UFZ HELMHOLTZ Zentrum für Umweltforschung

Subsurface reactivity dominates regional patterns of riverine nitrate concentration variability

Andreas Musolff[1], Pia Ebeling[1], Jan H. Fleckenstein[1], R. Kumar[1] & Rémis Dupas[2]
1 UFZ – Helmholtz-Centre for Environmental Research GmbH, Leipzig, Germany
2 UMR INRA/Agrocampus, Rennes, France

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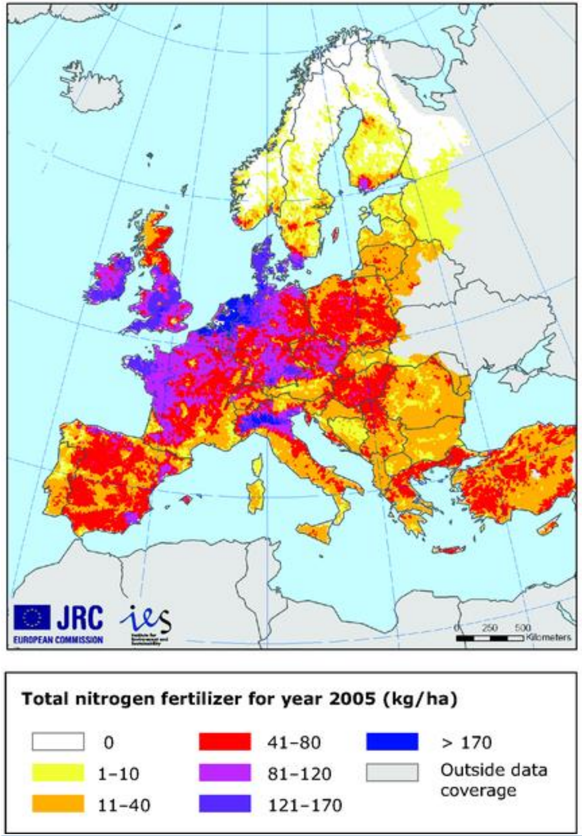
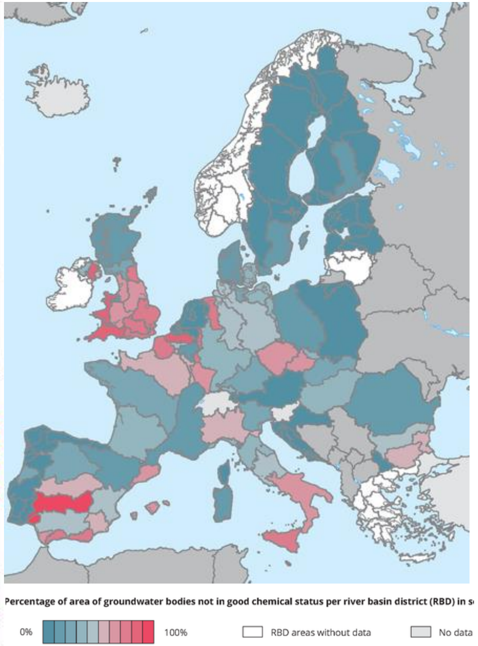
Introduction

Nitrate threatening water resources





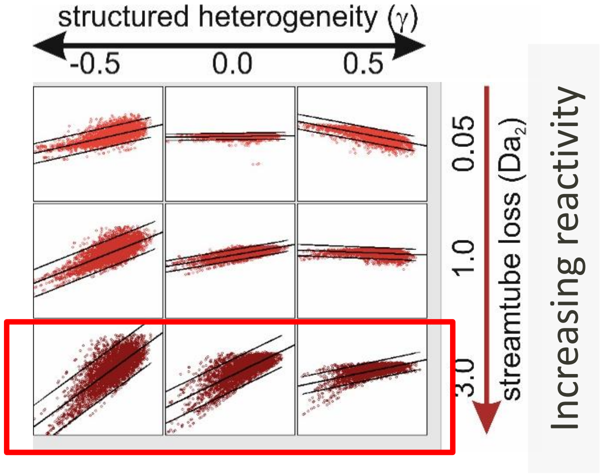
EEA 2018

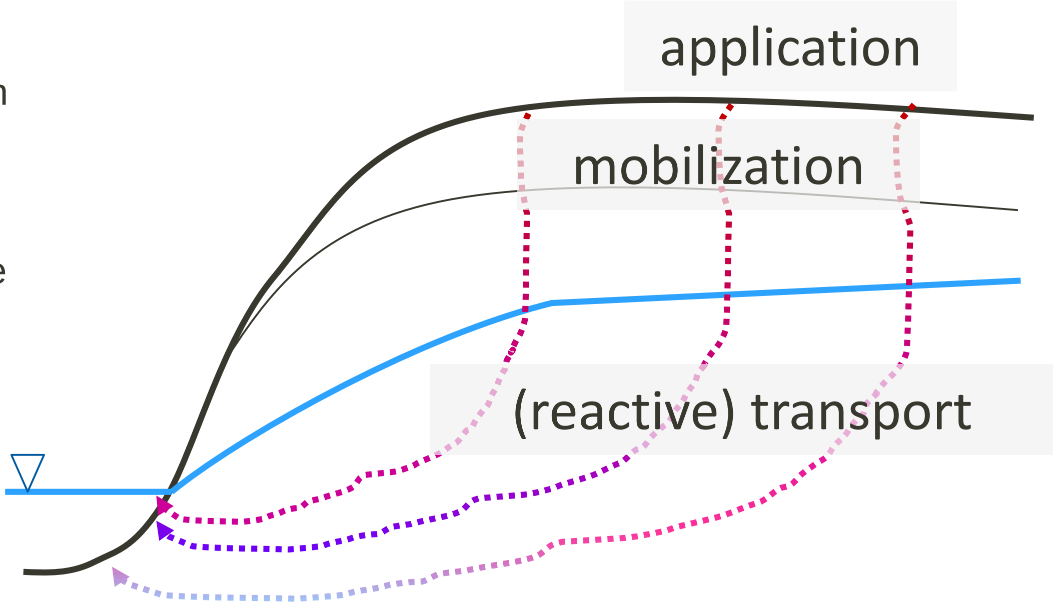
- A never ending story…
- Surface applications (left figure) and groundwater quality deterioration (right figure) do not always align
- How much of the observed pattern is driven by the fertilizer inputs and how much subsurface attenuation?
- Can we infer subsurface reactivity from patterns of surface water concentration?

Introduction
Model theory

- Strong subsurface reactivity will affect longer flowpaths/ older water more than shorter flowpaths/ younger water

- Assuming that higher discharge means younger water ages this will thus create positive C-Q relationships:



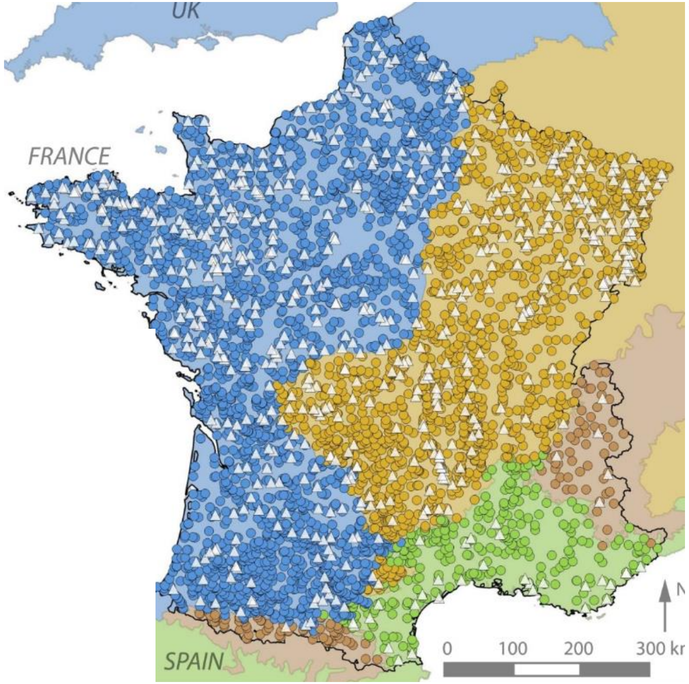


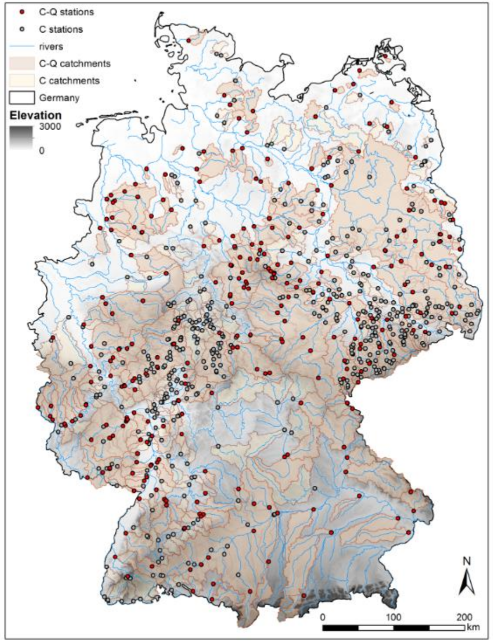
Musolff et al. 2017, GRL

Introduction
Objectives

- Can nitrogen input explain observed nitrate concentrations in surface waters?
  - Database of ~1400 catchments with C-Q time series in France and Germany
  - Do French and German catchments differ?
- Do we see a large scale evidence for subsurface nitrate attenuation across catchments
- Are concentrations and C-Q relations linked?

Databasis





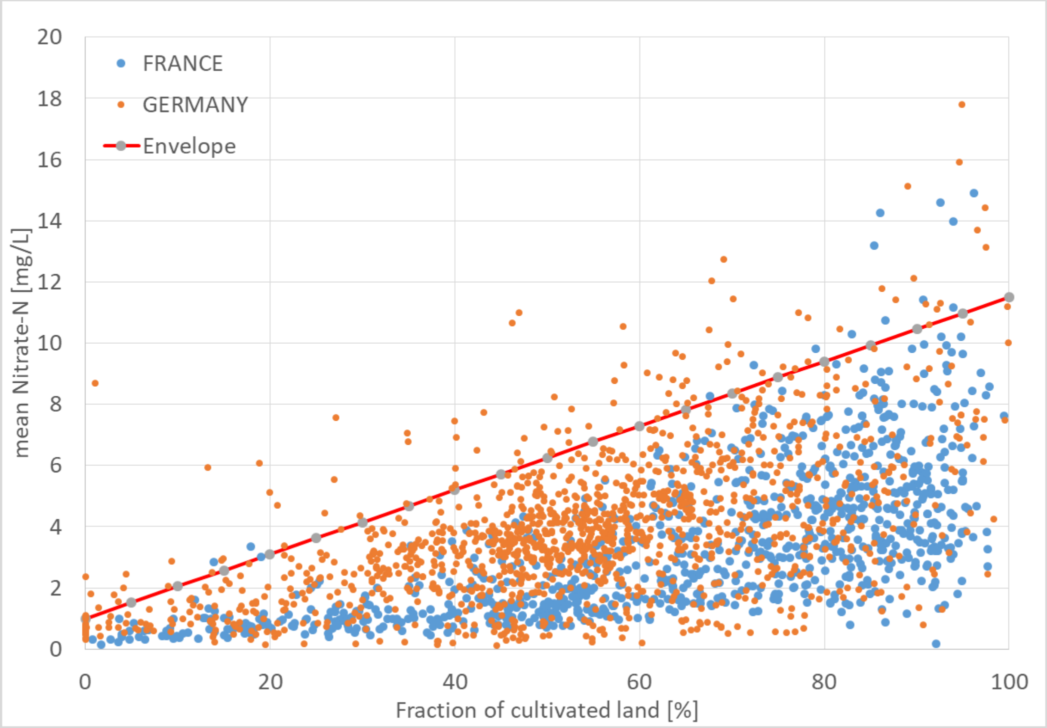
- Measured C-Q paired time series with a focus on more recent data (from year 2000 onward):
  - France: n=942
  - Germany: n=441 (1335 without Q)
  - Capturing atlantic to continental climates
  - Assuming a steady state between input and output

Dupas et al. (2019)

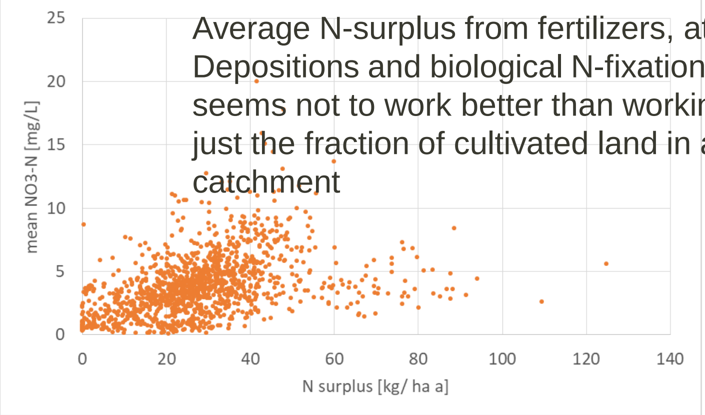
Ebeling et al. (in prep)

Results

Average nitrate concentration



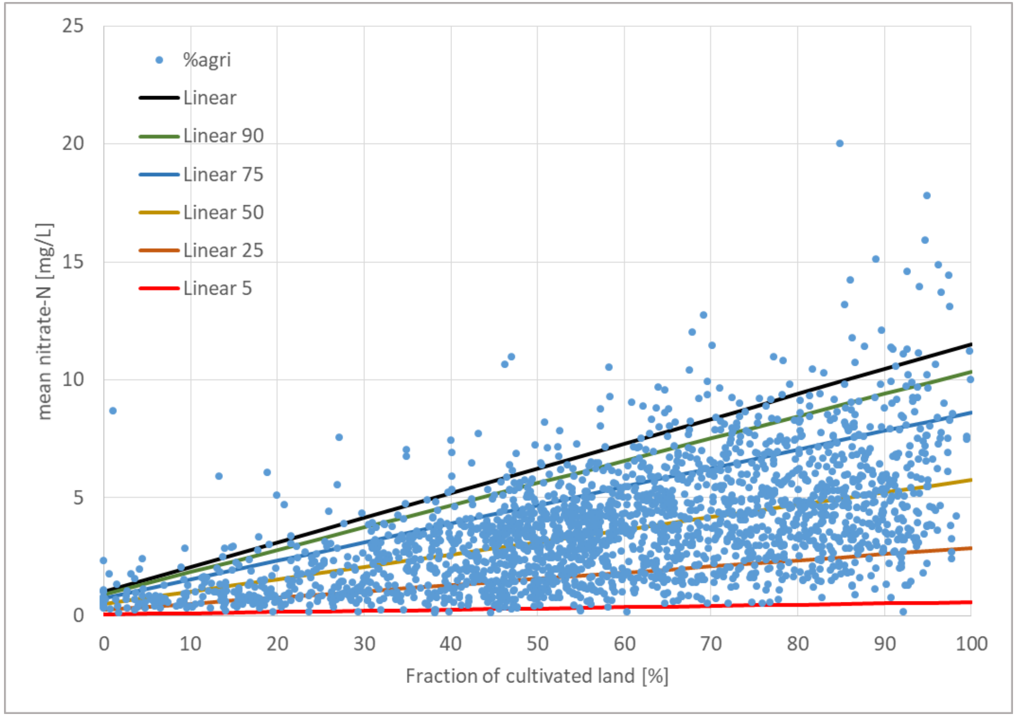
- Average nitrate-N
  - France: 3.46 ± 2.42 mg/L
  - Germany: 3.87 ± 2.41 mg/L
  - Not a big difference!
- Linear envelope function (95% of values are below that line) of mean nitrate vs. fraction of cultivated land



Average N-surplus from fertilizers, atm. Depositions and biological N-fixations seems not to work better than working just the fraction of cultivated land in a catchment

Results

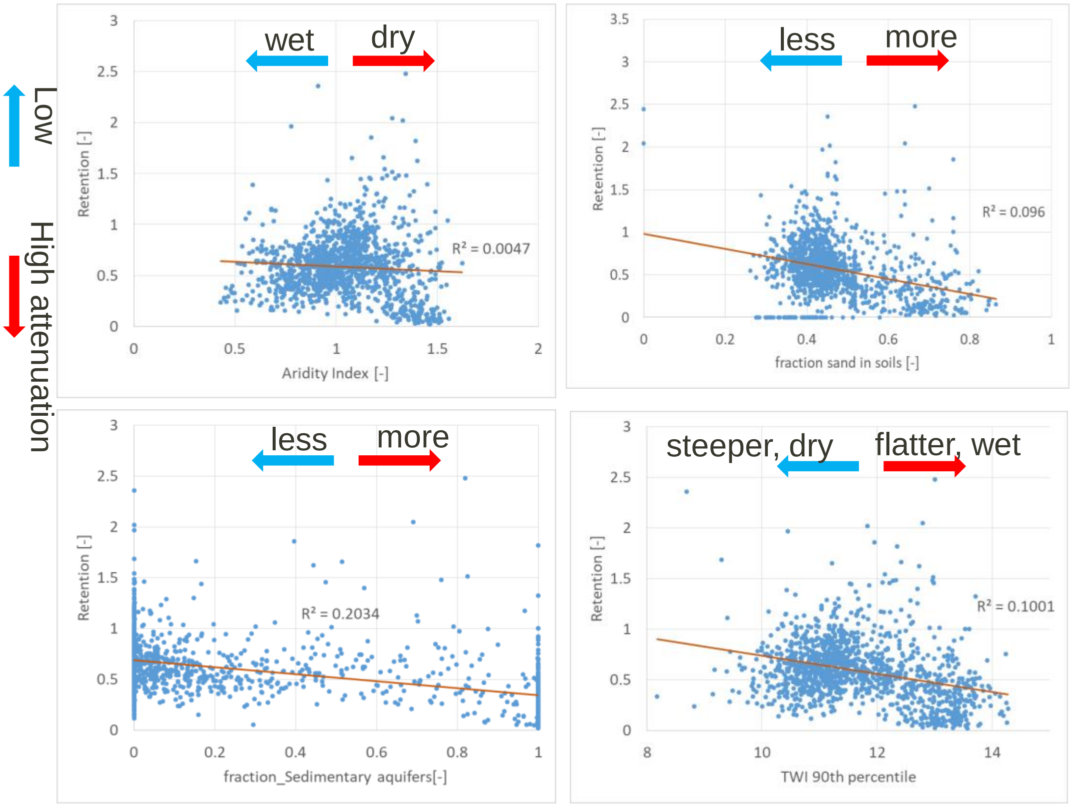
Nitrate retention



- Deviation from the linear input-mean nitrate envelope can be dilution or effective retention in subsurface and surface waters
- Introducing retention coefficient R to characterize that: How much is the observed mean concentration in a catchment deviating from the envelope function
- R=0.05 means that this catchment has a concentration of 95% smaller than expected from the input

Results

Nitrate retention (so far Germany only)



- Retention coefficient R vs other variables in a simpe correlation analysis

→Could be dilution: Aridity index shows no correlation to R

→Could be reaction:

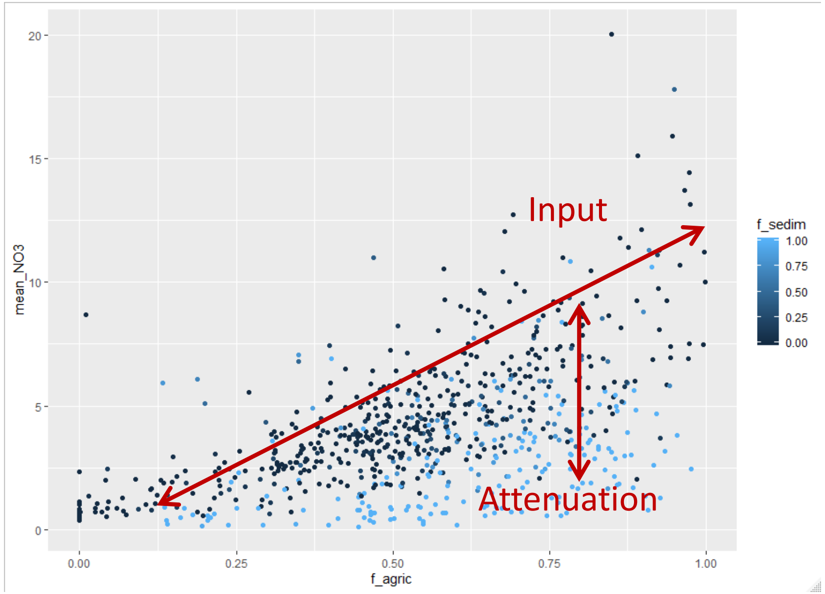
  →travel time: topographic wetness index TWI correlates negatively with R

  →reaction rate: sedimentary aquifers potentially high in carbon favor subsurface reactions (fraction sand in soils, fraction sedimentary aquifer in catchment are correlated with R

- Fraction of sedimentary aquifers, fraction of sand in soils and TWI are most promising (but correlated): r=0.66-0.81

Results

Predicting Nitrate concentrations (so far Germany only)



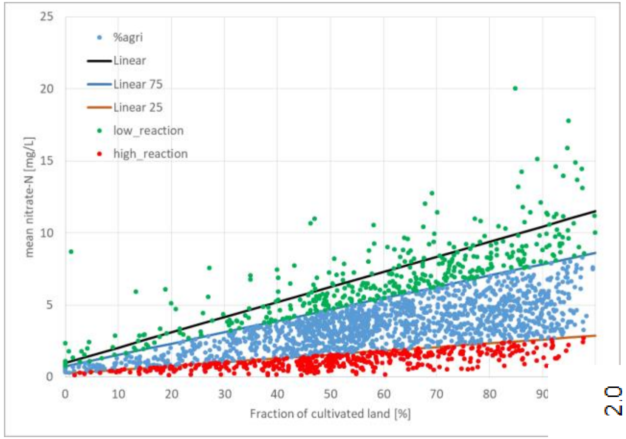
- Simple multiple regression model of mean nitrate concentrations as a function of fraction of cultivated land and other catchment characteristics:
- Mean NO_3 ~ f_cultivation R^2=0.30
- Mean NO_3 ~ f_cultivation +f_sedim R^2=0.49
- Mean NO_3 ~ f_cultivation +sand R^2=0.42
- Mean NO_3 ~ f_cultivation +TWI R^2=0.41

Note: adding aridity index does not help, N surplus instead of f_cultivation does not help

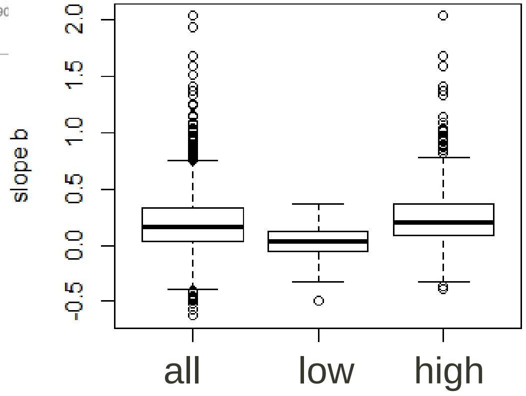
→ mean surface water nitrate can be explained to 50% by input and attentuation

Results

Mean nitrate concentrations – attenuation and C-Q relationships

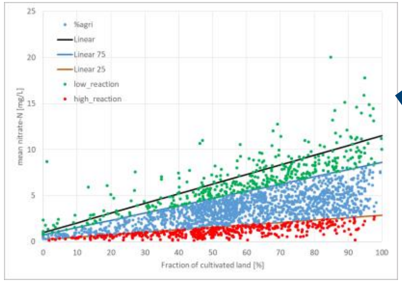


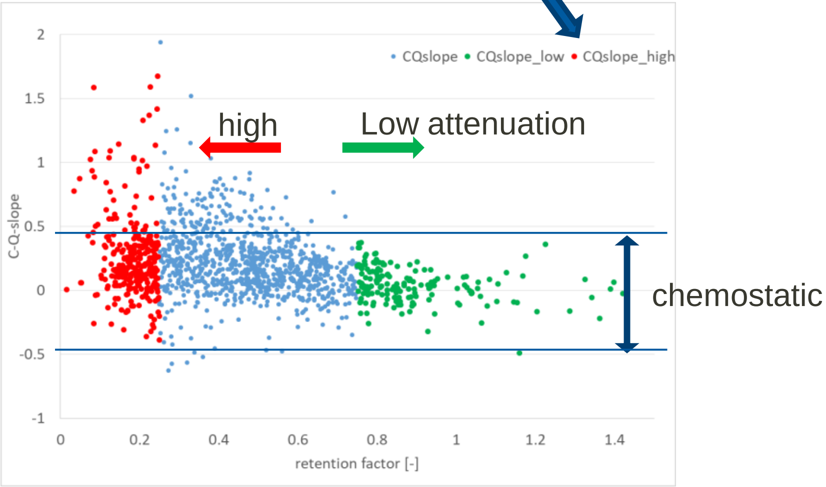
- Dividing data to high and low reactivity catchments:
  - Low reactivity catchmente have retention factors >0.75
  - High reactivity catchments have retention factors <0.25
- Do these catchment groups systematically differ in their C-Q relationship?
  - Yes: Significant higher slope b for „high reaction" catchments

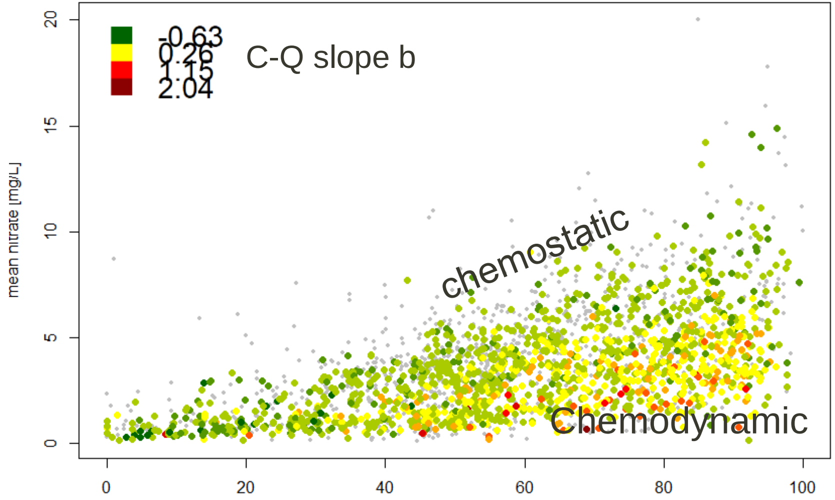


Results

Mean nitrate concentration – attenuation and C-Q relationships







- high nitrate concentration variance/ steep positive CQ-slopes occur, where attenuation is high
- Low attenuation means always chemostatic C-Q!
- Steep CQ-slopes are always connected to high attenuation!

Conclusions
Take home messages

- Large-scale databasis revealed a surprising consistent behavior:
  - Average surface water nitrate concentration can be explained by input (mainly agriculture) and subsurface attenuation
  - Fraction of cultivated land is suprisingly robust compared to actual nitrogen surplus
  - Steep C-Q slopes only occur, when attenuation is high
  - Low attenuation always results in C-Q slopes around zero (=chemostasis)

- → Steeply positive C-Q slopes of nitrate may be used as an indicator of subsurface attenuation efficiency

- → What are implication for a long-term perspective (i.e. decreasing denitrification potential in a catchment) – can this be seen in long-term time series by decreasing slope b?

References

- Musolff, A., Fleckenstein, J.H., Rao, P.S.C., Jawitz, J.W., 2017. Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. Geophys Res Lett, 44(9): 4143-4151. DOI:10.1002/2017GL072630

- Dupas, R., Minaudo, C. & Abbott, B.W., 2019. Stability of spatial patterns in water chemistry across temperate ecoregions. Environ Res Lett, 14(7)