Vertical distribution of solute input shapes concentration-discharge relations

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Data collection

585 stations with synchronized discharge (Q) and concentration (C) data

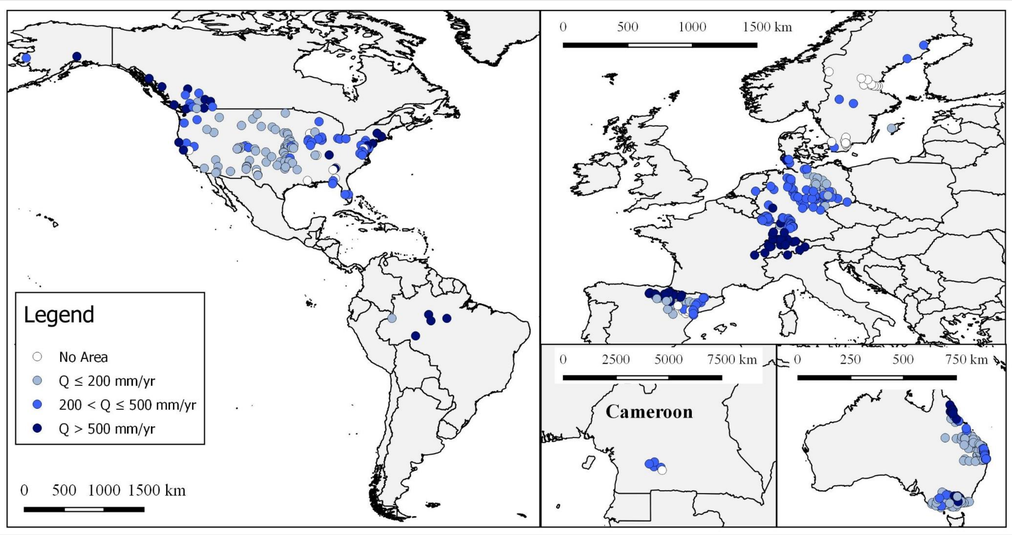

Figure 1.
Location of the water quality and discharge stations. The stations are classified based on the mean annual discharge normalized by catchment area.

HP 1: The input frequency is the main driver of the solute export dynamics

HP2: The depth of the solute generation is the main driver of the solute export dynamics

Hypotheses testing

Synthetic modelling experiments
The WATET model

Experimental setup

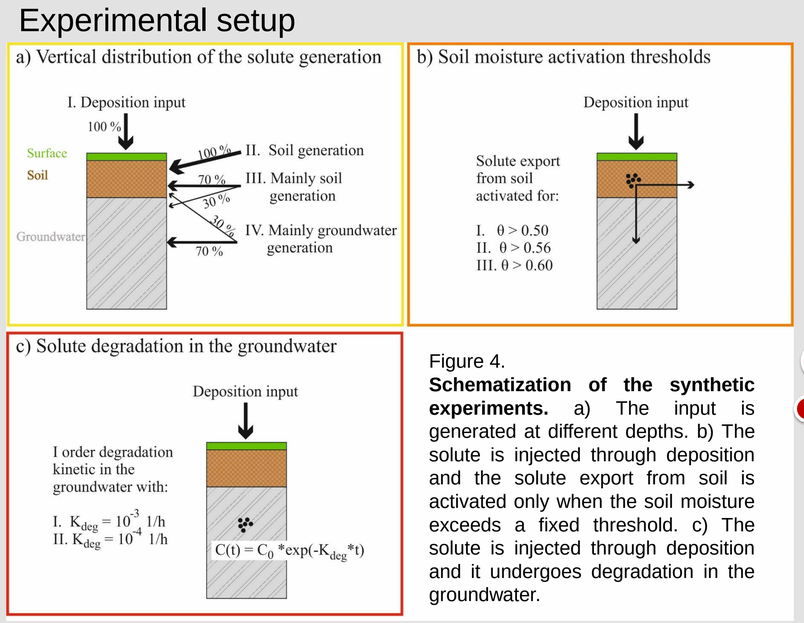

Figure 4.
Schematization of the synthetic experiments. a) The input is generated at different depths. b) The solute is injected through deposition and the solute export from soil is activated only when the soil moisture exceeds a fixed threshold. c) The solute is injected through deposition and it undergoes degradation in the groundwater.

Number of experiment runs

Figure 5.
Number of runs of the synthetic experiments. For each setup a constant amount of solute is injected with a different number of injections throughout the year, from all in once to constant small injections every day.

Coming soon
Botter et al., WRR, (in review)

Conclusions

The solute input/generation frequency adds some uncertainty to the solute export behavior, but the depth of solute generation and the consequent different of concentration in soil and groundwater water are the main drivers of the C-Q relations.

Evidences from data analysis

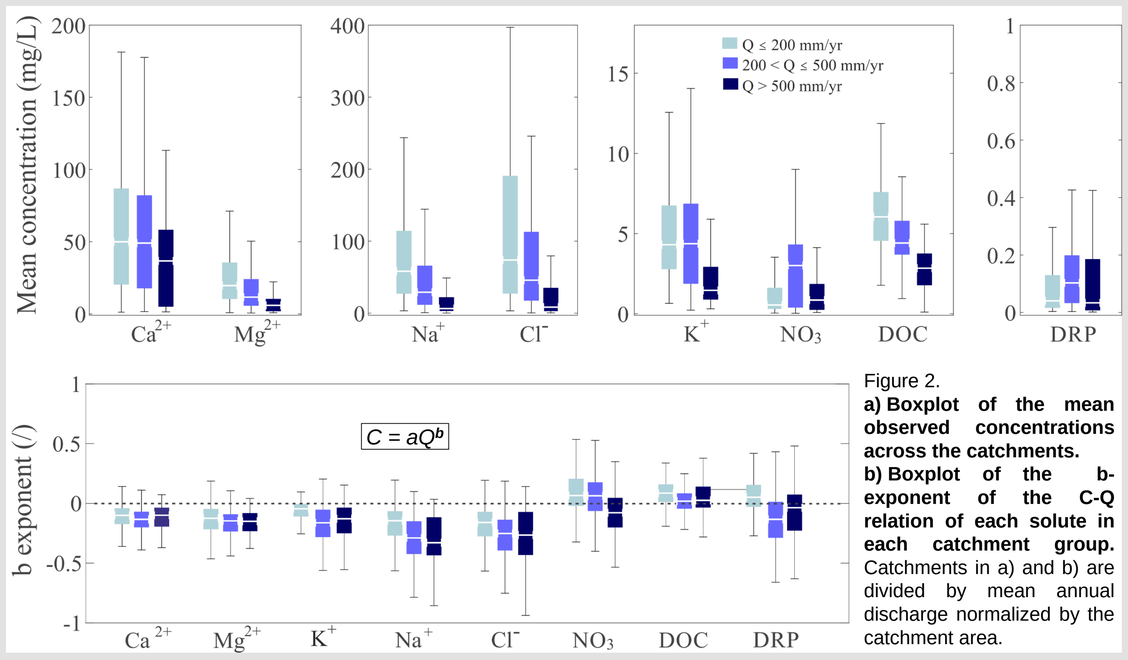

Figure 2.
a) Boxplot of the mean observed concentrations across the catchments.
b) Boxplot of the b-exponent of the C-Q relation of each solute in each catchment group. Catchments in a) and b) are divided by mean annual discharge normalized by the catchment area.

- Higher dilution with higher discharge except for nutrients K^+, NO_3 and DRP.
- Geogenic solutes Ca^{2+}, Mg^{2+}, K^+ exhibit moderate dilution.
- Na^+ and Cl^- strong and highly variable diluting behavior.
- DOC shows a consistently slightly enriching behavior.

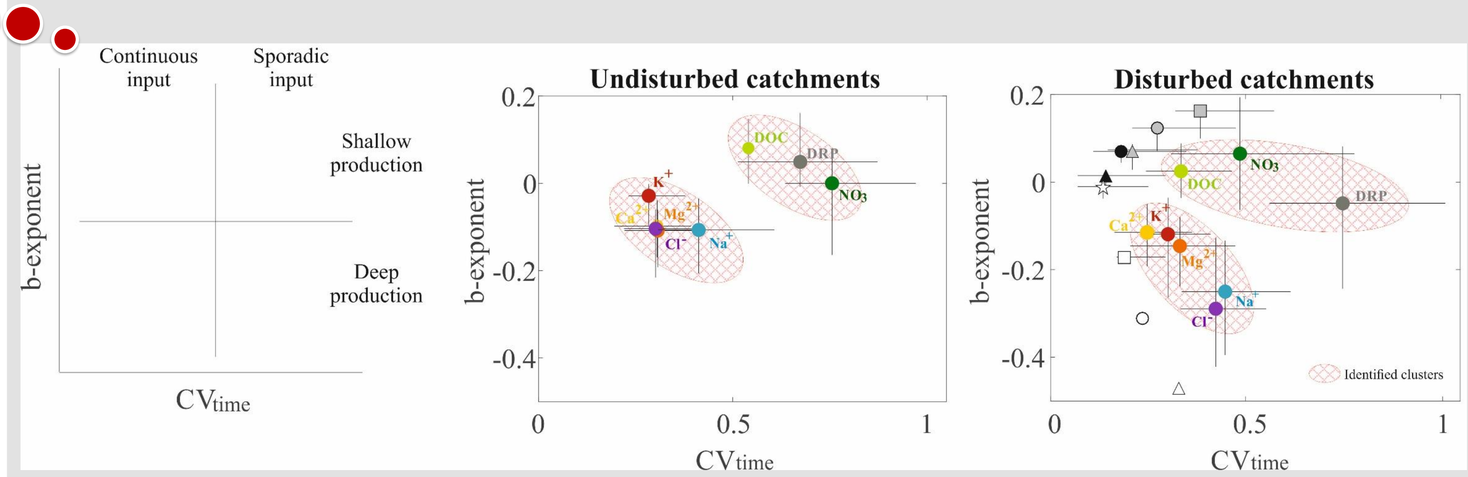

Figure 3.
CV_{time} VS b-exponent relation per each solute. The catchments are divided into undisturbed (i.e., mean NO3 concentration ≤ 1 mg/L) and disturbed catchments (i.e., mean NO3 concentration >1). The uncertainty bars span between the 25th and the 75th percentile.

- Geogenic solutes (Ca^{2+}, Mg^{2+}, K^+) and the salt solutes (Na^+, Cl^-)
  → low temporal variability (CV_{time}) and pronounced dilution behavior (negative b).
- Nutrients (NO_3 and DRP) and DOC
  → larger and highly variable CV_{time} and nearly zero or slightly positive b-exponents.
- Anthropogenic perturbation
  → increased uncertainty of both time variability (CV_{time}) and behavior (b-exponent).
- Unique behavior of DOC: CV_{time} comparable to geogenic solutes but behavior similar to nutrients.

Results

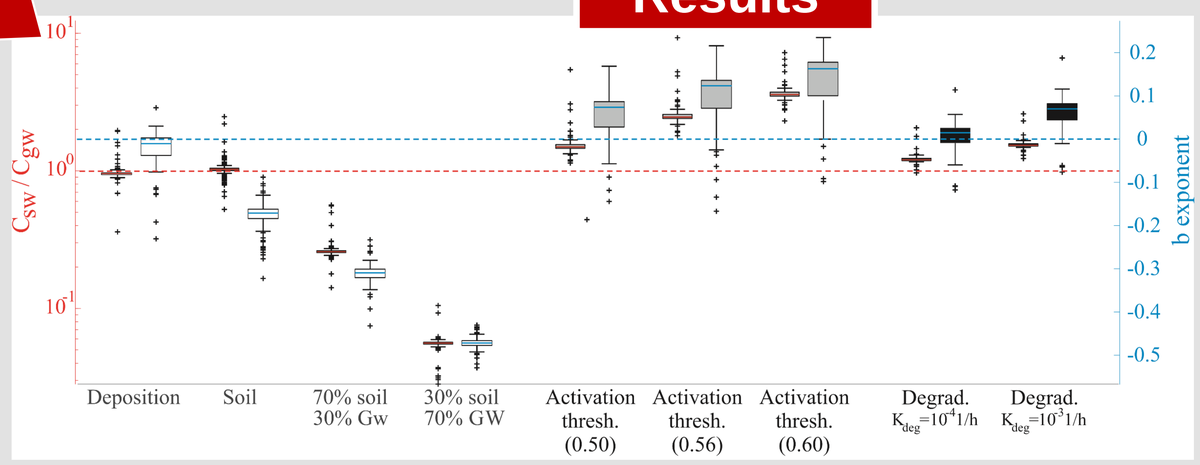

Figure 6.
b-exponent and Csw/Cgw resulting from the different experiments. The yellow boxes refer to the vertical distribution of solute generation experiments, the orange boxes to he activation threshold experiments and the red boxes to the degradation experiments.

- Both b-exponent and Csw/Cgw decrease with increasing depth of solute generation.
- The behavior spans between biogeochemical stationarity (deposition) and strong dilution (mainly groundwater generation) in the vertical distribution experiments.
- The higher the concentration in the groundwater water compared to the soil water the more diluting is the behavior.
- The higher the concentration in the soil water compared to the groundwater water the more enriching is the behavior (soil moisture threshold and groundwater solute degradation).
- Soil moisture threshold and solute degradation experiments exhibit enriching behavior and Csw/Cgw>1
- The timing of the input adds some uncertainty to the solute export behavior.

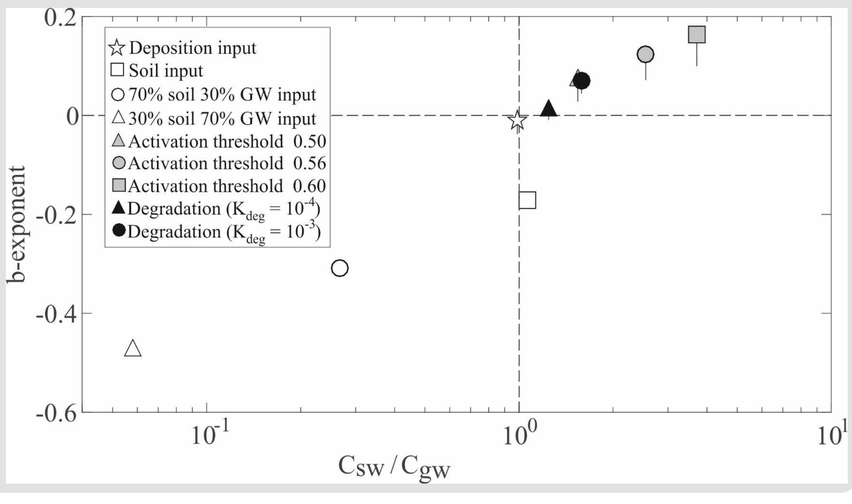

Figure7.
C_{sw}/C_{gw} VS b-exponent relation resulting across the experiments. The uncertainty bars span between the 25th and the 75th percentile.

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