DR. ANDREAS MUSOLFF (Orcid ID : 0000-0002-0115-1359)
DR. KLAUS-HOLGER HOLGER KNORR (Orcid ID : 0000-0003-4175-0214)

Article type : Response to Editor

Corresponding author mail id:- andreas.musolff@ufz.de

Response to the editor: Does iron reduction control the release of dissolved organic carbon and phosphate at catchment scales? - Need for a joint research effort.

A. Musolff[1*], B. Selle[2], O. Büttner[3], M. Opitz[4], K.H. Knorr[5], J.H. Fleckenstein[1], T. Reemtsma[6] and J. Tittel[7]

[1]Department Hydrogeology, UFZ – Helmholtz-Centre for Environmental Research, Permoserstr. 15, 04318 Leipzig, Germany

[2]Department III - Civil Engineering and Geoinformation, Beuth University of Applied Sciences, Luxemburger Str. 10, 13353 Berlin, Germany

[3]Department Aquatic Ecosystem Analysis, UFZ – Helmholtz-Centre for Environmental Research, Brückstr. 3a, 39114 Magdeburg, Germany

[4]IDUS Biologisch-Analystisches Umweltlabor GmbH, Radeberger Str. 1, 01458 Ottendorf-Okrilla, Germany

[5]Institute of Landscape Ecology, WWU Münster, Heisenbergstr. 2, 48149 Münster, Germany

[6]Department Analytical Chemistry, UFZ – Helmholtz-Centre for Environmental Research, Permoserstr. 15, 04318 Leipzig, Germany

[7]Department Lake Research, UFZ – Helmholtz-Centre for Environmental Research, Brückstr. 3a, 39114 Magdeburg, Germany

[*]corresponding author

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/gcb.13758

We welcome the comment by Kalbitz *et al.* (2017) on our recent paper in which we examined long-term time series of concentrations of dissolved organic carbon (DOC) and phosphate from 110 streams in Germany. We concluded that increasing concentrations of both DOC and phosphate were governed by the reduction of iron(III)-minerals in riparian soils and the associated release of the adsorbed compounds. We explained the decreasing stability of the iron minerals by declining nitrogen depositions and thus decreasing nitrate redox buffers in riparian wetland soils (Musolff *et al.*, 2017). Kalbitz *et al.* (2017) raised three major points to challenge our conclusions, which we accordingly address:

(I) *The ratio at which DOC and iron increased in our streams (molar DOC:Fe ratio: 39) was much higher than the typical adsorption capacity of iron oxides for organic carbon (OC) in soils (≤ 6-10).* We think that it is not the adsorption capacity that matters here, but rather the ratio at which DOC and iron are *mobilized* through reductive processes. Indeed, experimental studies demonstrated a joint reductive mobilization from wetland soils with OC:Fe ratios of 15-52 (Cabezas *et al.*, 2013) and 38-41 (Grybos *et al.*, 2007; Grybos *et al.*, 2009) which is comparable to our observations. In addition, a significant fraction of mobilized iron is precipitated or fixed as colloids at the soil-stream interface further increasing the OC:Fe ratio in the dissolved phase (Neubauer *et al.*, 2013). We recognize that the criticized remark in Musolff *et al.* (2017) did not sufficiently address these issues.

(II) *Nitrogen depositions in Europe and North America began to decrease only in the last decade while DOC concentration increases started much earlier.* Nitrogen depositions steadily declined in the EU between 1985 and 2007 to 71% (Fig. 1). In the US, regional deposition patterns changed after 1990-1992 (Li *et al.*, 2016). Considering that pronounced DOC increases were recorded in the 1990s and afterwards, we see no temporal mismatch between trends in nitrogen deposition and stream DOC.

(III) *Increased phosphate mobilization does not indicate reductive processes but may be related to temperature and changing pH.* Within the studied streams we note a significant correlation between trends of phosphate and dissolved iron (R^2 = 0.60, $P < 0.001$). In contrast, neither trends of phosphate and pH (R^2 = 0.03, $P > 0.1$) nor trends of phosphate and water temperature (R^2 = 0.00, $P > 0.1$) were related.

In a non-linear system of redox-buffering and with low nitrate availability, small changes in nitrate can induce strong non-stoichiometrical responses in iron reduction (Achtnich *et al.*, 1995). The critical nitrate concentrations may differ between sites as iron reduction is influenced by a suite of parameters such as concentration of iron, other electron acceptors (e.g. sulfate), pH, aluminum and aggregation of Fe-nanoparticles.

In conclusion we state that increasing reductive dissolution of iron minerals in riparian soils is a plausible biogeochemical control of the observed increasing concentration of phosphate and DOC in streams. Its significance for DOC-export at catchment scales is owed to the role of riparian zones as major source zones of event discharge in temperate climates (Dunne & Black, 1970). A joint effort of both data analyses and experimental work is needed to further explore the significance of iron reduction for the water quality issues discussed above.

Figure 1: Long-term records of nitrogen depositions in European countries as well as of average stream solute concentrations for 13 selected German stream. (a) Nitrogen (reduced plus oxidized) deposition (MSC-W, 2014). (b) Relative concentrations of DOC, dissolved iron and of nitrate from the 13 streams. For each stream, annual mean concentrations were calculated from Box-Cox transformed data. The annual means were then standardized relative to the first year of the observations. For individual years, medians were calculated from the standardized values of all streams. The selected streams represent those from (Musolff *et al.*, 2017) with significant DOC increases and pH values ≤6.

Acknowledgements

The work was supported by the Federal Ministry of Education and Research Germany (BMBF, 02WT1290A). The authors declare no conflict of interest.

References

Achtnich C, Bak F, Conrad R (1995) Competition for Electron-Donors among Nitrate Reducers, Ferric Iron Reducers, Sulfate Reducers, and Methanogens in Anoxic Paddy Soil. *Biology and Fertility of Soils,* **19**, 65-72.

Cabezas A, Gelbrecht J, Zak D (2013) The effect of rewetting drained fens with nitrate-polluted water on dissolved organic carbon and phosphorus release. *Ecological Engineering,* **53**, 79-88.

Dunne T, Black RD (1970) Partial Area Contributions to Storm Runoff in a Small New-England Watershed. *Water Resources Research,* **6**, 1296-&.

Grybos M, Davranche M, Gruau G, Petitjean P (2007) Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? *Journal of Colloid and Interface Science,* **314**, 490-501.

Grybos M, Davranche M, Gruau G, Petitjean P, Pedrot M (2009) Increasing pH drives organic matter solubilization from wetland soils under reducing conditions. *Geoderma,* **154**, 13-19.

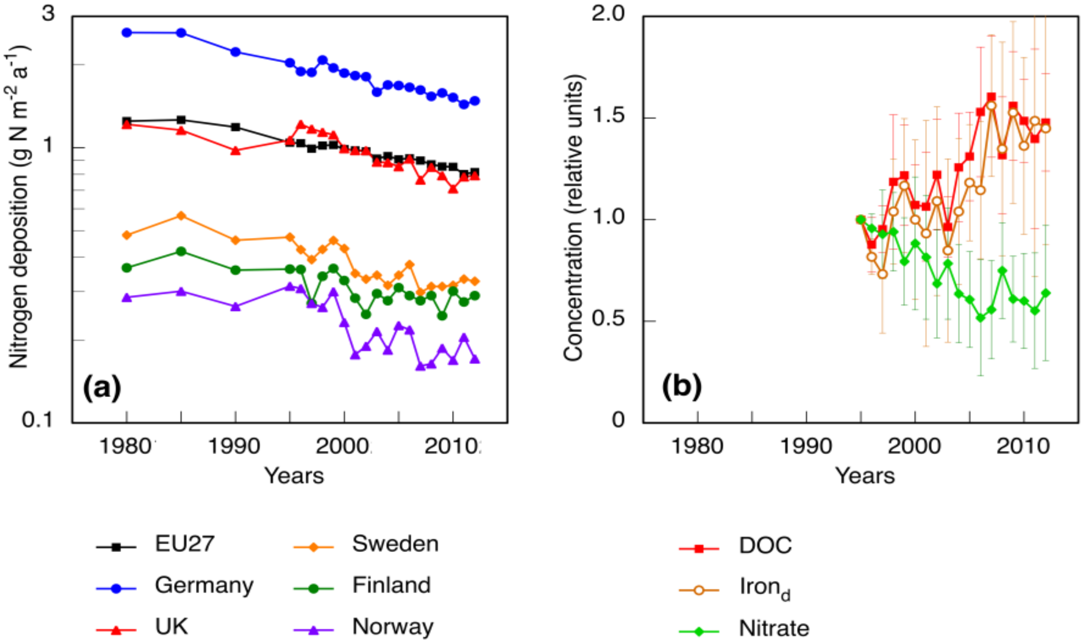
Kalbitz K, Kaiser K, Mcdowell WH (2017) Nitrate decline unlikely to have triggered release of dissolved organic carbon and phosphate to streams. *Global Change Biology*.

Li Y, Schichtel BA, Walker JT *et al.* (2016) Increasing importance of deposition of reduced nitrogen in the United States. *Proceedings of the National Academy of Sciences of the United States of America,* **113**, 5874-5879.

Msc-W (2014) EMEP/Meteorological Synthesizing Centre - West (MSC-W). http://www.emep.int/mscw/index_mscw.html.

Musolff A, Selle B, Büttner O, Opitz M, Tittel J (2017) Unexpected release of phosphate and organic carbon to streams linked to declining nitrogen depositions. *Global Change Biology,* **23**, 1891-1901.

Neubauer E, Von Der Kammer F, Knorr KH, Peiffer S, Reichert M, Hofmann T (2013) Colloid-associated export of arsenic in stream water during stormflow events. *Chemical Geology,* **352**, 81-91.


Nitrogen deposition (g N m-2 a-1)
3
1
0.1
(a)
1980
1990
2000
2010
Years
Concentration (relative units)
2.0
1.5
1.0
0.5
0
(b)
1980
1990
2000
2010
Years
EU27
Germany
UK
Sweden
Finland
Norway
DOC
Iron_d
Nitrate