

## ***Interactive comment on “Extreme dissolved organic nitrogen fluxes in the human impacted Pamba River, Kerala, India” by S. Elizabeth David and T. C. Jennerjahn***

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Reviewer # 1

1. The number of samples collected is rather low to quantify fluxes and yields for DON (monthly sampling over 9 months). I would be useful to show any relationships between discharge and DON concentrations, or at least provide the full data so that the reader can reconstruct these.

Reply: We do not think that our data set is too small to quantify fluxes. In contrast, it is a time-series that is much larger and more detailed than many other budgets that just use annual or seasonal data. We include a new figure that displays the full set of data

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for dissolved organic nitrogen (DON) and dissolved organic carbon (DOC).

2. Please provide some additional methodological details, e.g.

(i) Which standards were used to analyze TDN?

Reply: Standards used for TDN analysis: Low concentrations- Hansell standard (“Deep Seawater” Hansell Laboratory, University of Miami, RSMAS); High concentrations- NIST Merck Nitrate Standard with 1000 ppm NO<sub>3</sub><sup>-</sup> (diluted 1:100). Measurement was done according to German industrial norms DIN EN 12260 (H34) and DIN 38402-30 (A30).

(ii) How were DIN samples taken and preserved ?

Reply: For the dissolved inorganic nutrient analyses 50 mL of water were filtered through single use Sartorius syringe filters into a rinsed polyethylene (PE) bottle and fixed with 150  $\mu$ L HgCl<sub>2</sub> solution (35 gL<sup>-1</sup> HgCl<sub>2</sub> added to 1000 mL solution). The samples were carefully closed, shaken and stored at 4°C in the dark until analysis.

(iii) the detection limits mentioned for TDN analyses seem very high compared to what is typically reported in the literature for these types of instruments, the authors mention a detection limit of 0.29 to 0.32 mg N L<sup>-1</sup> for their instruments (equivalent to 20 to 23 M – which would be a better unit to use given that this is used throughout the rest of the ms to report concentrations). Stubbins and Dittmar (2012, L&O Methods 10, 347–35) for example report detection limits between 0.6 and 11 M, Shimadzu itself suggests detection limits to be around 4 M.

Reply: The lowest TDN concentrations measured during the analysis is 0.7 mg N L<sup>-1</sup> (50.09  $\mu$ M) during February 2012 (Fig.3). Therefore, the detection limit for TDN analyses in this study is uncritical because of high concentrations.

3. DIN analyses are mentioned in the Methods section, but data are not shown in detail – reference is made to a paper under revision but we have no access to this at the moment. It would be good to describe the DIN data in more detail in this paper.

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Reply: DIN is not in the focus of this paper. We have included one sentence about the DIN in section 4.2., mentioning that during the pilgrim season both the DON and the DIN exhibit variations. We will provide the submitted paper for reviewer's reference.

4. While we have no objective reason to question the data, the concentrations and fluxes are obviously extremely high compared to data from other systems globally. A number of questions and suggestions in this context: -The fluxes/yields reported here (90-1976 kg N ha<sup>-1</sup> y<sup>-1</sup>, i.e. 9000-197600 kg N km<sup>-2</sup> y<sup>-1</sup>) are so much higher than in other systems that it's hard not to raise an eyebrow. The authors have a few strong arguments to suggest the system here is indeed exceptional (e.g. calculations based on number of pilgrims) but these estimates, which don't take possible loss terms and N processing into account, still fall short at reaching the N yield observed. For comparison, the NEWS model output for calibration and validation catchments (Harrison et al. 2005) report DON yields up to 1000 kg N km<sup>-2</sup> y<sup>-1</sup>, global output up to 2200 kg N km<sup>-2</sup> y<sup>-1</sup>; and the data compilation by Alvarez-Cobelas et al. (2008, reference below) has empirical data that do not go higher than 500 kg N km<sup>-2</sup> y<sup>-1</sup>. The fact that the authors here find a DON yield of approximately 9000 kg N km<sup>-2</sup> y<sup>-1</sup> for the upper catchment (section I), which is reportedly pristine with a population density < 1 inhabitant per km<sup>2</sup> is therefore suspect. The authors should convince us their numbers are correct and if so, provide a hypothesis on why their DON yields from the pristine upper catchment would be so much higher than that reported in even highly anthropogenic catchments elsewhere. Alvarez-Cobelas et al. (2008) Export of nitrogen from catchments: A world-wide analysis. *Environmental Pollution* 156 (2008) 261-269. - I can only assume that the authors have also measured concentrations of dissolved organic carbon (DOC). These would be very useful to have a little more insight as to what the major form of DON might be (low DOC/DON ratios expected if e.g. labile compounds such as AA or urea contribute substantially); and as a quality check to constrain the DON concentrations. DOC:DON ratios have a global average of around 20, but can vary substantially. Even if we assume a relatively low DOC:DON ratio of 10 (as observed e.g. by Seitzinger et al. 2002 in agriculturally dominated systems), the DON

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data reported here would translate into huge DOC concentrations unseen elsewhere. DOC analyses are thus a good check to confirm the validity of the data.

Reply: When compared to the other segments in the Pamba catchment, DON flux in the upstream forest segment (segment I) is low. In this segment there is little "disturbance" compared to the other downstream segments of the Pamba catchment. Water for sampling was collected from the middle of the reservoir and is a point of concentration of suspended and dissolved organic matter. Because of the fact that water collected for sampling is not from a "running" river, but from an artificial lake, there might be accumulation occurring related to a possibly increased primary production and subsequent release of DON, inputs from tourists as well as to leaching from the forest soils. The resulting load and yield calculation might therefore be an overestimate for that segment. We will address this in the manuscript. In addition to this reason, the very upstream of the Pamba River is a place of touristic attraction resulting in anthropogenic activities therein. Therefore, all the above mentioned activities can be the reason for high DON concentrations and fluxes in the upstream forest region. The term "undisturbed forest region" for this segment will be rephrased as "upstream forest region" in the manuscript.

5. The Discussion section mentions a few other parameters such as TSS, BOD, pH which are not described in the Methods section and it's unclear where these data come from.

Reply: TSS, BOD and pH mentioned in section 4.2 are the values observed in the Ganges River during Kumbh festival. The sentence is modified accordingly.

6. Page 16149 top lines: It is mentioned here that pH decreased from  $7.3 \pm 1$  to  $7.1 \pm 0$ , then increased to  $7.1 \pm 1$ . Given the errors reported I doubt we can classify these as a clear or significant decrease and increase.

Reply: Sentence is rephrased.

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7. It is often hard to follow the arguments and trace the numbers being cited. For example, on page 16149 you mention a DON flux of 606 kg (organic N) ha<sup>-1</sup>, based on the number of pilgrims and the average organic N content in human waste. Does this number only refer to the 10 km<sup>2</sup> area where the pilgrimage is concentrated in, or is this extrapolated over the segment, or the entire catchment? Is this per day, per year? Why is this number different from the 271 kg DON ha<sup>-1</sup> yr<sup>-1</sup> mentioned in Table 3?

Reply: For the DON flux calculation from the temple region, we first considered 50,000,000 pilgrims during the pilgrim season. These are the number of pilgrims during the peak pilgrim time. In addition to this, the temple is open during the first five days of the Malayalam month/calendar (Malayalam calendar is a solar and sidereal calendar used in Kerala, India, [http://en.wikipedia.org/wiki/Malayalam\\_calendar](http://en.wikipedia.org/wiki/Malayalam_calendar)) throughout the year. Therefore, we now considered 55,000,000 pilgrims visiting the temple throughout the year. When taking this number of pilgrims into account, there is a slight variation in the DON flux from that calculated before. DON input calculated from the pilgrim activity amounted to 667 kg ha<sup>-1</sup> yr<sup>-1</sup> in the temple area. The yields and the respective discussion will be modified accordingly in the manuscript.

8. A little explanation is provided on page 16155: "As discussed before a DON input of 606 kg ha<sup>-1</sup> was calculated from the 10 km<sup>2</sup> temple area and when normalized to the whole catchment, the input from the pilgrim activity amounted to 271 kg ha<sup>-1</sup> yr<sup>-1</sup>.", but I don't see the link between the numbers 606 kg ha<sup>-1</sup> for a 10 km<sup>2</sup> area, how does this convert to 271 kg ha<sup>-1</sup> yr<sup>-1</sup> for a catchment of 2235 km<sup>2</sup>?

Reply: We recalculated the DON input from the pilgrim activity and corrected and rephrased the above mentioned sentence accordingly.

9. The total potential DON input is calculated as 514 kg N ha<sup>-1</sup> yr<sup>-1</sup>, and the range mentioned is 477-752 kg N ha<sup>-1</sup> yr<sup>-1</sup>. While Table 3 lists the numbers for individual components that add up to 514 kg N ha<sup>-1</sup> yr<sup>-1</sup>, it's not clear how the estimated range was calculated.

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Reply: The sentence is corrected and rephrased accordingly.

10. P16138 L 14: rephrase this sentence, "inadequate sewage treatment" is not a land use practice.

Reply: Sentence is rephrased accordingly.

11. P16150 line 12: ambiguous to where these numbers refer to (your study or those of the study in Spain).

Reply: 'When compared with the Pamba catchment, the % composition of DON in south-east Spain catchment was found similar (99 %), while the concentrations (36 to 29 302  $\mu$ M) were in a much lower range'. These values refer to the Pamba catchment. We rephrase it in the manuscript.

12. Also on line 23 of the same page "application rate was about 8-fold higher": ambiguous in which of the two studies it was higher.

Reply: Urea application rate is 8-fold higher in the Pamba catchment than in Guadalquivir catchment. We clarify it in the manuscript.

Reviewer # 2

1. In several places there are statements indicating that DON has been largely ignored (e.g., Page 2, Line 9; Page 4, Line 3). This may have been true 15 years ago, but since then there has been progress in measuring and monitoring DON. I think these comments should be toned down, for example by stating that DON has received less attention than inorganic N.

Reply: Sentence is rephrased accordingly.

2. The authors refer to "pilgrims" several times before much of a description is given. It would be helpful to briefly explain what is meant by the term "pilgrim" where it is first mentioned.

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Reply: Explanation is included in the manuscript.

3. It would be useful to attach some values to statements made in the abstract. (Sewage is a major source of DON; The pilgrim event accounts for most of it; DON makes up a significant portion of anthropogenic nitrogen.

Reply: The pilgrim contribution is included in the abstract.

4. The authors state that they were unable to quantify all the N losses in the segment wise calculations, which resulted in negative load values in some cases. Nevertheless, they went on to report loads for segments I, II, and IV. Even though values from these areas were positive, it seems like they could be underestimated for the same reasons they were negative in other areas. The unbalanced budget indicates that the uncertainty in the estimates is very large.

Reply: In the manuscript we mentioned that uncertainties are large and therefore budgets were only calculated for some segments which, nevertheless, also have their uncertainties.

5. The calculation of DON produced by pilgrim waste assumes that all the N makes it to the stream. I think it is safe to assume that much of it is retained in the soil. The authors should at least mention this.

Reply: We will mention that part of the pilgrim waste can be retained in the soil. However, as the pilgrims in a way form a "point source" and discharge most of their waste directly into the river, it is conceivable that major part of it is directly introduced.

6. DON values recorded after the pilgrim event are lower than the values recorded during (and even before) the event. This suggests that the systems are fairly resilient.

Reply: DON values are always high, much higher than in other rivers. We don't know what is meant with the term "resilient" in this context.

7. In the conclusions, it could be stated that there are methods for better evaluating

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sources of DON. For example using methods such as optical properties and molecular size. This is a burgeoning field of research that could shed light on the sources of DON.

Reply: Indeed, we need better methods and more studies to quantify DON in rivers and determine the sources. We will add this in the manuscript.

Specific comments:

Page 2, Line 9. Even though it is in the title, it would be good to restate that the Pamba River is in India.

Reply: Changes are done accordingly.

Page 2, Line 14. Fertilizer application and inadequate sewage treatment are not really land use practices.

Reply: Sentence is rephrased accordingly.

Page 2, Line 25. Delete the word "of"

Reply: Corrected

Page 3, Line 1. Change "i.e." to "e.g."

Reply: Changes are done accordingly.

Page 3, Line 13. Delete the word "the" before "ecosystem functioning"

Reply: Corrected.

Page 3, Line 18. Change "lead" to "leads"

Reply: Corrected.

Page 3, Line 20. Change "algal bloom" to "algal blooms"

Reply: Corrected.

Page 3, Line 23. Insert a comma after "activities".

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Reply: Changes are done accordingly.

Page 3, Line 24. Insert "source of" before "N contributing"

Reply: Changes are done accordingly.

Page 3, Line 27. Insert "the" before "microbial".

Reply: Changes are done accordingly.

Page 4, Line 10. Replace "from" with "for"

Reply: Corrected.

Page 4, Line 16 Insert commas before/after ", including India,"

Reply: Corrected.

Page 4, Line 17. Insert "water" after "drinking"

Reply: Changes are done accordingly.

Page 4, Line 20. Insert a period after the citation.

Reply: Done.

Page 4, Line 21. Change to "Water resources in many parts of India are getting depleted because of the rapid increase in the population and increasing demand for water used in irrigation and human and industrial consumption."

Reply: Changes are done accordingly.

Page 4, Line 27. Change to "A unique feature of the Pamba River catchment is the Sabarimala temple, the largest pilgrim center in the world. In addition to pilgrim activity, other major anthropogenic sources of N in the catchment are agricultural land use practices, livestock farming, and sewage effluent."

Reply: Changes are done accordingly.

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Page 5, Line 2. Relationships between what?

Reply: Cause-effect relationship between human interventions such as pilgrims, agriculture and sewage disposal and the seasonal variations of dissolved organic nitrogen concentrations in the Pamba catchment. This is mentioned in the manuscript. Page 5, Line 14. "into" is one word

Reply: Corrected.

Page 5, Line 16. Replace "making up" with "comprising"

Reply: Changes are done accordingly.

Page 5, Line 19. Replace "is obtained" with "occurs"

Reply: Changes are done accordingly.

Page 5, Line 25. Consider changing to "The major land use category in the Pamba basin is forest, comprising 44% of the total land area."

Reply: Changes are done accordingly.

Page 6, Line 2. Insert "The" before "Sarbarimala" Insert a comma after "world"

Reply: Changes are done accordingly.

Page 6, Line 7. Replace "comprises" with "are located in"

Reply: Changes are done accordingly.

Page 6, Line 8. This seems redundant with Line 6 because both sentences indicate that this type comprises 14% of the land area.

Reply: In line 6, 14% of the total land area refers to forest plantations, while in line 8, 14% refers to settlement with mixed tree crop (SMT) area. Refer table 1. Detailed land use categories and percentage of the total land area is given in Table 1. In order to clarify, we rephrase this in the manuscript.

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Page 6, Line 15. Change “comprises of” to “is comprised of” Page 6, Line 23. Change “is the main land use” to “are the main land uses”

Reply: Changes are done accordingly.

Page 7, Line 8. Insert a comma after “analysis”

Reply: Changes are done accordingly.

Page 7, Line 11. Replace “in a” with “with a”

Reply: Changes are done accordingly.

Page 7, Line 15. Insert “a” after “using”

Reply: Changes are done accordingly.

Page 7, Line 17. Replace “were” with “was”

Reply: Changes are done accordingly.

Page 8, Line 6. Till?

Reply: The Pamba catchment is divided into 8 segments for the segment wise budget calculation (Fig 2). Area of each segment is described in detail in Table 2. As mentioned in the calculation, Discharge per segment =  $A_s \times Q$  where,  $A_s$  is the area of the segment and  $Q$  is the respective discharge ( $0.2 \text{ km}^3\text{km}^{-2}$ ) of that segment.

Page 9, Line 18. Insert a comma after “April”

Reply: Changes are done accordingly.

Page 9, Line 18. Replace “displayed” with “recorded”

Reply: Changes are done accordingly.

Page 11, Line 23. Change “comprising” to “comprised”

Reply: Changes are done accordingly

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Page 12, Line 1. Change to “, for instance in Latin America, Africa, and Oceania, BNF comprises 85% of the total N: :”

Reply: Sentence is rephrased accordingly.

Page 12, Line 2-5. These sentences are unclear and need to be rewritten.

Reply: Will be rewritten in the manuscript.

Page 12, Line 11. Change to “Various activities were observed such as bathing with soap, discarding trash, and urinating and defecating on the river banks.”

Reply: Sentence is rephrased accordingly.

Page 12, Line 15. Replace “was taken” with “took”

Reply: Changes are done accordingly.

Page 12, Line 16. Change to “took part in ritualistic bathing in the river, which led to: :” Reply: Changes are done accordingly.

Page 13, Line 5. Delete “the” before “DON”

Reply: Deleted.

Page 13, Line 25. Delete the term “considered as”

Reply: Deleted.

Page 14, Line 6. Replace “comprised” with “reported”

Reply: Replaced.

Page 14, Line 7-10. These sentences are poorly formed and need to be rewritten.

Reply: Will be rewritten in the manuscript.

Page 14, Line 13. Delete “the” before “rainfall”

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Reply: Deleted.

Page 14, Line 18. Not sure what is meant by “natural calamity”

Reply: In this context natural calamity refers to flooding in the he downstream of the Pamba catchment.

Page 14, Line 21. State where the Guadalquivir catchment is located.

Reply: Included.

Page 14, Line 25. Insert “of DON” after “source”

Reply: Inserted.

Page 15, Line 18. Delete “thereby”

Reply: Deleted.

Page 15, Line 19. Change “fowls” to “domestic fowl”

Reply: Changed.

Page 15, Line 19. Delete the word “is”

Reply: Deleted.

Page 16, Line 15. Delete “to this”

Reply: Deleted.

Page 16. Line 24. This sentence is poorly written and needs to be reworded

Reply: Will be reworded in the manuscript.

Page 17, Line 18. Comma should be before “thereby” rather than after

Reply: Changes are done accordingly.

Page 17, Line 24. Comma should be before “thereby” rather than after

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Reply: Changes are done accordingly.

Page 18, Line 11. Change to “Domestic sewage inputs, despite being high, do not balance: : :” Reply: Changes are done accordingly.

Page 18, Line 19. Insert “a” before “high”

Reply: Inserted.

Page 18, Line 20. What is meant by “adjusted” human water security threat?

Reply: According to Vörösmarty et al (2010), “adjusted” human water security threat refers to a condition where basic water services such as clean drinking water and sanitation are the major issues. Most of Africa, large areas in central Asia and countries including India, China, Peru and Bolivia struggle with these basic water services and emerge as regions with greatest “adjusted” human water security threat. We explain this better in the manuscript.

Page 18, Line 22. Insert “a” before “high”

Reply: Inserted.

Page 18, Line 27. Insert a period at the end of the sentence.

Reply: Done.

Page 18, Line 27. Delete “the” before “sewage”

Reply: Deleted.

Page 19, Line 6. Capitalize “Export”

Reply: Changed.

Page 19, Line 19. Replace “is concluded” with “appears”

Reply: Changes are done accordingly.

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Page 19, Line 24. Insert a comma after “before”

Reply: Inserted.

Page 19, Line 27. Change “It comprised of” to “DON from pilgrim activity comprised”

Reply: Changed accordingly.

Page 20, Line 6. Change “. It amounts to” to “, amounting to”

Reply: Changes are done accordingly.

Page 21, Line 3. Change to “sufficient toilets to accommodate the pilgrims: : :”

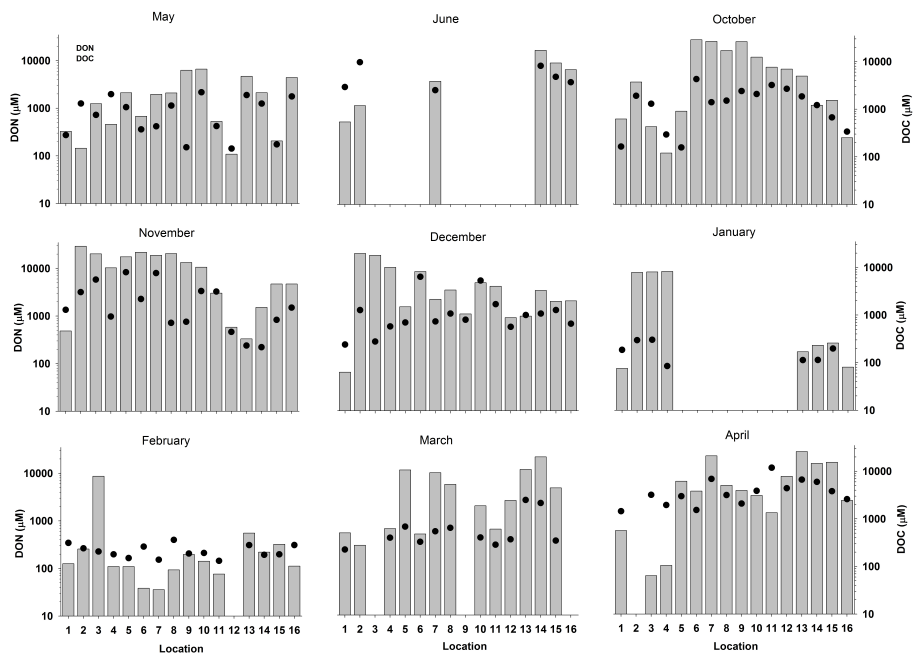
Reply: Changed accordingly.

Page 21, Line 5. Sentence needs to be reworded.

Reply: Reworded in the manuscript.

Interactive comment on Biogeosciences Discuss., 10, 16137, 2013.

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**Fig. 1.** Monthly variations in dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) concentrations in the Pamba River.

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