Subsurface reactivity dominates regional patterns of riverine nitrate concentration variability

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Introduction
Nitrate threatening water resources

- 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?
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-superflus 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 simple 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 $\text{NO}_3 \sim f_{\text{cultivation}} R^2=0.30$
  - Mean $\text{NO}_3 \sim f_{\text{cultivation}} + f_{\text{sedim}} R^2=0.49$
  - Mean $\text{NO}_3 \sim f_{\text{cultivation}} + \text{sand} R^2=0.42$
  - Mean $\text{NO}_3 \sim f_{\text{cultivation}} + \text{TWI} R^2=0.41$

Note: adding aridity index does not help, N surplus instead of $f_{\text{cultivation}}$ does not help

→ mean surface water nitrate can be explained to 50% by input and attenuation
Results
Mean nitrate concentrations – attenuation and C-Q relationships

- Dividing data to high and low reactivity catchments:
  - Low reactivity catchments 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?