PRESENT AND PAST NITROGEN TURNOVER IN THE DANUBE ESTUARINE TRANSITION ZONE

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Abstract

After decades of heavy eutrophication the NW Black Sea Shelf slowly recovers towards a natural state. During two cruises we investigated the turnover of nitrogen in the Danube estuarine transition zone. Isotopic patterns of dissolved and particulate N-species highlight the River Danube as dominant source in spring but they give also evidence for diazotrophic N_2 fixation during summer. Sedimentary $d^{15}N$ records track the temporal changes of dominant N sources and the current recovery from eutrophication.

Keywords: Nutrients, River input, Black Sea, Danube Delta

The Danube Delta–Black Sea shelf region has overall received dynamic nutrient loads from the River Danube that rose to critical levels in the 1970s and 1980s but decreased sharply in the 1990s due to the collapse of eastern European economies. However, nutrient release from organic rich sediments retarded the recovery of the ecosystem for another decade. During two cruises (spring 2012 and summer 2013) in the Danube River Delta–Black Sea transition zone, we analyzed dissolved nutrients, dual isotope signatures of nitrate, and $d^{15}N$ of suspended particulate matter across the salinity gradient. Water column data were complemented by a series of short sediment cores that were analyzed for organic carbon and nitrogen contents as well as for $d^{15}N$. During high run-off (May 2012) data highlight the Danube as a point source of nutrients to a nutrient starving sea. Data further indicate intense drawdown of river-borne nutrients in the river plume - and spatial isotopic patterns of nitrate and suspended N clearly attribute this drawdown to assimilation over entire salinity gradient [1]. However, an unusual 1.9 : 1 but very strict enrichment of $d^{18}O_{NO3}$ to $d^{15}N_{NO3}$ questions the usually uniform 1 : 1 enrichment that is attributed to assimilation by phytoplankton [2]. Similar ratios are known only for heterotrophic bacteria in laboratory experiments [3] but have never been observed in field studies. Moreover, the relatively low isotopic enrichment factor e^{15} of -2.7 ‰ in residual nitrate is in good agreement with the fractionation expected for heterotrophs [3]. Consequently, this aberrant fractionation pattern could evidence the occurrence (and dominance) of heterotrophic bacteria in the Danube estuarine transition zone. These bacteria generally may play a more important role in coastal N-turnover than previously thought. However, the dominance of heterotrophic nitrate consumers is probably a seasonal feature that only plays a major role if large quantities of nitrate as well as suspended and dissolved organic matter are available. During low run-off August 2013 nitrate concentrations were too low for isotope measurements but $d^{15}N$ values of suspended matter strongly suggest a seasonal shift from a single (riverine) source to a two endmember mixing of isotopically even more enriched particulate nitrogen (derived from residual riverine nitrate) and isotopically depleted particulate marine nitrogen. Possible sources for isotopically light marine nitrogen are diazotrophic N_2 fixation (postulated by several researchers but not observed yet in the Black Sea), incomplete NO_3^- uptake due to phosphorous limitation or the atmospheric deposition of anthropogenic NO_x as observed in the Eastern Mediterranean Sea [3, 4]. However, spatial and temporal patterns in sedimentary $d^{15}N$ witness the shift from past severe eutrophic conditions to the currently recovered ecosystem. A significant role of nitrogen fixation as a consequence of phosphorous release from organic rich sediments is evidenced by a depth decrease of sedimentary $d^{15}N$ values in the outer plume. Isochronous time-slices at depth imply a two endmember mixing of isotopically enriched riverine nitrate with isotopically depleted nitrate from the shelf that turns to the presently dominant one endmember. Overall, all N species analyzed exceptionally clearly illustrate the isotopic coherences that characterize the present and the past nitrogen turnover.

References

1 - Möbius, J. and Dähnke, K. 2015. Nitrate drawdown and its unexpected isotope effect in the Danube estuarine transition zone. *Limnology and Oceanography* 60 (3),1008-1019.

2 - Granger, J., D. M. Sigman, J. A. Needoba, and P. J. Harrison. 2004. Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton. *Limnology and Oceanography* 49: 1763-1773.

3 - Granger, J., D. M. Sigman, M. M. Rohde, M. T. Maldonado, and P. D. Tortell. 2010. N and O isotope effects during nitrate assimilation by unicellular prokaryotic and eukaryotic plankton cultures. *Geochimica et Cosmochimica Acta* 74: 1030-1040.

4 - Mara, P., Mihalopoulos, N., Gogou, A., Daehnke, K., Schlarbaum, T., Emeis, K.C., Krom, M., 2009. Isotopic composition of nitrate in wet and dry atmospheric deposition on Crete in the eastern Mediterranean Sea. *Global Biogeochem. Cycles* 23.

5 - Emeis, K.C., Mara, P., Schlarbaum, T., Möbius, J., Dähnke, K., Struck, U., Mihalopoulos, N., Krom, M., 2010. External N inputs and internal N cycling traced by isotope ratios of nitrate, dissolved reduced nitrogen, and particulate nitrogen in the eastern Mediterranean Sea. *J. Geophys. Res. Biogeosci.* 115.