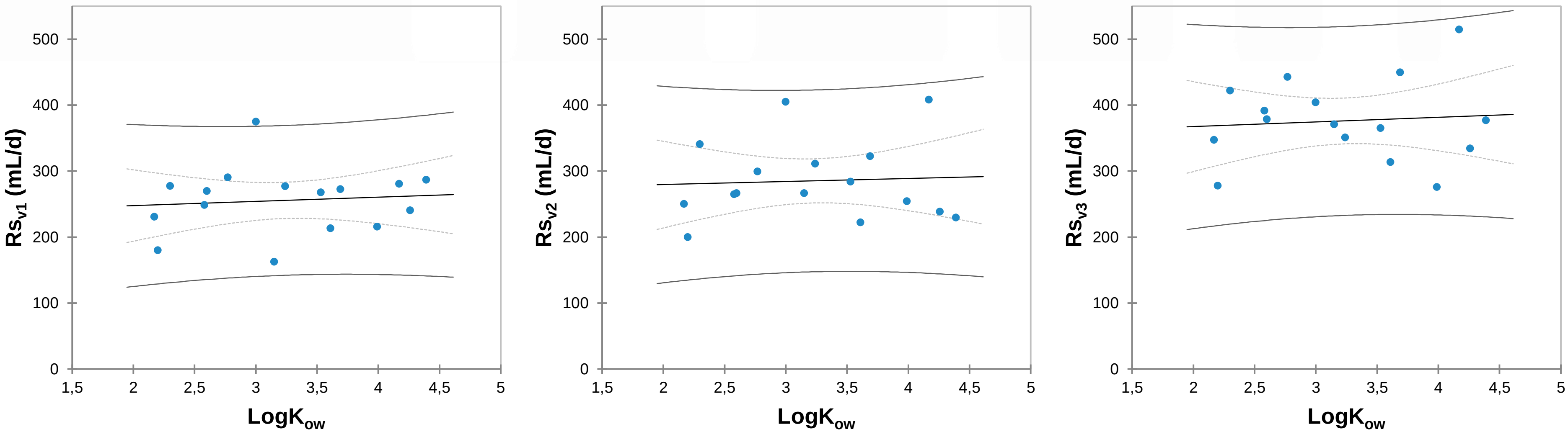


$$Rs_{v3} = 174 \times LogK_{ow} + 119$$
$r^2 = 0.744$

- Confidence interval of 95%
- Differences between experimental and theoretical for Rs: from -25 to +60%
- Rs_{v3}: same equation obtained by Li *et al.*, 2010:

$$Rs = 171 \times LogK_{ow} + 196$$
$r^2 = 0.84$

Results and discussion – Linear regression for pharmaceuticals with 0 < $LogK_{ow}$ < 2

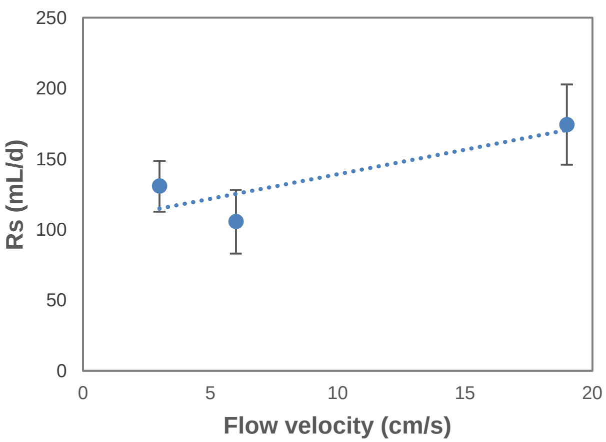


- Confidence interval of 95%
- $Rs_{v1\text{-}max}$: 255 ; $Rs_{v2\text{-}max}$: 285 and $Rs_{v3\text{-}max}$: 375 mL/d
- Differences between experimental and theoretical: from -50 to +40%

- Literature:
  - Rs_{max} obtained from $LogK_{ow}$ ≈ 1.7 (Alvarez *et al.*, 2007), 2.5 (Mazzella *et al.*, 2007), 2.7 *(Thomatou et al., 2011)* or 3 (MacLeod *et al.*, 2007)

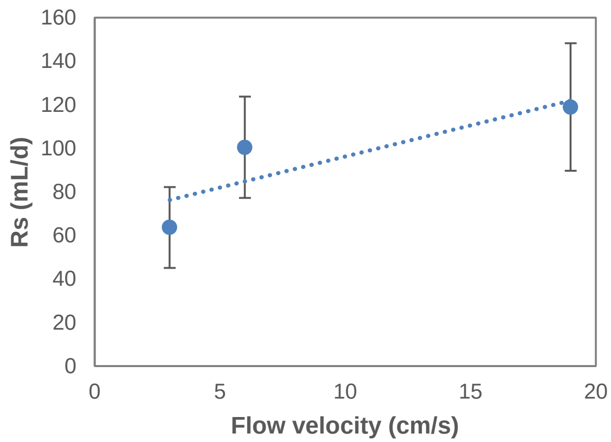
Results and discussion – Relationship between parameters from $Rs=f(LogK_{ow})$ vs. flow velocity

Slopes of linear regression



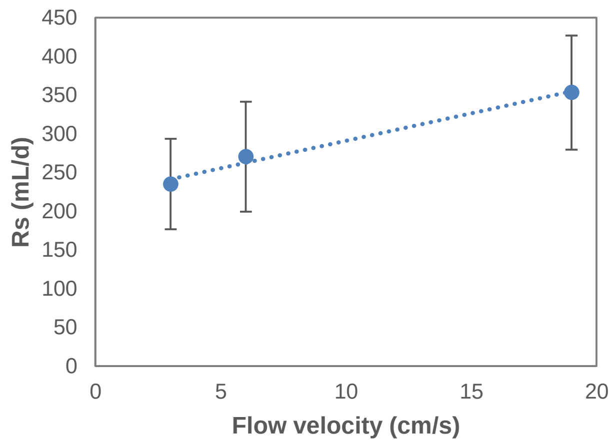
$$Rs = 3.49 \times LogK_{ow} + 104$$
$r^2 = 0.729$

Intercepts of linear regression



$$Rs = 2.85 \times LogK_{ow} + 68$$
$r^2 = 0.740$

Intercepts of equilibrium



$$Rs = 7.08 \times LogK_{ow} + 220$$
$r^2 = 0.986$

- Link between parameters from $Rs=f(LogK_{ow})$ and flow velocites
- Slopes and intercepts increase with flow velocity
- Usefull to recalculate parameters of equation to estimate Rs in the range [2-20cm/s]

Conclusion about calibration of POCIS for pharmaceuticals

- Estimation of 38 sampling rates out of 44 parmaceuticals tested
- 12 new Rs (not available in literature):
  - ✓ Dexamethasone, flunixin, griseofulvin, indomethacin, metronidazole, paraxanthine, perindopril, praziquantel, pyrantel, salbutamol, sulfadiazine and sulfamethoxypyridazine.
- No estimation of Rs for 6 pharmaceuticals:
  - X Econazole, fenbendazole, fenofibrate, metformin, thioridazine, triclabendazole
- 4 flow velocities tested: 0 (no stirred); 2-3; 6-7 and 20 cm/s with increase of Rs with flow velocities
- Mathematical model to estimate Rs from pharmaceuticals LogK_{ow} (range 0-5) : non-linerar relationship selected

$$Rs_{\mathrm{v1}} = -284 \times e^{-1.51 \times LogK_{ow}} + 270$$

$$Rs_{\mathrm{V2}} = -230 \times e^{-0.96 \times LogK_{ow}} + 302$$

$$Rs_{\mathrm{V3}} = -340 \times e^{-1.34 \times LogK_{ow}} + 393$$

- Difference between estimated and experimental values of Rs: ± 60% which is consistant with literature

Tank you for your attention !