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Interactive comment on “Nitrogen balance and fate in a heavily impacted watershed (Oglio River, Northern Italy): in quest of the missing sources and sinks” by M. Bartoli et al.

Anonymous Referee #1

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In their manuscript the authors describe a detailed investigation of nitrogen pollution within the Oglio River basin, a sub basin of the Po watershed in northern Italy. Along the river a sudden increase in the nitrate concentration is visible in a reach without significant contributions from point sources or tributaries. The authors clearly show that these large diffuse N inputs in that area originate from nitrate-rich groundwater. A detailed budget approach which included calculations of N inputs from agricultural, domestic and industrial sources furthermore showed that only 34% of the calculated N surplus is exported from the watershed. However, applied in-situ measurements of denitrification rates via isotope pairing and stable isotope ratios of N and O in nitrate showed that denitrification in wetlands and in river sediments seem to be responsible

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for only 45% of the total N retention within the catchment. The overall conclusion the authors draw is that the groundwater in the Oglio River basin might act not only as a long-term source of N in some regions but can also be a short-term nitrogen sink.

Generally the authors present a very interesting study and used a wide variety of different methods (analytical as well as mathematical) to describe the input and fate of anthropogenic N within the Oglio River Basin. The manuscript is well written and the used scientific methods are state of the art. Therefore I think that the manuscript is worthwhile for publication in Biogeosciences. However since some parts of the manuscript are not totally clear and sometimes a little bit confusing some revisions are necessary.

The authors have chosen a different manuscript structure which has some positive but also some negative effects. On the one hand, the authors are able to guide the reader step by step through the applied investigations, methods and drawn conclusions. This makes it easy to follow and works very well for chapters 1 to 5. However chapters 6 and 7 don't show that clarity anymore and are somewhat confusing. In chapter 6 that deals with the role of the groundwater as a sink or source of N the authors first describe that the northern parts of the catchment show higher groundwater nitrate concentrations than the rest of the catchment. This statement is in my opinion not in agreement with Fig. 7, which shows the highest nitrate concentrations in groundwater sampled in the middle of the catchment. Apart from this discrepancies the authors further write, that in the lower parts of the basin nitrate is often absent from groundwater and that there are additional signs indicating a 'rapid denitrification'. From this I would assume that the groundwater in the lower part of the catchment is a sink of N, since N is removed quite quickly via denitrification whereas in the northern parts the groundwater is more an N source. The authors however conclude that the northern part of the Oglio watershed acts as short-term N sink, which is an argumentation that I cannot follow by means of the text (P.9215 L. 17-21). Maybe I misunderstood something here and the authors can explain this more detailed.

In the second part of chapter 6 the authors well describe the reasons for the observed

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‘nitrate-anomaly’ in the Oglio River basin. Here it is easy to follow their conclusions.

In chapter 7 the authors describe more detailed the function of the large numbers of springs that are located in the ‘spring belt’ in the middle of the catchment. I’m not sure if it is necessary to put this information into an extra chapter since it is strongly related to chapter 6. Furthermore I’m not sure if all the given information is necessary and what conclusions can be drawn from it. My impression was that it is quite confusing and difficult to understand. Where is the estimated N input of 4-8tNd-1 coming from? How was it calculated? Is it really only one aquifer? At the end of chapter 7 the authors draw a first conclusion that groundwater in the Oglio River Basin acts as a short-term N-sink and long term N source and present a time interval of >20 years. How have you calculated his interval?

Chapter 8 which is named with ‘Discussion and Conclusion’ has more the function of a summary, since most of the points were already discussed in the previous chapters. Therefore I would suggest revising and renaming it to ‘summary and conclusions’ or something similar.

One disadvantage of the chosen structure is that there is a lack of information due to the absence of a real ‘Material and Methods’ sections. Especially the description of the used methods for the stable isotope analysis and the Isotope Pairing incubations must be more detailed (analytical precision, methods, standards, used instruments). Absolutely no information is given about the analysis of the $\delta^{18}\text{O}$ -values in water (P. 9216 L. 4ff). As far as I could see most of the analyses are published in other publications, but these seem to be mainly conference proceedings which I was not able to get. Therefore I would suggest that the authors should provide more information about the analytical part in the respective chapter or should add an extra chapter with the description of the analytical methods. Furthermore a discussion about possible uncertainties and errors in the budget calculations (chapters 2.2 to 4) is missing.

Specific comments:

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Try to be more concise with the notation of the catchment area. I was a little bit confused about the different regions within the catchment. Is the whole catchment area which is presented in Fig 1 (left) named 'lower Oglio River Basin' or is it only the southern part? Sometimes in the text you write 'Oglio river Basin' sometimes 'lower Oglio River Basin', northern part, southern part,...

P.9208 L.14-15: Can you put the NUE from the Oglio River Basin in context to some NUEs from other regions here?

P.9208 L.17-19: Please add the references through which you obtained the information about population and the per capita N production.

P.9209 L.18ff: Chapter 3.3:

- Very simplified calculation, many uncertainties, input from tributaries treated as point source (it can be assumed that most of the nitrate comes from a diffuse source).
- Since it becomes clearly obvious from chapter 2.2 that the dominating inputs come from diffuse sources, I think that chapter 3.3 and fig. 4 can be deleted.
- If the section remains in the manuscript the header should be changed since all calculations are based on nitrate.

P. 9210 L.10-11: Why were N inputs from Lake Iseo into the watershed subtracted / what is the contribution? Should N export not include N from all sources?

P 9210 L.20-23: I'm not really sure if the authors' statement that N export from a catchment can be predicted by population density withstands a more detailed investigation. To be on the safe side I would suggest to weak the statement.

P.9211 L.20/21: Is it possible to mark the stations where denitrification was measured in the map (fig1 left)?

P.9212 L.4: LOI should be explained or at least written out.

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P.9212 L.17/18: I don't think that a Dn share of up to 40% is negligible.

P.9213 L.17: what is meant by 'organic matter contribution to stream nitrate'? If you think that this nitrate might be generated by nitrification of manure-N, you should write it more clearly and maybe cite some references.

P. 9213 L.17-20: From fig 6 it is not possible to distinguish between isotope values of middle and downstream stations. All are displayed by empty triangles. Can you use different symbols?

P.9213 L.21ff: How can you be sure that you can exclude nitrate assimilation as process decreasing the nitrate concentration and increasing the isotope values of the NO₃? Especially since you have done your investigations during summer.

P. 9215 L.2: Fig. 7: Isn't the highest NO₃ concentration found in the middle part of the catchment, and there especially at two spots, one close to the eastern border and the second one close to the western border of the catchment? Furthermore Fig7 matches very well with Fig 3.

P.9215 L.10: Again: anthropogenic organic matter = nitrification of manure N?

P. 9216 L.9ff:

- How was the share of groundwater to the river water calculated? What end-member values were used? How large was the difference between the end-member δ -values?

- The presentation of calculated and measured $\delta^{15}\text{N}$ values and nitrate concentrations in the text would be helpful here.

- What do you mean with 'nitrate that has been recycled in the environment'? Nitrate generated during nitrification? Why should that nitrate show higher $\delta^{15}\text{N}$ values than the nitrate deriving from groundwater which might be partly denitrified?

P.9217 L.2: What data is the basis for Fig 7? Are the concentrations which were measured in the 50 springs included?

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P. 9217 L.11: Where is the NO₃ data from the one aquifer coming from? Is it displayed in Fig 7? Where is the aquifer located?

P.9217 L. 12: How have you calculated the input of 4 to 8 tN d⁻¹ from the one aquifer to the river? What about the other aquifers in that area? How much do they contribute? What do you mean with recycled?

P9217/9218: Section 8: Since most of the data was discussed in the previous sections I would suggest using this section only for summary and conclusions, to avoid redundancy. All remaining discussion should be moved to the respective previous sections.

Technical corrections:

Try to be more concise with the used units (either $\mu\text{mol l}^{-1}$ or mg l^{-1} , either kg N yr^{-1} or t N yr^{-1}).

P.9205 L.12: add space after 'consequence, '

P.9211 L.24: delete space after 'isolated.'

P.9215 L.6: corn = maize (P.9204 L.19)?

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