

Interactive comment on “Dissolved and particulate reactive nitrogen in the Elbe River/NW Europe: a 2-year N-isotope study” by T. Schlarbaum et al.

Anonymous Referee #1

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Review of Schlarbaum et al. The nitrogen cycle is massively perturbed by human action and we urgently need to better understand the impact of this excess nitrogen in the environment. Isotopic techniques provide a very valuable tool with which to better understand the cycling of nitrogen. This very well conducted study from a very experienced research group provides a valuable new contribution to our understanding. In particular this study attempts to tackle the particularly challenging issue of the cycling of dissolved organic nitrogen which is poorly characterised, poorly understood and difficult to measure, since it must be done by difference between total N and nitrate measurements. The Elbe estuary studied here is rather well chosen for this study because the relative proportions of DON to nitrate are high enough to allow rather precise measurements of the isotopic composition of the DON by difference, and the complicating issue of ammonium contribution to DON seems to be rather minor. I would offer

C3470

some comments on particular aspects of this paper that I think should be considered before its final publication. The authors note the revision of the nitrate standard composition in 2.3.1. It might be useful for readers to know if they need to convert to the new standard if this is a simple linear change or if it is more complicated. The analyses presented here are of very high quality and the uncertainties seem to have been very carefully assessed, particularly the complex ones arising from error propagation for the DON. The authors suggest the average uncertainty on their DON isotopic data is +1.2. In Table 2 average values for nitrate and DON concentration and isotope composition are presented. I note that the environmental variability of nitrate isotopic composition is about 20 times the analytical variability, but the equivalent environmental variability of the isotopic composition of DON is similar to the analytical variability. If this is correct it does emphasise that the DON variability the authors discuss is very close to the analytical limits of the method. The seasonality reported for DON and its isotopic composition is intriguing. The winter maximum in concentration seems well defined, but the summer maximum is rather modest in such an inevitably noisy signal and the seasonal difference in DON isotopic composition 5-5.9 summer, 6.3-7.5 in winter is again quite close to the precision. The authors carefully evaluate the drivers of the observed seasonality and I would only query a few of the details of their discussion. P7554 line 8 I suspect light rather than temperatures drives the seasonality. I would suggest that the authors clarify that they are assuming no fractionation in sedimentary denitrification. I agree with them that water column denitrification is unlikely, but denitrification within agricultural fields as well as within the body of the river is probably important. P7555 I agree entirely that the PN will have mixed sources, but I would query the interpretation around line 21 that changes in PN reflect changes in resuspension with flow as well as consumption. Firstly the resuspended PN is likely to have rather limited bioavailability. The correlation of DON and PN isotopic signal may indeed reflect processes such as the authors describe, but could also be a coincidence, or reflect the significant analytical uncertainties in both values, or could reflect both DON and PN responding to similar physical driver such as increased flow and resuspension. Section 4.3.1. As noted from

C3471

the various references, the bioavailability fraction of DON is generally rather low, so it seems hard to create a significant seasonality in its cycling, particularly when the concentrations of readily bioavailable nitrate and ammonium are quite high. 4.3.2. My understanding is that nitrogen loss from fields in summer is often rather small because of high crop requirement and low water loss, so I wonder if inputs from agriculture really can drive much of a seasonality. I would also query the logic of the argument about summertime DON cycling which seems to require DON release under nutrient limitation (DOC certainly but perhaps not DON) and then rapid utilisation of this DON. In summer nitrate concentrations are low but not limiting for production. Phosphate may fall to low concentrations but that may not mean it is limiting since it can be rapidly cycled and DOP may also be available. In this sense I would suggest that rivers such as the Elbe differ from coastal waters where inorganic nutrient concentrations do fall to levels low enough to induce real nutrient limitation on algae. 4.3.3. I would suggest the authors clarify the mechanism they suggest for DON sedimentation, and I would note dilution is an alternative explanation. 4.3.4. I do not know this catchment, but my understanding was that fertiliser use in autumn was restricted since the crops do not need it during the non-growing season.

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C3472