Stoichiometry on the Edge

Humans induce strong imbalances of reactive C:N:P ratios in streams

Alexander Wachholz[1], Joni Dehaspe[1,2], Pia Ebeling[1], Rohini Kumar[1], Andreas Musolff[1], Felipe Saavedra[1], Carolin Winter[1,3], Soohyun Yang[1,4] and Daniel Graeber[1]

1 Helmholtz Center for Environmental Research (UFZ)
2 Flemish Institute for Technological Research NV- VITO, Mol, Belgium
3 Department of Hydrology, Albert-Ludwigs-University of Freiburg
4 Department of Civil and Environmental Engineering, Seoul National University, Seoul, Republic of Korea

alexander.wachholz@ufz.de

UFZ HELMHOLTZ Zentrum für Umweltforschung

Executive summary

What is stoichiometry? The ratio between reactants in chemical reactions (e.g., how much C is needed to denitrify one mol of NO_3-N).

Why is it important in aquatic ecosystems? Together with nutrient concentrations, their stoichiometry (e.g., C:N:P ratios) controls the reaction rates of important ecosystem services, such as nutrient retention.

How does human activity change it? Human activities drive C:N:P ratios away from conditions in pristine catchments by introducing too much N (and P) while removing sources of bioavailable OC. This can limit e.g. bacterial retention of nutrients in rivers and adjacent ecosystems.

Motivation & Hypotheses

Ecosystem functions are not only affected by the over-abundance of a single macronutrient but also by the stoichiometry of the reactive (r) forms of dissolved organic carbon (rOC), nitrogen (rN), and phosphorus (rP).

Many studies focus on single macronutrients or stoichiometric ratios such as N:P or C:N independent from each other. We argue that a mutual assessment of reactive nutrient ratios rOC:rN:rP relative to organismic demands enables us to refine the definition of nutrient depletion versus excess including its linkage with hydro- biogeochemical processes. We hypothesize that

(I) average reactive C:N:P ratios in agriculturally-impacted catchments show a stoichiometric imbalance towards high rN

(II) rOC:rN:rP at the catchment outlet to show distinct intra-annual variability that can be linked to key hydrological and biogeochemical processes within the catchment

Data & Methods

- 6 years of C, N, and P time series from 574 catchments -> average seasonal pattern
- normalization of nutrients according to the Redfield ratio

$$(I) \quad M_{RFC} = \frac{b_M\, M}{\frac{b_{OC}\, TOC}{106} + \frac{b_N\, DIN}{16} + b_P\, SRP}$$

where M is any macronutrient (OC, N, P) concentration [*mol/ l*] and b is the bio-availability of the macronutrient

- classification of catchments according to depletion (RFC < 20 %) and intra-annual rOC:rN:rP variability

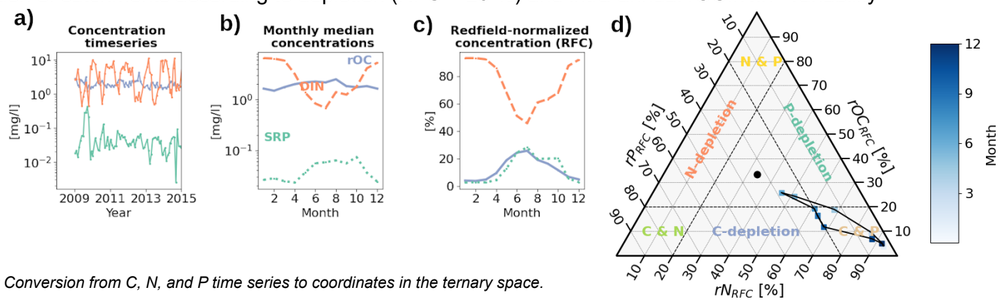
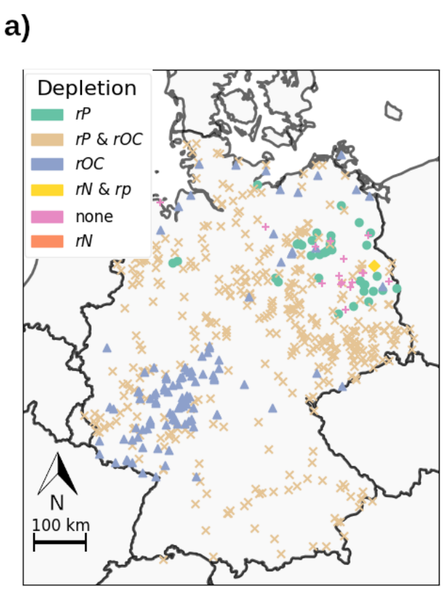


Figure 1: *Conversion from C, N, and P time series to coordinates in the ternary space.*



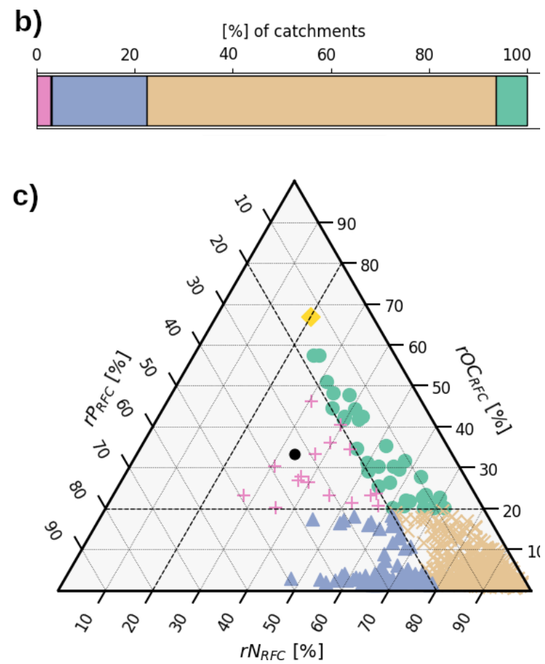


Figure 2: *Distribution of annual mean depletion patterns among 574 German catchments. "Depletion" refers to Redfield-normalized concentrations (RFC) which are < 20 % (see. Eq.I). The prefix "r" represents the reactive fraction of N, P, and organic C.*

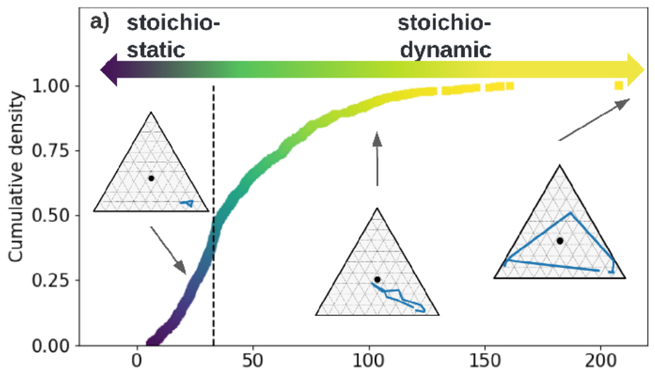


Figure 3: *Distribution of the intra-annual C:N:P variability () among German catchments. The dashed line marks the separation between stoichio-static and -dynamic catchments (33rd percentile).*

Results & Conclusions

- This study presents the first large-scale, systematic assessment of reactive C:N:P ratios across river networks
- Among catchments and seasons, reactive C:N:P ratios are imbalanced towards excessive N compared to well-known stoichiometric requirements
- This is not only true for agricultural catchments, which illustrates the ubiquity of excess rN in anthropogenically influenced landscapes
- In contrast to our expectation, we show that not all catchments show an evident intra-annual variability in reactive C:N:P ratios, but some are **stoichio-static**
- We link **stoichio-static** behavior to high nitrate concentrations with little variability throughout the year
- This mask changes in nutrient ratios that could have been caused by the variability of C and P
- This imbalance will likely have strong consequences for (i) catchment nutrient retention due to the stoichiometry of the key biological processes and (ii) for alterations in the integrity and functioning adjacent ecosystems

Future research

- How do seasonal reactive C:N:P ratios appear in pristine catchments(i.e., what goals could we set for restoration)?
- How do in-stream reactive C:N:P ratios affect species compositions in streams and adjacent ecosystems?
- Where & when becomes stoichiometry a limiting factor in aquatic ecosystems?

DOI