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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.

M. Bartoli et al.

marco.bartoli@unipr.it

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Dear Editor we have revised the manuscript integrating all the different suggestions and comments made by the reviewers; we did our best to improve the paper according to their expert and helpful opinion. This manuscript integrates original data (i.e. watershed mass balance of N for the year 2000, river and tributaries N analyses, point and diffuse N source calculations, etc.) together with recently published data (Laini et al., 2011; Racchetti et al., 2011; Sacchi et al., 2011; Soana et al., 2011). It is organized and presented in a not conventional way, as a story that guides the reader and follows the advancement of different years of research at the macro and microscale in this

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geographical area. We are happy that the reviewers appreciated this attempt even if they both evidenced that this presentation can create confusion in some sections and requires anyway, for each macroarea, clear objectives and methods. We improved the paper accordingly and we now believe, thank to their suggestions, that the manuscript is more readable and clear.

Answers to the comments of two anonymous reviewers

Reviewer #1 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.

Authors' response: We agree with the reviewer and have modified the text accordingly: higher nitrate concentrations in the Oglio basin were found in the central part of the watershed. We have furthermore clarified that groundwater in the central part of the basin is a site of temporary accumulation of nitrate (and thus a "sink" of the surface N excess) with probably little denitrification going on while the southern part of the basin is a real N sink where denitrification removes nitrogen from the groundwater. Nitrogen temporarily accumulated in the groundwater of the middle portion of the basin can then be recycled to the surface through the springs and pollute the surface water. To avoid confusion, we have moved the sentences p.9215 L 11-16 to the end of paragraph 7.1

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and included the following short summary “We thus conclude that groundwater can be a large potential sink for N, especially in the southern portion, where N is permanently removed from the basin via denitrification. On the other hand, in the northern and central part, nitrate accumulates in groundwater and, in the long term, is substantially recycled to the surface, acting as an internal source of pollution”.

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?

Authors’ response: We agree with the reviewer and we have rearranged these last chapters. The revised version of the paper has now a chapter 7 (The relevance of groundwater for N-cycling in the Oglio River watershed) and two paragraphs (7.1. Temporary accumulation and net N loss in the central and southern portion of the basin and 7.2. Linking ground and surface water: the springs belt). As paragraph 7.2. deals with a peculiarity of this watershed and in general of the interface between higher and lower plain in the Alpine side of the Po River watershed, with over 700 springs censused, we would prefer to keep this paragraph as an individual section. We agree that it cannot be a new chapter of the story. We have reformulated some sentences of this paragraph in order to make it more clear to the reader. In particular, we removed the speculation on the time interval of 20 years and the estimated input of 4-8 tons of N per day, that was already explained in chapter 3 of the revised version. All details about the unconfined aquifer are provided in Sect. 2. Due to its depth and thickness, this is the only aquifer

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interacting with the Oglio river.

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.

Authors' response: We agree with the reviewer and we have renamed and shortened this section.

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.

Authors' response: We have included more details on M&M in each section and we have removed those references dealing with conference proceedings that are difficult to get. We have to say that in the cited manuscript (i.e. Racchetti et al., 2011, Biogeochemistry, the IPT is described in detail, together with all the analytical methods, instruments and so on.

Furthermore a discussion about possible uncertainties and errors in the budget calculations (chapters 2.2 to 4) is missing.

Authors' response: In Soana et al. 2011, that contains all calculations performed for the year 2008, we report the errors associated to the N budget at the basin level and

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this is one of the few papers if not the only reporting the error associated to input and output N terms. We have included in the revised version some comments on the uncertainties and errors in budget calculations.

Specific comments: 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,. . .

Authors' response: We agree and we have made more clear that the subject of this study is the lower Oglio River, that originates from Lake Iseo and flows into the Po River. There is also another alpine portion of the Oglio River that flows into the Iseo Lake that was not considered in the present study.

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

Authors' response: We have added a range of NUEs from other studies.

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

Authors' response: We have added the appropriate references.

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.

Authors' response: We agree in part with the reviewer comment as this calculation is robust as it is based on a number of concentration and flow measurements. We also

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believe that it provides another important evidence of the main N sources polluting the Oglio River. In section 3.3 we consider the nitrate input to the Oglio river course; from the Oglio River perspective, tributaries can be considered point sources since the location of the source can be readily identified at the rivers' confluence. On the other hand we consider "non point sources" any other diffuse input in the river bed, such as the input of groundwater, which may occur by little seepages over long distances. In order to clarify this point we changed the section title in "Point and diffuse nitrate sources in the Oglio river course" and rearranged some sentences in the paragraph.

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?

Authors' response: The subtraction was made as N loads from the Lake are produced outside the basin of the lower Oglio River that, as we better explained in the paragraph 2 and in the legend of figure 1, has its km 0 at the Iseo Lake.

P. 9210 L.120-23: 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.

Authors' response: We agree and we have reformulated the sentence.

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

Authors' response: We tried, but the resulting map is rather confused due to the very small dimension of the wetlands. In Racchetti et al. 2011 a detailed map showing the location of the sampling sites is reported.

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

Authors' response: We explained what is LOI.

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

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Authors' response: We agree and we have reformulated the sentence.

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.

Authors' response: The term "anthropogenic organic matter" indicates any type of organic matter input related to human activities, including manure spreading on soils and septic effluent leaching (e.g. Widory et al., J. of Contaminant Hydrology 72, 2004). Nitrate isotopes do not allow distinguishing manure-derived from sewage-derived nitrates, since these sources have overlapping isotopic signatures. We have specified this in the text.

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?

Authors' response: We agree and we have modified the figure accordingly.

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.

Authors' response: We agree that assimilation by phytoplankton may also occur, especially in summer, but we observe decreasing nitrate concentrations and enriched isotopic compositions also during the autumn and winter sampling campaigns. We have modified the text of the paragraph to account also for this explanation. Furthermore, chlorophyll a concentrations in the Oglio River (not reported in the present study) are generally low (<10 µg l⁻¹) so we believe that N uptake is probably a minor pathway for this element in this system.

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

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second one close to the western border of the catchment? Furthermore Fig7 matches very well with Fig 3.

Authors' response: We agree, there was a confusing use of the terms middle, northern and central plain and watershed. Here and in the other sections we made the text clearer.

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

Authors' response: As stated above, this term indicates both manure-derived and sewage-derived nitrates. We have specified this in the text.

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 -values? - The presentation of calculated and measured ^{15}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 ^{15}N values than the nitrate deriving from groundwater which might be partly denitrified?

Authors' response: We refer here to an ongoing work, only partially published in conference proceedings (Delconte et al., 2011b), aiming at evaluating the amount of groundwater entering the Oglio river based on different chemical and isotopic tracers. We agree with the referee comment that the choice of the right end-members for establishing the water budget is crucial, and that a more detailed explanation would be necessary to provide a sound estimate of this field evidence. On the other hand, information on the stable isotope and trace element composition of groundwater in the area is still missing. At present, we cannot be sure that water outflowing from the springs is fully representative of the groundwater characteristics. Therefore, since we considered that the water budget definition is out of the scope of this paper, we have eliminated the whole paragraph. With the terms "recycled nitrate" we indicate the fraction of this ion temporarily transferred to groundwater and then transported back to the surface water

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by springs.

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

Authors' response: We clarified that the figure 7 was realized with NO₃ concentration data collected from the ARPA monitoring network of groundwater (ARPA Lombardy, 2009) and not with data from the monitored springs. We have also clarified in a previous answer that in this area there is only one aquifer.

P.9217 L. 12: How have you calculated the input of 4 to 8 tN d⁻¹ from the one aquifer to the river?

Authors' response: This question was raised by the reviewer also in the general comments. We have removed from this section the estimated amount of nitrogen transferred by groundwater to the river in this specific reach as the same numbers are reported in paragraph 3. As accurate flow measurements and nitrate concentration analyses were available we performed N-mass balances along different reaches of the Oglio River. One of the reaches included the area where the nitrate anomaly was evidenced, which is the part of the river course where nitrate augments significantly but where no point sources are present. As this reach overlaps the springs belt we speculate that this nitrogen input (varying seasonally from 4 to 8 tons N d⁻¹) comes from river-groundwater interactions. We have multiple evidences of this, also from other conservative tracers analyses not presented here.

What about the other aquifers in that area? How much do they contribute?

Authors' response: All details about the unconfined aquifer are provided in Sect. 2. Due to its depth and thickness, this is the only aquifer interacting with the Oglio river.

What do you mean with recycled?

Authors' response: Recycled = returned. We explained before that we consider the

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groundwater of the central part of the basin a temporary site of accumulation of nitrate. Variable fractions of the accumulated nitrate can be returned (or recycled) to the surface via the numerous springs present in this area.

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.

Authors' response: We agree and have renamed and reduced the length of this final section.

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}).

Authors' response: We agree and we went through the whole manuscript and homogenized the units.

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

Authors' response: We added the space.

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

Authors' response: We deleted the space.

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

Authors' response: We replaced corn with maize.

Reviewer #2 Since a part of the paper is focused on point sources, I would recommend including in the introduction a sentence summarizing the contribution of point sources to N cycle alteration.

Authors' response: We agree and we have modified the introduction accordingly.

Howarth et al. (2011) have demonstrated how N fluxes are partially controlled by climate. Climate characteristics of the Oglio catchment should be provided by the authors

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in the catchment description paragraphs.

Authors' response: We have added some information on the climate of this geographical area.

Howarth et al. (2011) are well cited in P9218 L14. However citation in P9204 L2 is not the most proper.

Authors' response: We have removed the citation.

P9204L4-5. I recommend citing here one of the most classic works dealing with these aspects (Van Breemen et al., 2002 Biogeochemistry 57/58).

Authors' response: We have included the suggested citation.

P 9204 (L21-27) Study objectives: This paper is not presented in the traditional way but in many sections, with their own M&M, results and discussion sections. I agree with authors and I consider that a paper of this nature is more understandable in this manner. I consider, however, that authors should clearly and separately present the aim of each one of the sections.

Authors' response: We agree with the reviewer and have added to each section a clear hypothesis and a clear aim.

Section 2.1 should be presented in an individual section (Study area) apart from section 2

Authors' response: We agree with this suggestion and we have created a new section (chapter 2) with the study area.

Section 2.1 Proportion of arable land should be provided.

Authors' response: We included the % of arable land within the basin.

Information on the type of crops should also be provided. Are there maize crops only?

Authors' response: Maize represents a major fraction of cultivations (65%), this per-
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centage was included.

P9205 L12 “consequence,water” Please include the space

Authors’ response: We included the space.

P9205 L16. What do you mean with “unregulated exploitation”?

Authors’ response: We wanted to remark that in Italy there is a general overexploitation of the resource water for irrigation purposes and water demand and use exceeds concessions by Provinces. We have anyway removed this aside from the text.

P9206 L1 Please indicate the period (2007-2010)

Authors’ response: We indicated the period.

P9206 L5 Please include a space in rivercourse

Authors’ response: We included the space.

P9206 L7 How many sites (aprox.) for tributaries? Authors’ response: We indicated the number of tributaries and sewage treatment plants

P9206 An “increasing spatial” trend

Authors’ response: This comment is not clear to us. In this section we describe nitrate trend in the Oglio River and we refer to a steep increase in the concentration of this ion within a narrow reach.

Section 2.2 and figure 2. Authors should maintain a unit coherence throughout the paper. In P 9215 they express concentrations as mg/L. Since the results of the paper have a policy dimension, I would recommend using mg/L.

Authors’ response: We checked the manuscript and homogenized the units.

P 9207 L3. Please do not present this as an “only-one-sentence paragraph”, and include it as the first sentence in the next paragraph. Please apply the same criteria in

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other parts of the paper.

Authors' response: We agree and have removed all the "one sentence paragraphs" from the manuscript.

P9208 L9 "N mass balance between 2000 and 2008 shows that the situation did not improve over the eight years". Not only the situation is not improving, it is clearly getting worse.

Authors' response: Yes, this is the output from our calculations. We have remarked it in the manuscript.

P9208 L 5-10 Has this area been declared as Nitrate Vulnerable Zone?

Authors' response: Yes.

Section 3.3 Please re-write M&M of this section, like this it is very difficult to understand.

Authors' response: We agree, this paragraph was reformulated.

Fig 4. Authors comment in 3.2 section that industrial and human pollution can account for about 6% and +- 8% of the total inputs. According to point 3.3, however, the contribution of these sources can be higher, mainly in the winter. Please connect these two approaches in a new sentence.

Authors' response: We have connected the two approaches with a new paragraph.

P9210 Section 4. To which period finally corresponds the estimated annual flux?

Authors' response: The estimated annual flux is based on data from the period 2000-2010.

P9210 L18 Why do you express export as N-NO₃-?

Authors' response: Our data suggest that more than 95% of N exported from the Oglio River is in the form of nitrate. We express export as N-NO₃- for two main reasons: the first is that this is the major fraction of the total and the second is that we want to

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compare our export with those reported by Caraco and Cole (expressed as N-NO₃).

P9210 L18 A comparison of these results (I mean river export) with the values for European rivers recently summarized in the ENA report will be enlightening.

Authors' response: We agree and we have added a reference that links the reader to the chapter of the ENA report dealing with N export from European Rivers.

P 9210 L 25-27 "basin represents about 34% of the N surplus calculated into the watershed, which means that some 26 000 tN are somehow retained within the basin, by processes still to be identified." These calculations are for 2008 balance, please indicate.

Authors' response: We indicated that calculations refer to 2008.

P 9212 L 4. Please indicate that LOI is "loss-on-ignition"

Authors' response: We have specified it.

Fig 6. (Legend) "2 - Mineralized synthetic fertilizer" Do you mean nitrification + urea hydrolysis?

Authors' response: The term "mineralization" is normally used to indicate the transformation of organic N to ammonium. However, Clark and Fritz 1997 use the term "Mineralized NH₄-NO₃ fertilizer" to indicate the isotopic composition shown by nitrate after all processes causing its formation from synthetic sources, including nitrification. But since nitrification is the dominant process causing the change stable isotope compositions, especially in the $\delta^{18}\text{O}$ ratios, we changed the legend of Fig. 6 in "Nitrified synthetic fertilizers".

P9214 L 9 Are all "low-order ditches" irrigation channels?

Authors' response: Yes, mainly and we have specified this in the manuscript.

P9214 "We extended the maximum theoretical denitrification rate all over the surface

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actually occupied by the ditch network (about 6250 ha) in this geographical area.”
Please explain better.

Authors’ response: We have reformulated the entire paragraph better clarifying our calculations.

P9214 L25 Do you mean again for 2008 calculations?

Authors’ response: Yes, it is the same period and we have specified it in the text.

P9215 L 18 According to section 2.1 irrigation period is May-September

Authors’ response: Yes, we have corrected the text.

P9216 L22. Since authors entitled the section as a question form, a final summarizing sentence is needed.

Authors’ response: We have included the following sentences: “We thus conclude that groundwater can be a large potential sink for N, especially in the lower plain, where N is permanently removed from the basin via denitrification. On the other hand, in the higher plain, nitrate accumulates in groundwater and, in the long term, is substantially recycled to the surface, acting as an internal source of pollution.

P9217 L 1. As I said before, all the units should be the same, please transform to mg/L.

Authors’ response: We agree and homogenized all units.

P9217 L 21 I recommend citing here a recent paper by Bouraoui and Grizzetti (2011; Sci Total Environ, 409)

Authors’ response: The paper was included.

P 9218 “even if at present no informations are available on when such N was added to the basin” Please re-phrase.

Authors’ response: We changed the sentence in “Available information suggests that the contamination of groundwater is an ongoing process, as nitrate concentrations

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keep increasing (ERSAF Lombardy, 2009), although the exact timing is presently undetermined.”

P 9218. L19-22 Please also consider here: ammonia volatilization and its effect on air pollution and also when it is deposited. Consider also N₂O emissions and consequences on climate change.

Authors’ response: We have added a comment dealing with potential implications for N₂O and NH₃ emissions.

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