Trace metals transfer in rivers: a semi-empirical formulation to describe a complex sorption – desorption process to be implemented in SWAT model.

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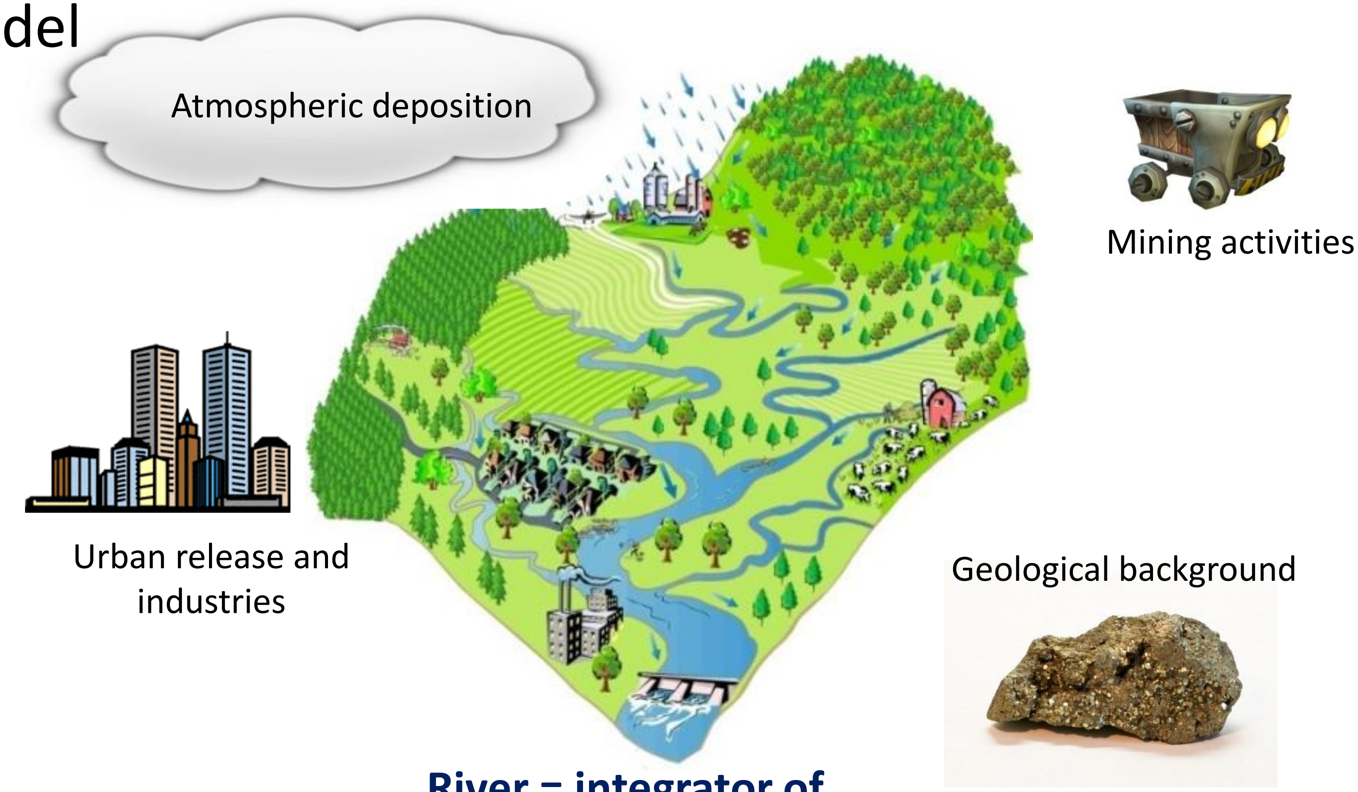
Trace Metal problematic in natural waters

- Exhibits a wide range of behaviour in natural waters
- Controlled by various environmental factors
- difficult to model



Atmospheric deposition

Mining activities

Urban release and industries

Geological background

River = integrator of pollution

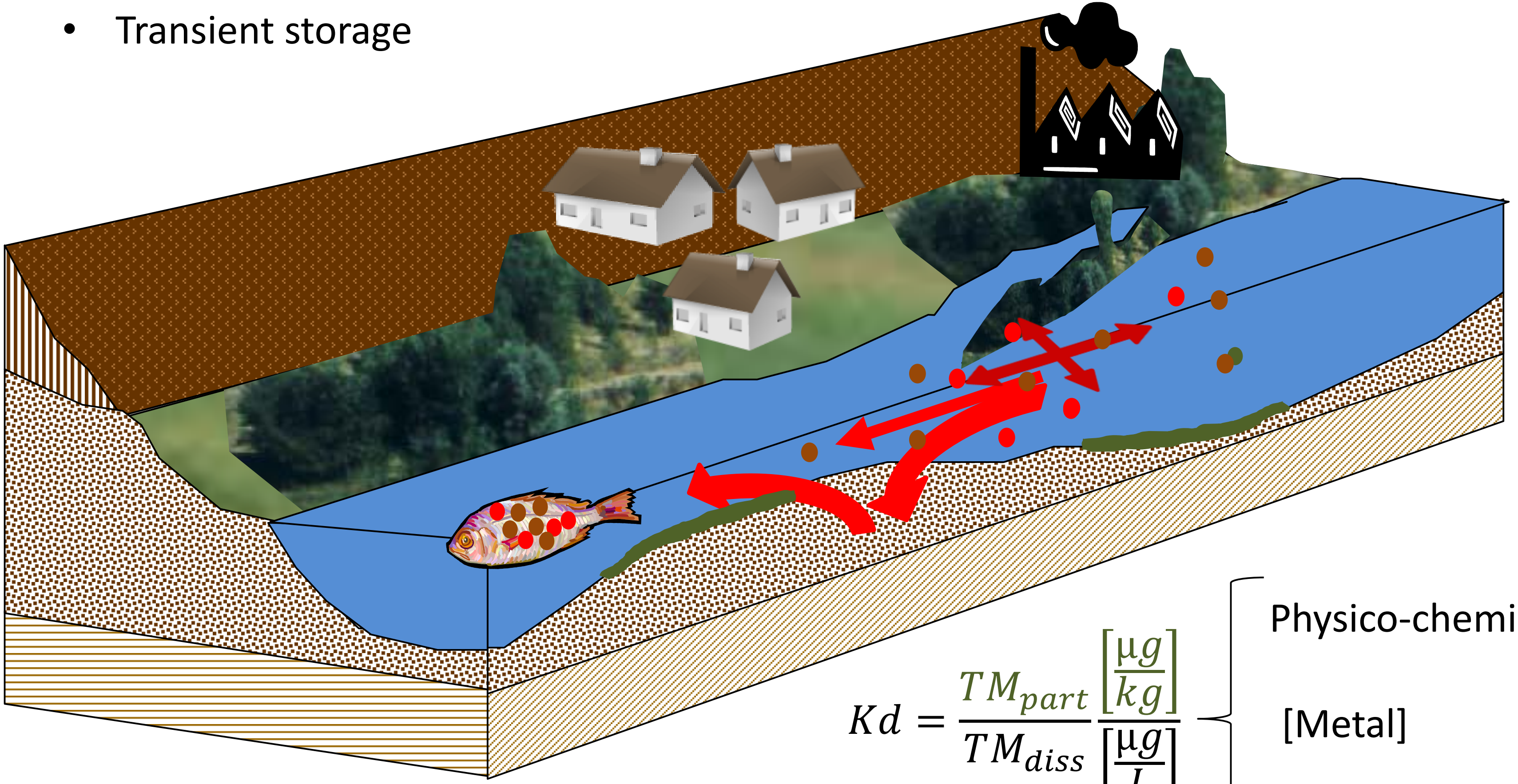
Transfer of trace metals in rivers

- Advection
- Dispersion
- Transient storage

- Sédimentation
- Érosion

🔴 Dissolved phase

🟠 Particulated phase



$$Kd = \frac{TM_{part}\left[\frac{\mu g}{kg}\right]}{TM_{diss}\left[\frac{\mu g}{L}\right]}$$

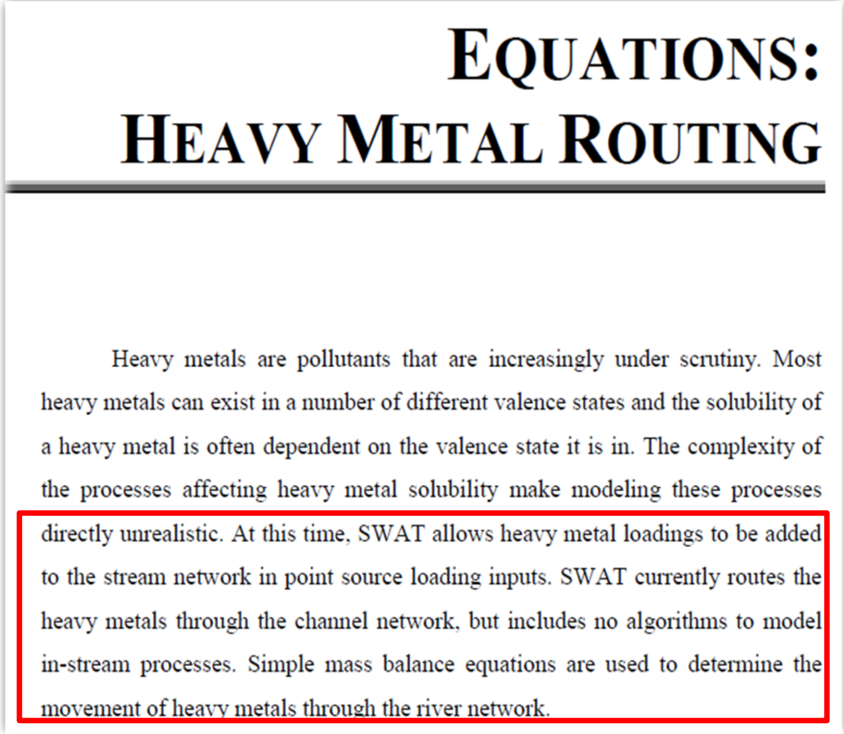
Physico-chemistry

[Metal]

Nature of SS

Modelling approaches : Sorption models

Trace element
Free adsorption site
Occupied adsorption site



EQUATIONS: HEAVY METAL ROUTING

Heavy metals are pollutants that are increasingly under scrutiny. Most heavy metals can exist in a number of different valence states and the solubility of a heavy metal is often dependent on the valence state it is in. The complexity of the processes affecting heavy metal solubility make modeling these processes directly unrealistic. At this time, SWAT allows heavy metal loadings to be added to the stream network in point source loading inputs. SWAT currently routes the heavy metals through the channel network, but includes no algorithms to model in-stream processes. Simple mass balance equations are used to determine the movement of heavy metals through the river network.

MINTEQA2 (Allison et al., 1991)

WASP (Ambrose et al., 1993)

WHAM (Tipping, 1993)

Modelling approach

- Different levels of modelling simplicity
  - SWAT: the TM are fully dissolved and transported from the inlet to the outlet.

$$TM_{diss_{out}} = TM_{diss_{ch}} \times \frac{V_{out}}{V_{ch}}$$

  - Two phases separation of TM: The TM exist either in a dissolved form or in a particulate one.

$$TM_{part_{ch}} = TM_{part_{ch,i}} + TM_{part_{eroded}} - TM_{part_{deposited}}$$

$$TM_{part_{out}} = TM_{part_{ch}} \times \frac{V_{out}}{V_{ch}}$$

  - Two phases separation with dynamic equilibrium: The two TM phases can interact to maintain an equilibrium based on the physico-chemistry.

$$Kd = f(physico - chemitry) = \frac{TM_{part}\left[\frac{\mu g}{kg}\right]}{TM_{diss}\left[\frac{\mu g}{L}\right]}$$

$$TM_{diss_{ch}} = \frac{TM_{total_{ch}}}{1 + Kd \times SPM}$$

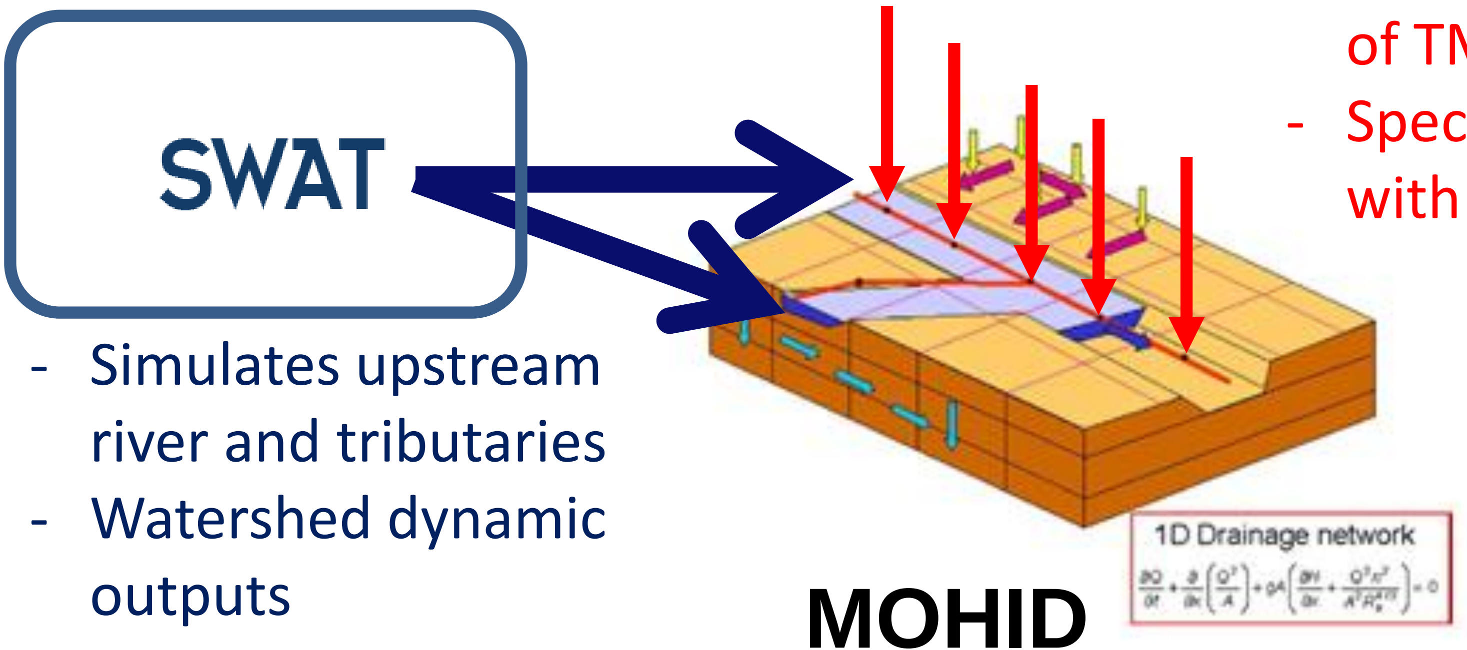
$$TM_{part_{ch}} = TM_{total_{ch}} - TM_{diss}$$

Objectives

- Propose an alternative modelling option for trace metal
  - Use two TM phases: dissolved and particulate
  - Use a dynamic Kd formulation based on available variables and quantities in SWAT

First step : we have to identify key parameters involved in Kd formulation

Complex modelling



WHAM

- Chemical speciation of TM
- Specific reaction with organic matter

SWAT

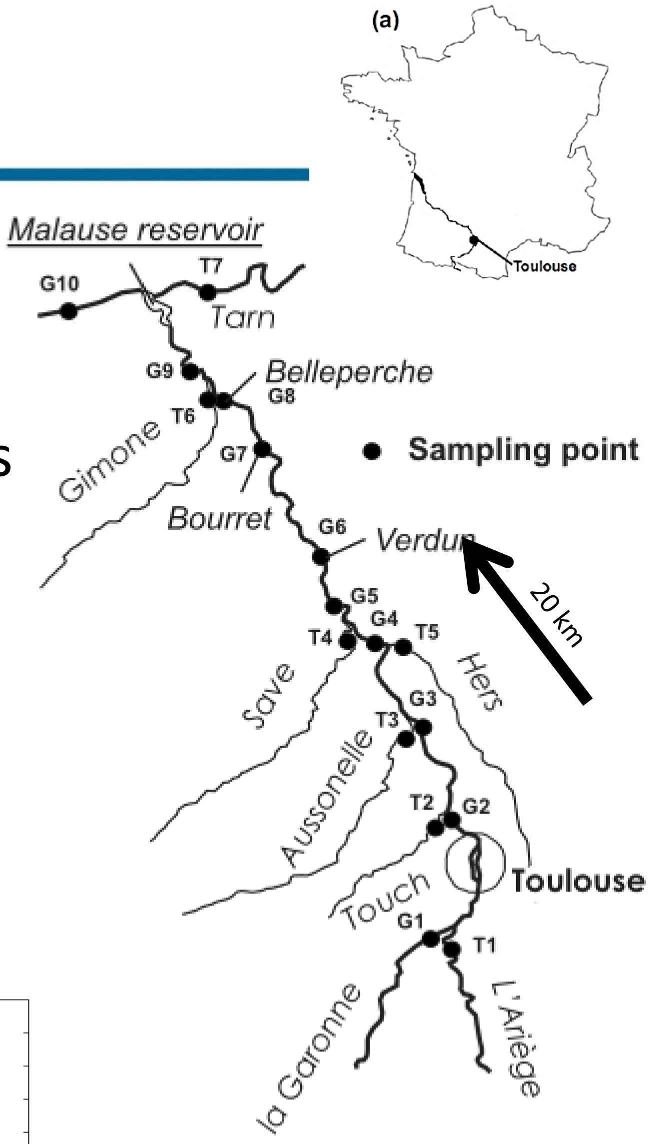
- Simulates upstream river and tributaries
- Watershed dynamic outputs
- SPM concentration

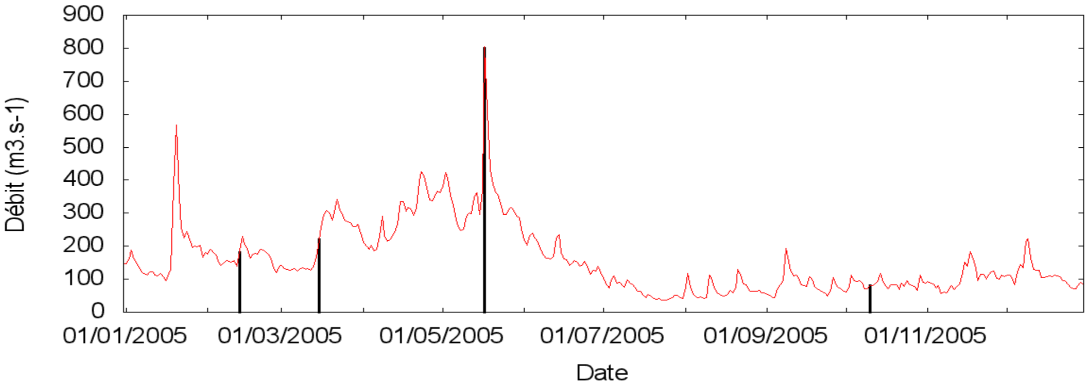
MOHID

- Full St-Venant equations
- Advection – diffusion equations
- Transient storage
- Erosion – deposition equations

Study case

- The Garonne River sector
  - Reach of 80 km (watershed 13800 km^{2})
  - Monthly average discharge 75 to 341 m^{3}/s
- 4 campaigns in 2005 (13 sites)
    - Nutrients
    - Major ions
    - Physico-chemistry
    - 15 Trace metals





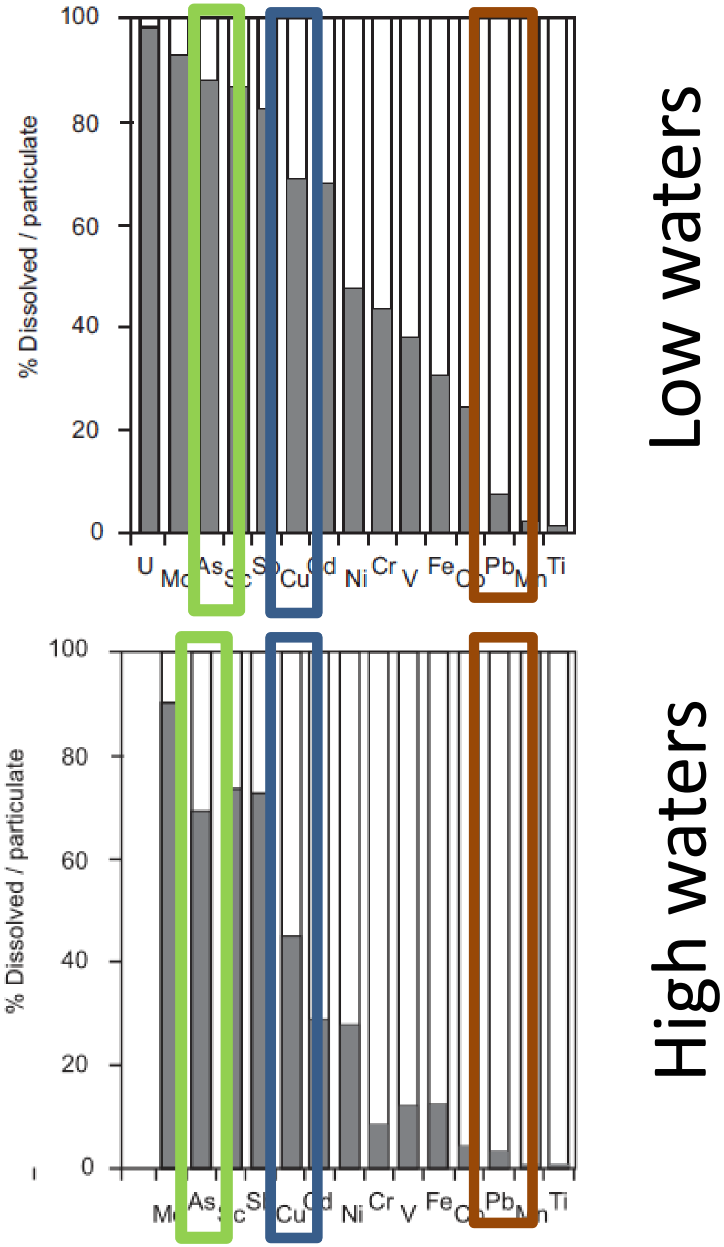
Study case

Choise of two trace elements

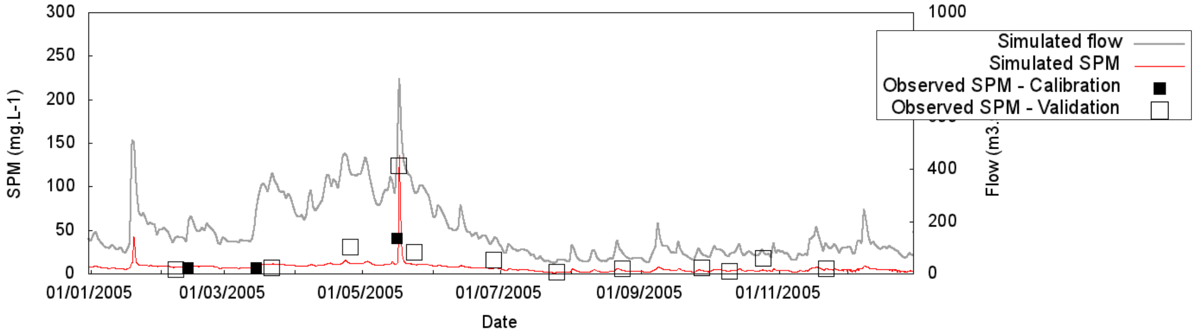
- Lead (Pb)
- Arsenic (As)
- Copper (Cu)

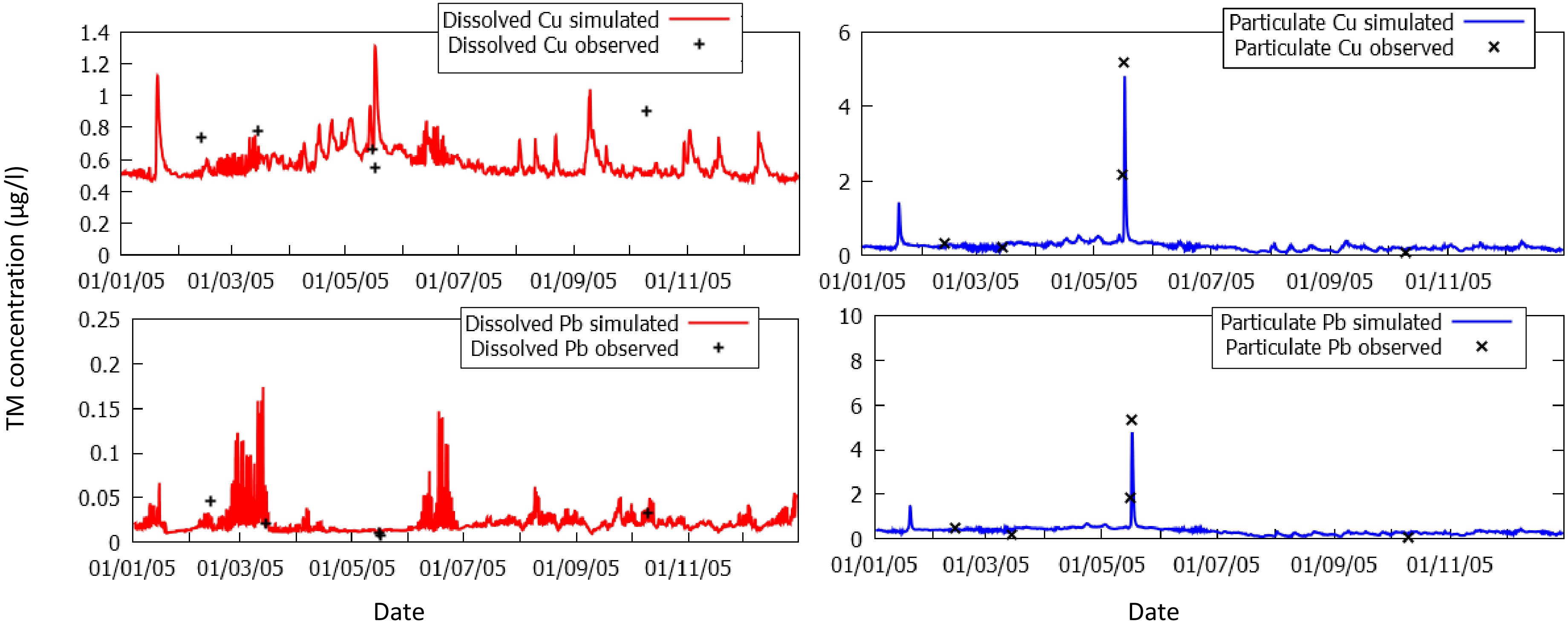
+

$$f_{COP} = \min\left(\frac{0{,}60}{SPM - 1.0} + 0.021;\ 0.24\right)$$

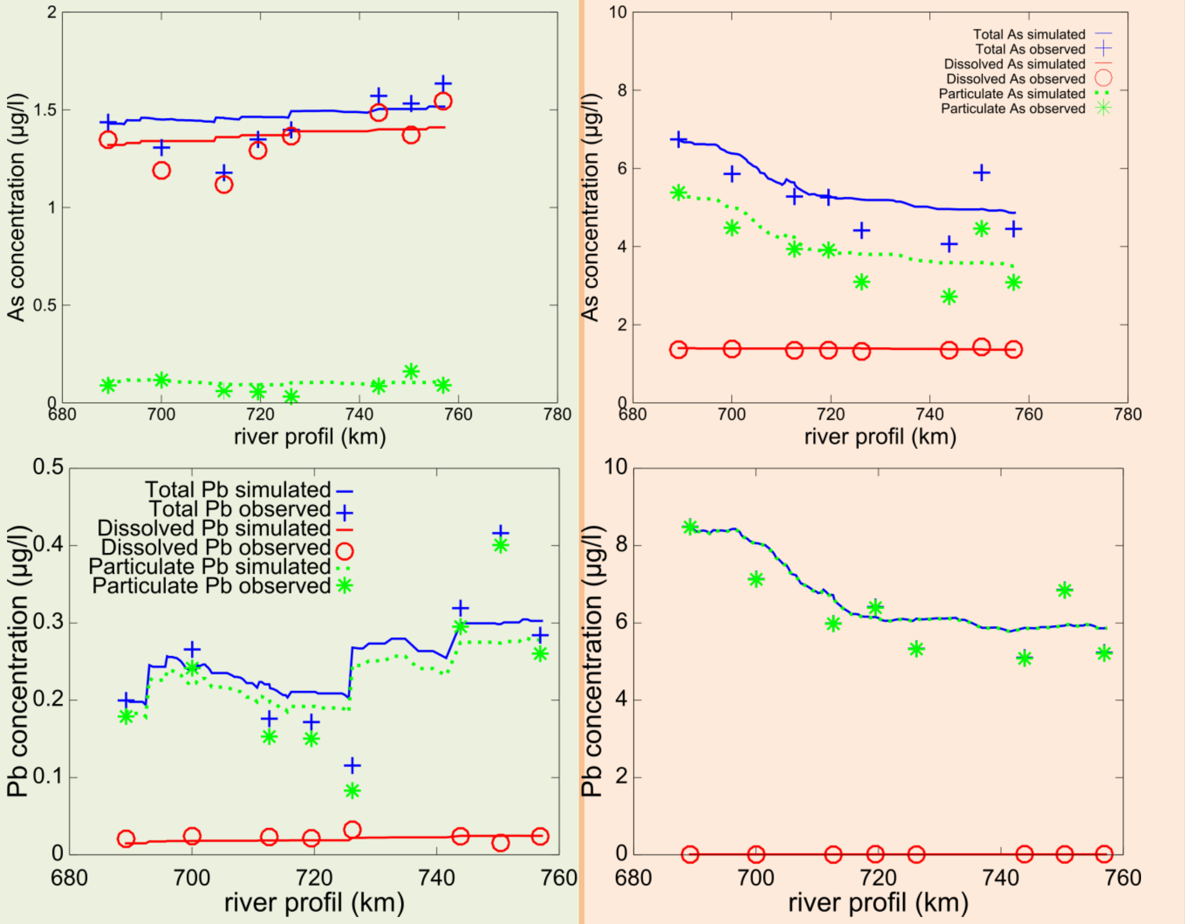


TM temporal concentration evolution





TM spatial concentration evolution

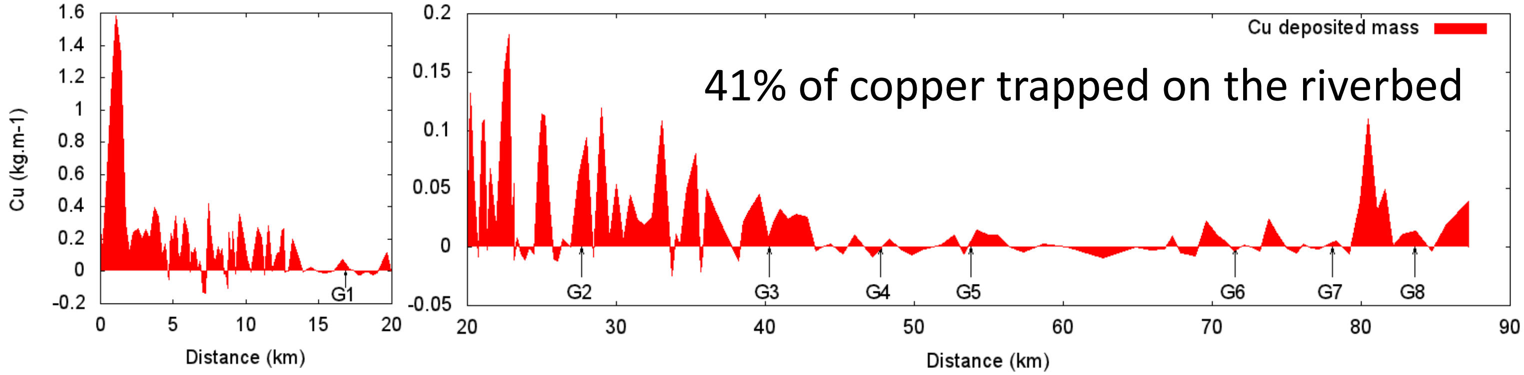


Low waters

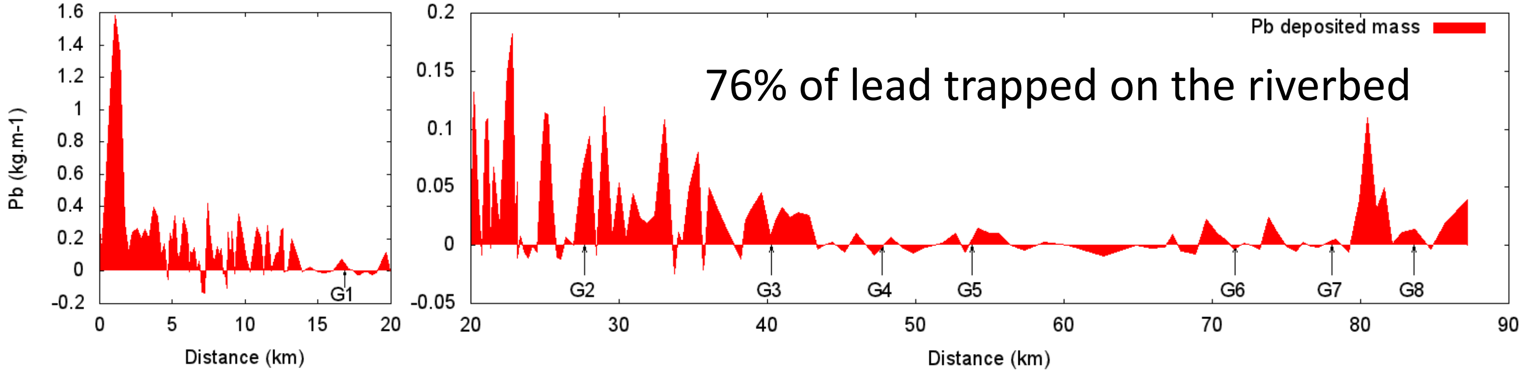
High waters

Key results

- The particulate phase is important to describe sources and sinks of trace metals



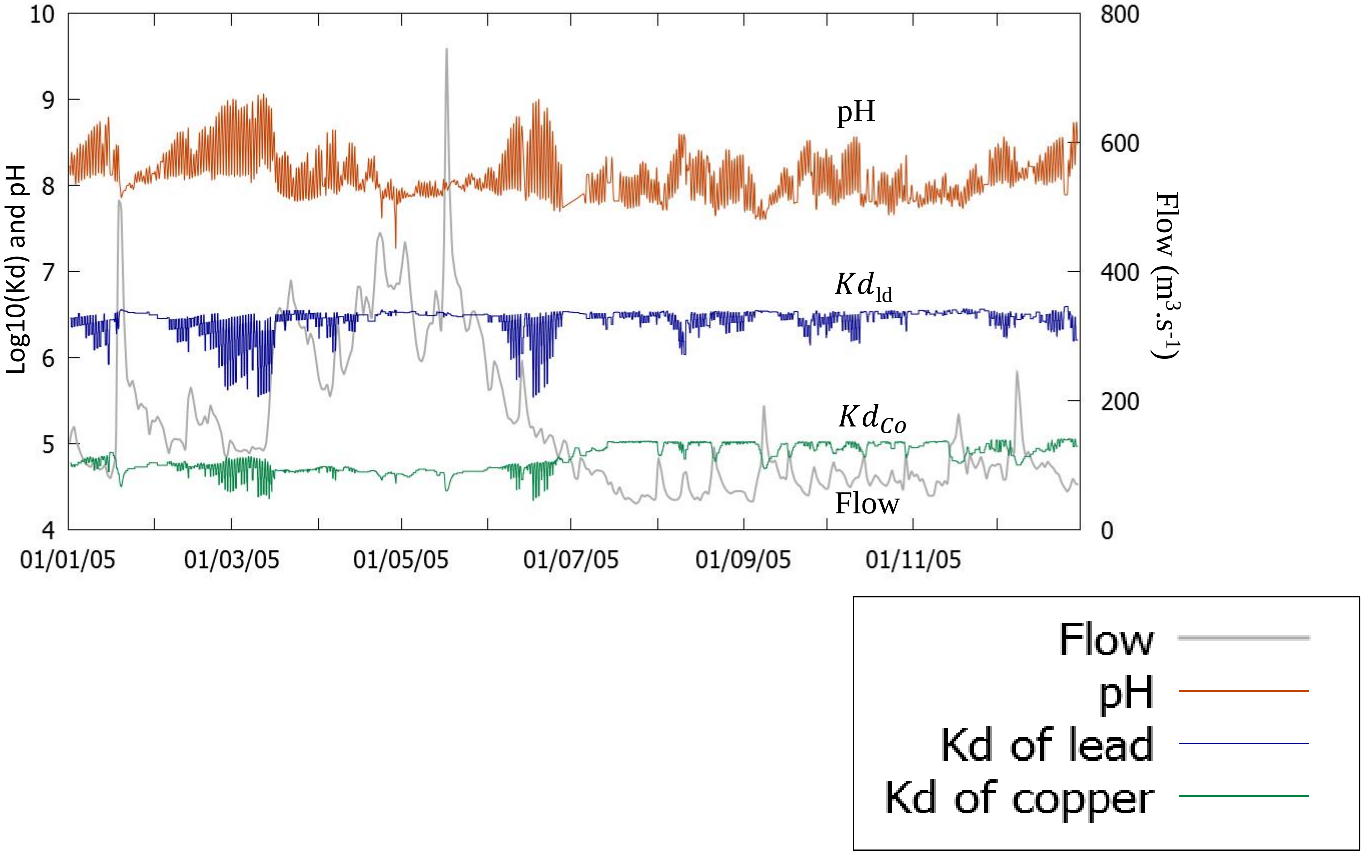
41% of copper trapped on the riverbed



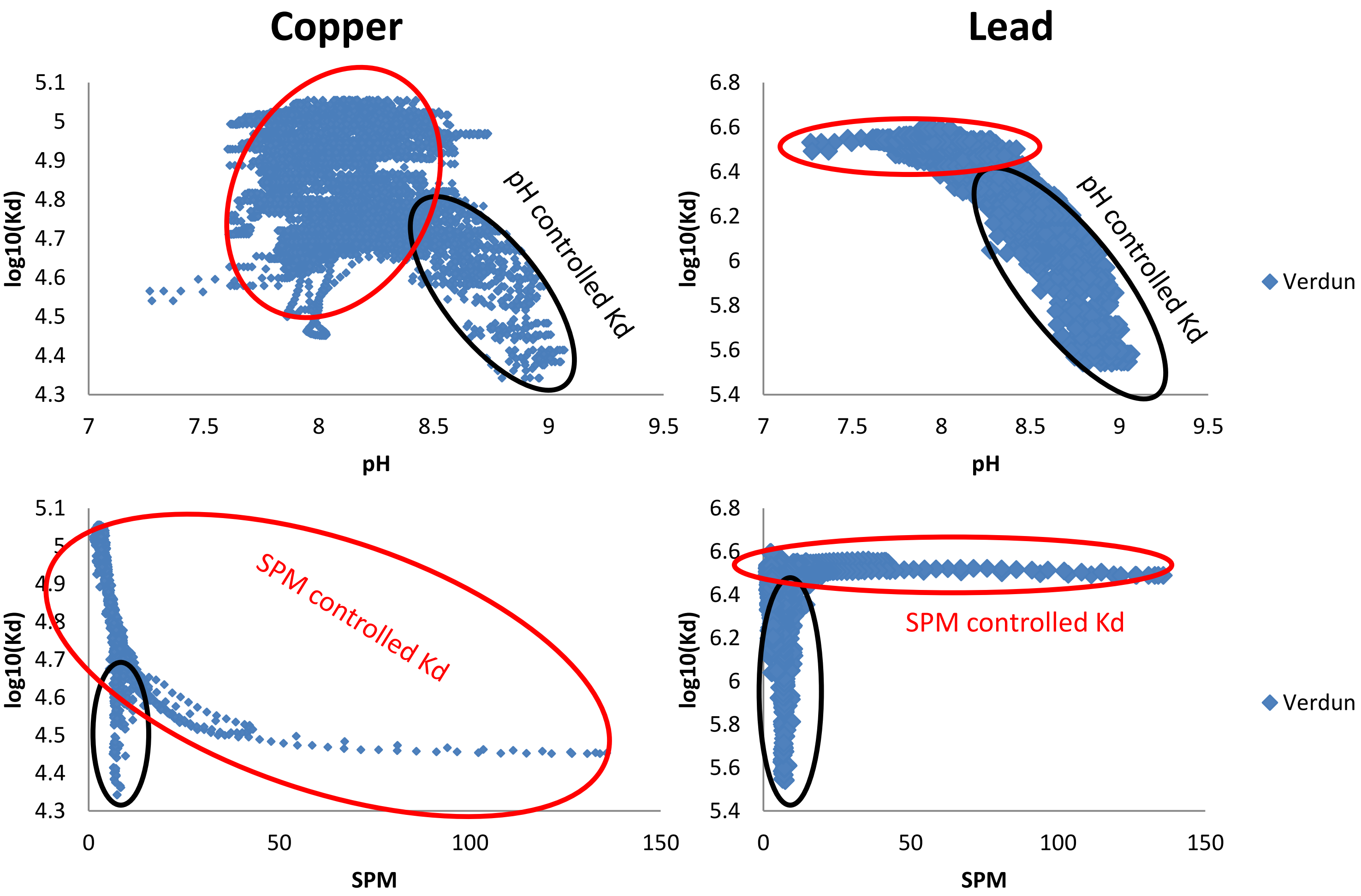
76% of lead trapped on the riverbed

Key results

- Physico-chemistry influence



Key results



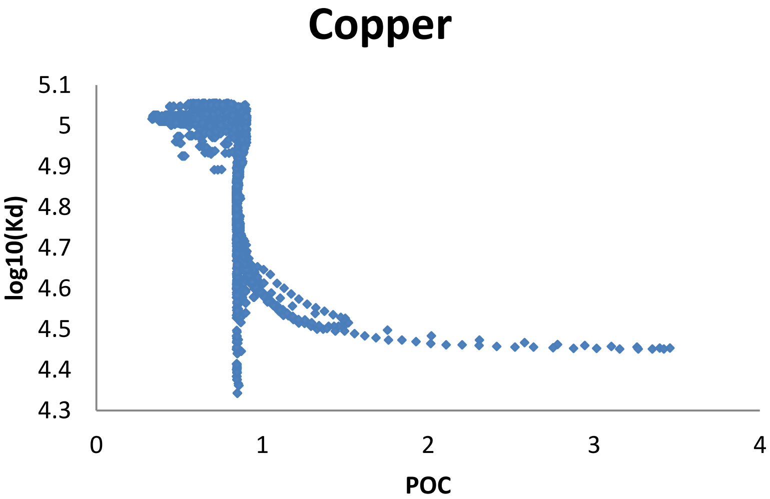
pH controlled Kd

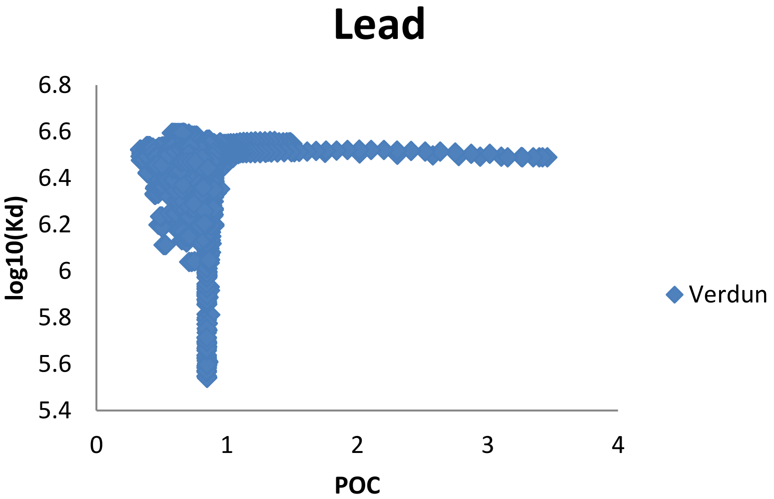
pH controlled Kd

SPM controlled Kd

SPM controlled Kd

Key results


Copper
log10(Kd)
5.1
5
4.9
4.8
4.7
4.6
4.5
4.4
4.3
0
1
2
3
4
POC


Lead
log10(Kd)
6.8
6.6
6.4
6.2
6
5.8
5.6
5.4
0
1
2
3
4
POC
◆ Verdun

Proposition

- Metal input generation
  - Anthropic sources: point-sources, atmospheric deposition, diffuse sources (fertilizers application)
  - Geogenic source: Based on soil maps, residence time and mixing models (Wade et al. 1999)
- Modelling requirements
  - Fixed Kd model: efficient for high Kd trace metal
  - Variable Kd model: efficient for low Kd
  - A simple empirical variable Kd model can be built on limited inputs variables (pH, SPM and POC concentrations)

Thank you for your attention