Reactive transport modelling to assess pesticide dissipation at river scale

G. Drouin, M. Fahs, B. Droz, G. Imfeld & S. Payraudeau

Laboratoire d'Hydrologie et de Geochimie de Strasbourg (LHyGeS)
1 rue Blessig 67000, Strasbourg, France
Université de Strasbourg, ENGEES, CNRS

Contact: guillaume.drouin@unistra.fr

Context & gap of knowledge

- **Pesticide contaminations are ubiquitous in surface waters, including in rivers[1]**
- **The Sediment Water Interface (SWI) is a highly reactive boundary of rivers where degradation occurs[2]**
  - Increased residence time
  - Favourable redox conditions for microbial and chemical degradation
- **Its reactivity is mainly controlled by transport of dissolved species into the sediment bed[3]**
  - **Hydrological forcing**
    - Horizontal water velocity (river flow)
    - Vertical water fluxes (ground-surface)
  - **Geomorphologic structures**
    - Large scale (meanders, dams, etc.)
    - Small scale (bed forms, vegetation, etc.)

→ **In-stream degradation of pesticides still unresolved**

- **Modelling transport at a fluid-porous interface is still challenging[4]**

Aims

1/ Developing a physically-based reactive transport model at the SWI:
- Without interfacial conditions
- Horizontal & Vertical fluxes

2/ Investigating the effects on solute transport of:
- A representative hydrological forcing
- Sorption

Ongoing

...

3/ Understanding the relationship between transport and degradation at the interface

Methodology

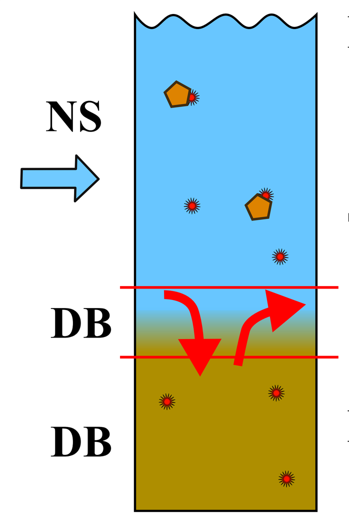
Aim 1/

Aim 2/ +

Aim 3/ +

Modelling transport at the SWI

Advanced numerical methods are coupled in an innovative way to solve the governing equations without any specific treatment of interfacial conditions.



Flow:
- Navier-Stokes (NS)
- Darcy-Brinkman (DB)

→ **Non conforming Crouzeix-Raviart finite elements**

Transport:
- Diffusion
- Dispersion + advection

→ **Discontinous Galerkin finite element**

Reactivity:
- Sorption

$$s_1 \bullet \frac{\rho}{\epsilon}\frac{\partial u}{\partial t} + s_2 \bullet \frac{\mu}{K}u + s_3 \bullet \frac{\rho}{\epsilon^2}(u\nabla)u - s_4 \bullet \frac{\nu}{\epsilon}\nabla(\nabla u)\nabla p = -\rho g \nabla z$$

(s_1, s_2, s_3, s_4) are used to switch from NS to DB, (u, p) are the state variables for water velocities and pressure and (ρ, ϵ, ν, K) the porous medium characteristics

Tracer experiments

Tracer experiments are used to investigate transport of dissolved species and validate the model

Tracers:

Conservative - $NaCl$

Adsorptive - Azo dye

$(K_d = 7.7 mL.g^{-1})$

Flow:

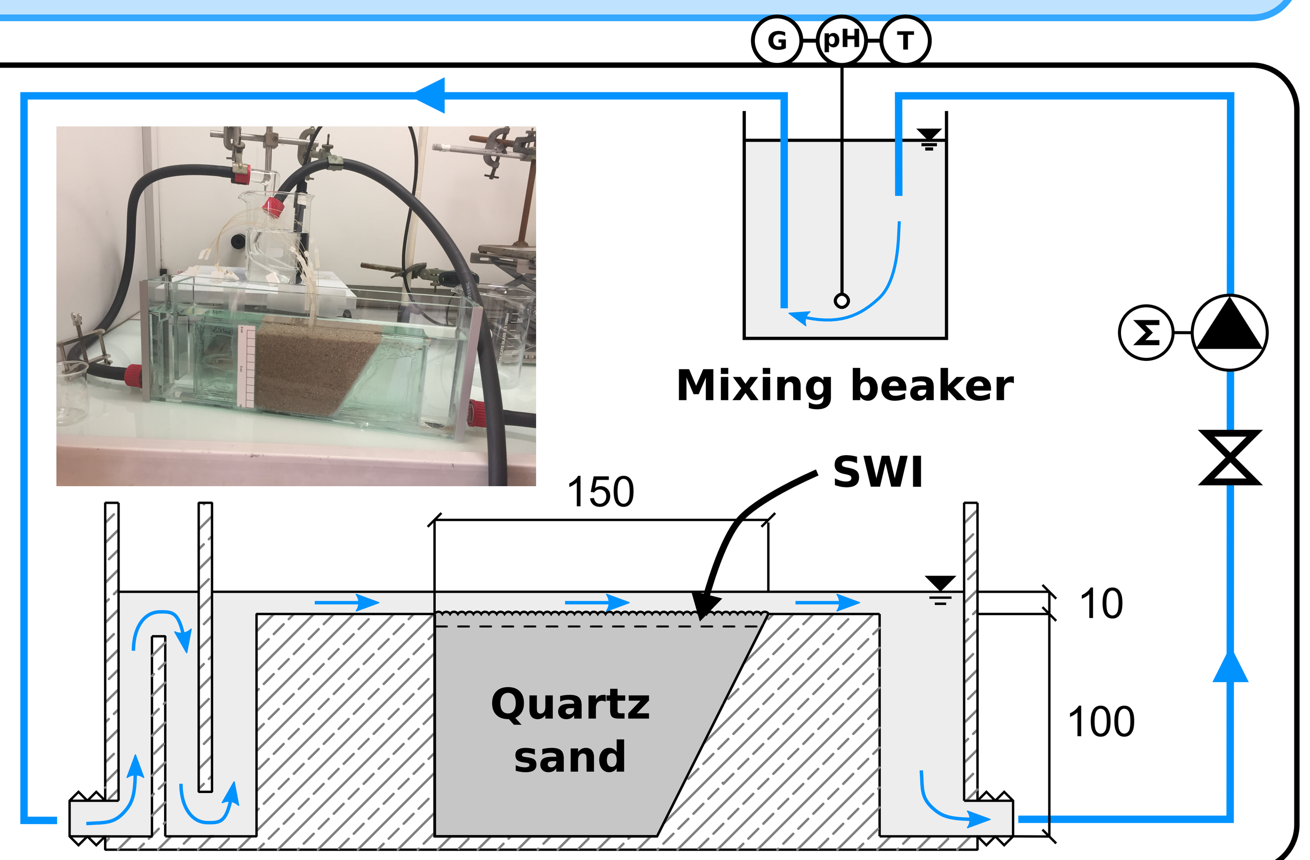
$1.5 < u < 4.5 \ cm.s^{-1}$

$150 < Re < 500$

Configuration:

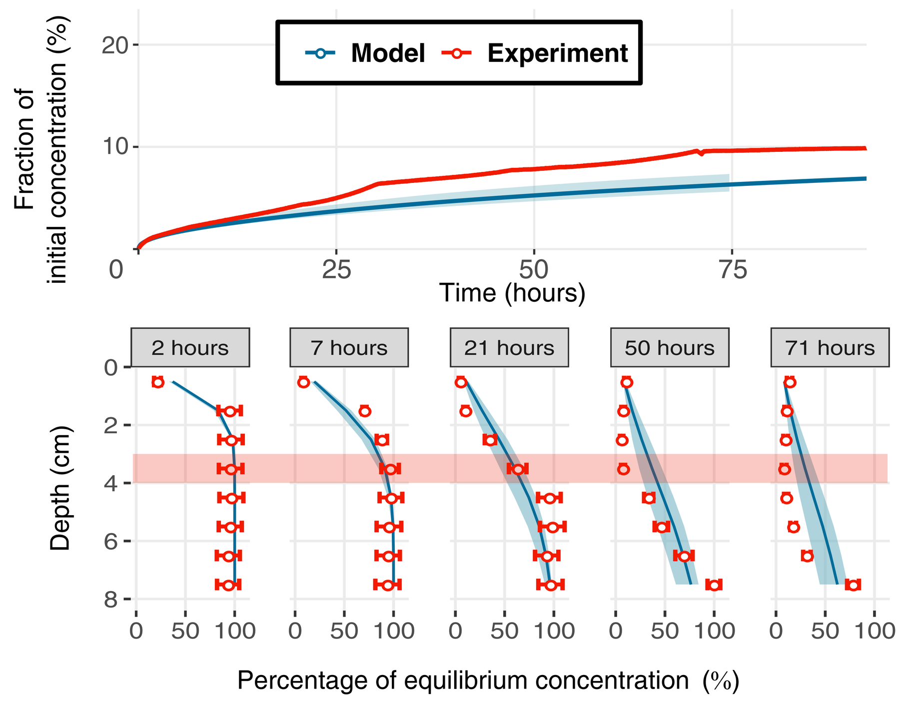
Export - groundwater

Incorporation - surface water



Model validation

Simulations fit well with experimental data & reveal that dispersive transport is dominant



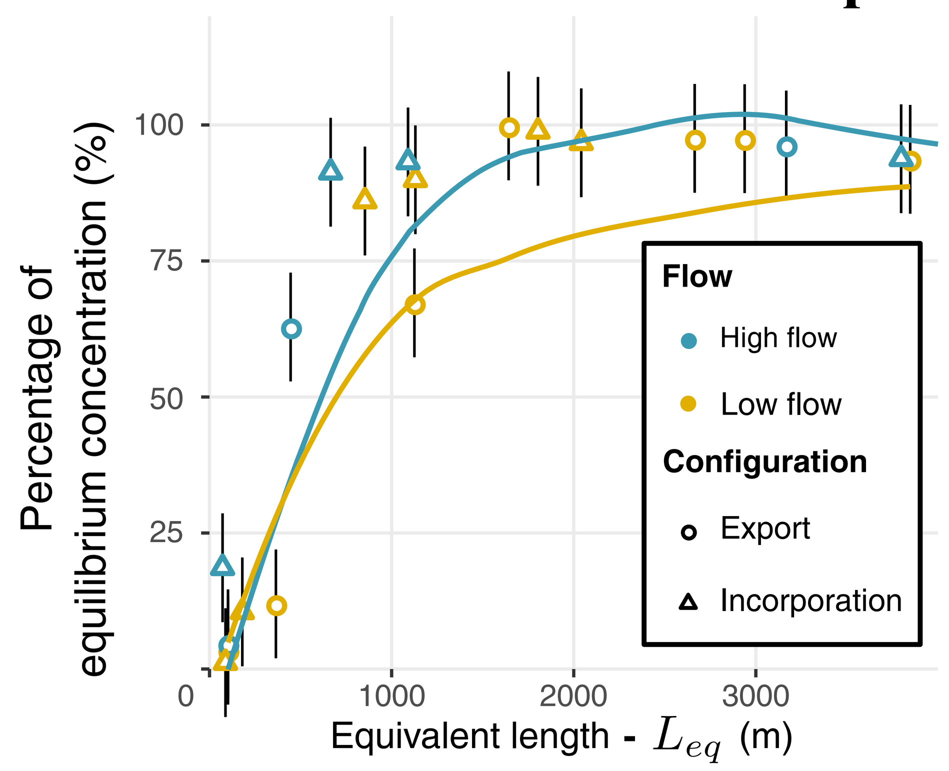
- **Numerical details**
  - Closed mass balance $< 0.01\%$
  - Mesh size sensitivity negligible $< 2mm$
- **Parameter sensitivity**
  - **Interface layer thickness**
    - Grain size = velocity penetration
  - **Dispersion coefficient**
    - Dispersion driven transport

$$\begin{cases} 10^1 < Pe < 10^6 \\ \frac{D_{eff}}{D_m} \approx 10^1 \end{cases}$$

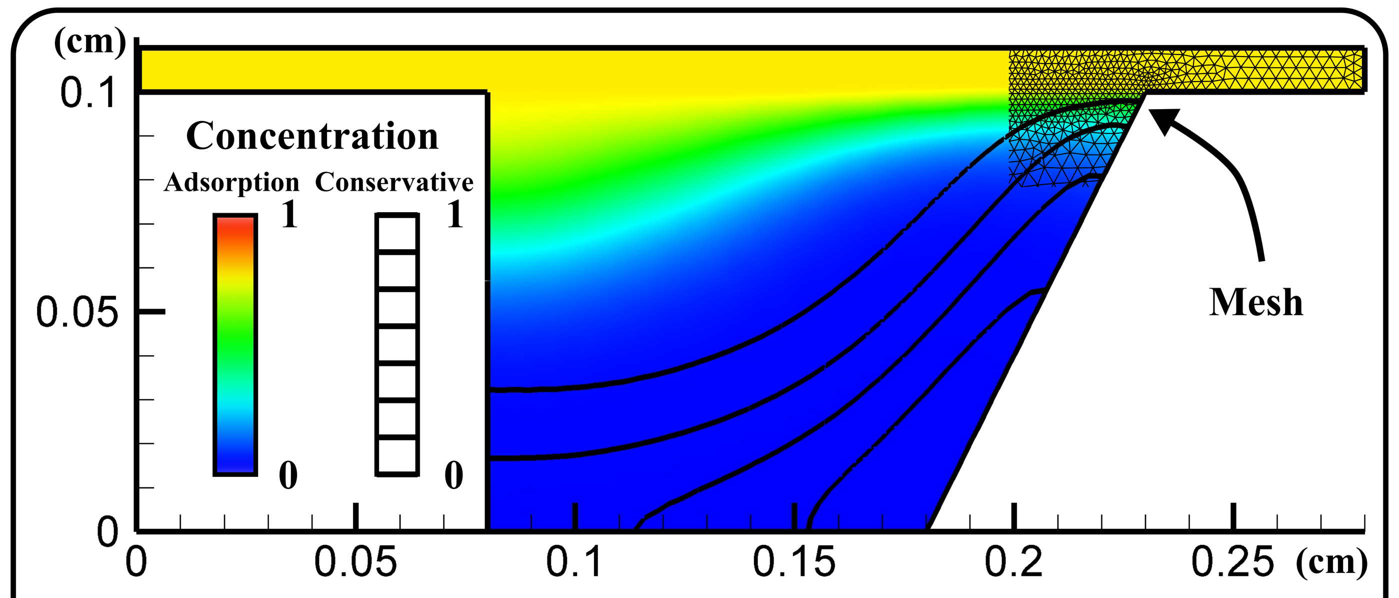
The effects of water flow and sorption on transport at the SWI

Water flow controls mass exchange rate but not capacity alongside a bounded river transect. Sorption favours pollutant removal by the sediment bed

Results at 3.5 cm deep



- **Export = incorporation**
- **Water flow dependancy**
  - ✓ **Temporal rates:**
    - Varying exchange rate & Penetration/export pace
    - Time required to reach 90% of the equilibrium:
    - $2 < T_{90\%} < 30\ h$
  - ✗ **Equivalent length scaling**
    - Constant exchange capacity
    - $L_{eq_{90\%}} \approx 2000\ m$



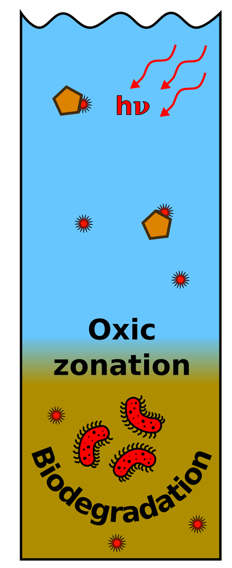
- **Sorption effect**
  - Enhanced/ hampered mass exchange
  - Limited penetration depth

River bed ~ sink

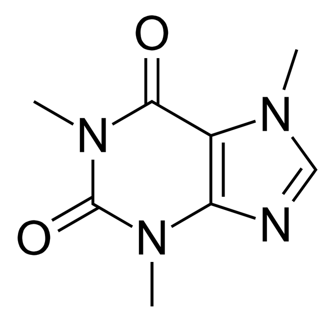
Conclusions & Perspectives

A promising tool to assess in-stream degradation at large scale

- **Suitable model for transport at the SWI**
  - For conservative and sorptive species
  - → **Degradation processes ?**
- **Sorption limits deep contaminations**
  - Contaminants sorb on the upper sediment
  - → **Influence on degradation ?**
- **Flow independant mass exchange**
  - Contaminant source (surface/groundwater)
  - Exchange capacity per river length
  - → **Simplified risk assessment in rivers ?**



Caffeine



- Short half life
- Organic contaminant

References

(1) de Souza et al., «Occurrence, impacts and general aspects of pesticides in surface water: A review», Process Safety and Environmental Protection (2020).

(2) Krause et al., «Ecohydrological interfaces as hot spots of ecosystem processes», Water Resources Research, 2017.

(3) Byrne et al., «Diffusive equilibrium in thin films provides evidence of suppression of hyporheic exchange and large-scale nitrate transformation in a groundwater-fed river», Hydrological Processes, 2015.

(4) Cardenas, Hyporheic zone hydrologic science: A historical account of its emergence and a prospectus, Water Resources Research, 2015.