

Interactive comment on “Export flux of unprocessed atmospheric nitrate from temperate forested catchments: A possible new index for nitrogen saturation” by Fumiko Nakagawa et al.

Anonymous Referee #1

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Overall Comment:

This manuscript by Nakagawa et al. present two-years of nitrate exports from three different forested catchments in Japan supposedly with different N saturation status. Using the triple isotope composition of nitrate in streams (3 catchments) and soils (one catchment), they conclude on the sources of nitrate to the streams (atmospheric vs remineralized) and insist on the use of the M_{atm}/D_{atm} (atmospheric nitrate export flux/atmospheric nitrate deposition flux) ratio as an indicator of the N saturation status in the studied catchments. While I strongly advocate for a more systematic use of the triple isotope composition of nitrate to better understand N cycling in catchments, I find

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this study lacking in several areas (see general and specific comments) and presents numerous flaws that, in my opinion, would require a lot more work before considered for publication. This would require more than major revisions to be amended, and believe that the manuscript in its current state should be rejected for publication.

General Comments: There are several points of concern that I would like to raise here:

First, the structure and presentation of the manuscript are not sound. There are several missing pieces of information in the Methods that are needed to correctly interpret the results presented here (see related specific comments). The number of nitrate isotopic data presented in Figures 3 and 6 do not correspond to the number of nitrate concentration, without any explanation as for why. A lengthy description of the results obtained for the catchments IJ1 and IJ2 is provided in the results section, but never discussed later on. The Figure 4 presents a line without any caption, nor associated equation. While the manuscript is understandable, a thorough English language editing will be needed, and should be favored before resubmitting the article.

Second, I am very concerned about the temporal resolution of the sampling performed in the study. While the authors say they sampled each stream about once a month (which I think is too low resolution to efficiently capture seasonal variations of atmospheric nitrate exports, especially during brief events like snowmelt that can occur in the course of two weeks (see Bourgeois et al., 2018)), the actual sampling frequency reported in Fig. 3 and 6 for nitrate isotopes is once every two months (7 data points per year). The authors should explain why this is so, and also justify that such a low temporal resolution is enough to capture the real seasonal variability of atmospheric nitrate exports.

Third, I would be more cautious regarding the simplification that high NO_3^- concentration in a stream is always the result of N saturation. N saturation is a complex biogeochemical state of ecosystems of which one, among many, symptom is increased N leaching from soils to streams. But a high NO_3^- concentration in streams can stem

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from numerous other sources (e.g., topography, nature of the catchment soil/rock substrate, land-cover, percentage of forest cover) that need to be eliminated before the authors can indisputably correlate high NO₃⁻ concentration in streams and more advanced N saturation stage. Here, the authors conclude on the N saturation stage of the three studied catchments exclusively based on atmospheric nitrate exports from the streams. Not only is this not a novel finding (see next comment), but other evidences (e.g., nitrification/mineralization rates, leaves N content, roots and leaves mass) of the different N saturation stage between catchments should be provided to confirm, or not, the authors' conclusion.

Fourth, the main result of the manuscript, according to the authors, resides in using the Matm/Datm ratio as a new and robust indicator of N saturation status in forested catchment. I hardly find anything new in that result. As the authors point out in their discussion, the correlation between N saturation and increased export of atmospheric nitrate date as far back as two decades ago (Durka et al., 1994), and confirmed since then (Rose et al., 2015). Assuming that the gradient of nitrate concentration across streams is really due to different N saturation stages between catchments, then the correlation between Matm (export flux of atmospheric nitrate) and N saturation stage is not novel. The authors fail to demonstrate what the use of the Matm/Datm instead of just Matm is more valuable, and of scientific importance.

Specific Comments:

Page 2

L.11: awkward use of the word “representative”. I think what you want to say is “most important”

L.13: remove “receiving”.

L.15-16: you need to remove “probably”. It is well-documented that N deposition is responsible for N saturation in forested ecosystems.

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L.23-25: Among the listed processes leading to nitrate removal should appear i) microbial immobilization (different from assimilation) and ii) nitrate leaching.

Page 3 L.5: you need to cite Kendall et al., 2007 here.

L.8-9: this is an awkward definition of unprocessed atmospheric nitrate. You need to find another word than “survives” here. A better definition would “atmospheric nitrate that has not undergone a full cycle of assimilation, mineralization and nitrification leading to the regeneration of nitrate, nor exchanged O atoms with H₂O after deposition.”.

L.12: This sentence should say “. . . we can quantify the proportion of unprocessed . . .”

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L.2: The first sentence doesn't really make any sense. It should say: “The natural stable isotopic composition of nitrate is represented by its d¹⁵N, D¹⁷O, and d¹⁸O values.”

L.5: You have introduced the NO₃-atm notation for atmospheric nitrate in page 2 line 23. Please make a consistent use of that notation throughout the text, instead of alternatively using “atmospheric nitrate” and “NO₃-atm”

L.8-10: you should specify here that remineralized nitrate also applies to atmospheric nitrate that has undergone a full cycle of assimilation, mineralization and nitrification.

L.12: you say that the D¹⁷O of NO₃-re is close to 0. This is very vague, please specify the range of D¹⁷O here, and/or what process are responsible for such value (different from 0).

L.15-17: I don't understand how you can conclude that based on the literature you provide. Only Tsunogai et al. (2016) presented a dataset of D¹⁷O-NO₃-atm longer than a year (3 years), and none of these studies say that the annual average of D¹⁷O-NO₃-atm is “almost constant” over time. Do you try to say the mean annual D¹⁷O-NO₃-atm is similar in all these studies? They range in a similar array of values, but can still vary by a few ‰ depending on the geographic location (see Alexander et al.,

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2009). This sentence needs to be much improved or utterly removed.

L.21: awkward use of “partial metabolism”. Please rephrase.

L.25: To use this equation, you must assume that $D17O-NO_3-re = 0$. This is not consistent with your statement line 12 that $D17O-NO_3-re$ is “close to 0”.

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L.7: I assume this is the associated error to the mean $D17O_{atm}$ you are using in this study. How does this error translate in terms of uncertainty in your calculations of C_{atm} , F_{atm} and M_{atm} ? I think this is an important, yet overlooked, piece that is missing in your manuscript. L.11: I am intrigued by how you choose your references: it is sufficient to cite the 3-4 works that first used this correction method (that would be Tsunogai et al., 2010 and 2011, Dejwakh et al. 2012 and Riha et al., 2014 I believe). Here it looks like you want to provide a list of all the works that used this method. This is neither necessary, nor actually accurate (i.e., you missed other works that also used it). L.25: Do you know the respective contribution of summer/winter precipitation to the annual total? If yes, please specify it here.

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L. 1 and 14: Do you know the surface proportion of each watershed actually being covered by forests? If yes, please specify it.

L. 2: Since you are talking here of high loading rate, please provide the value.

L. 3: the use of “enrichment” instead of “concentration” throughout the manuscript is very confusing and will need to be amended.

L. 4: So, you assume that this catchment is N-saturated, according to Aber et al. (1998) definition of N-saturation. Please say it in these terms here.

Page 7 L.7-9: Please indicate how the sampling was conducted: manually, autosampler, what kind of bottles, cleaning procedures, etc.

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L.13: I don't understand why you say “at each weir”. Does it mean that the IJ1 catchment has several outlets where you sampled water? Please correct accordingly.

L.15-17: That is a pretty big assumption. It would seem to me that the topography of a catchment would impact the discharge rate far more than its area, because topography would drive both snow height in winter and water residence time the rest of the year. You should at the minimum provide some references to explain why you can make such assumption.

L.22: Please provide the proportion of samples collected during the winter period vs the rest of the year.

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Section 2.4: I have several concerns regarding this section. First, regarding the extended amount of time you left the collecting bottle at the KJ site (around a month), and considering that in summer you have temperature as high as 34C (according to section 2.1), how can you be sure that your nitrate concentrations are not biased by partial evaporation of the rain water? Oppositely, do you have a heating system to melt the snow in winter? If not, how can you be sure that you really collect 100% of wintertime precipitation? Second, you state several factors that could impact the nitrate concentration in deposition samples (incomplete dry dep collects, possible nitrification). It would be useful that you provide an associated uncertainty to the estimated atmospheric NO_3-atm concentration due to these factors (and also water evaporation). Third, you say that the deposition collector at the KJ site was installed in an open field. You must be aware that rainfall in open field is not representative of throughfall that actually reaches the soils and streams under forest canopies. For instance, Guerrieri et al. (2015) suggested that in forests with high N dep (which is the case at the KJ catchment) canopies play a significant role in modifying both NO_3- concentration and isotopic composition from rainfall to throughfall. This is an important point that need to be clarified as it could impact the interpretation of your results (see below).

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L.14: Does it mean that in the end, all samples were analyzed, and none rejected?

L.15-21: So, the values given in the manuscript are the averages of these repeated analyses?

L.26: Please describe what would be the highest uncertainty caused by presence of nitrite in a sample on the D17O value of nitrate (highest uncertainty would be for $\text{NO}_2^- = 0.049 \text{ } \mu\text{mol.L}^{-1}$ and the lowest NO_3^- concentration you measured in your study). This would give the reader a better idea for why you regard nitrite concentrations as negligible.

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L.10-14: It might be worth illustrating this by a figure that you could place in the SI, for readers unfamiliar with the different definitions of D17O and their discrepancies.

Page 12 L.6-12: A detail, but I don't think that Matm , Mre , Mtot and Datm can be classified as "fluxes", but more as "annual loads". L.13 Add "annual" before "deposition". L.23: I disagree, in 2014 the flux is still higher in spring than in December. You could probably replace "December" by "winter period". L.25: In 2015, you also have a June-July maximum in Fatm that is noticeable.

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L.5: If I understood correctly, you calculated a Fatm value for every D17O value measured in the stream. Which means 15 points over two years, according to Figure 3. I think this temporal resolution is way too low to accurately catch the seasonality in stream atmospheric nitrate export (and for instance snowmelt in spring). How can you make a strong statement on this subject with seven samples per year? You really need to argue why such low sampling resolution is enough to describe the behavior of your catchment.

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L.6-7: It would be useful to the reader if you could compare here your stream nitrate concentration with other concentration measured in forested catchments outside of Japan, just like you do for the isotopic composition of nitrate later on.

L.15: up to 1.6 mmol.L^{-1} , or more? If it is more, then put the maximum value. As it is now, it does not make any sense.

L.23-27: This is interpretation of the results: therefore, it needs to be removed from the Results section and moved to the Discussion section.

Page 14 L.4-18: It is more standard to present deposition fluxes in $\text{kg-N ha}^{-1} \text{ yr}^{-1}$. This would be easier to compare with other studies and to understand how elevated deposition is on your catchments (and it is very elevated!). You may want to change your stream fluxes as well to be homogeneous on the units you use. L.17: Ok, so here is the error associated with your deposition estimation. Please refer to this section where appropriated earlier in your manuscript. L.21-22: Why don't you present also Fatm and Ftot for IJ2? If you don't present these results, then remove the section where you say that you extrapolated discharge data for IJ2 from IJ1 using the catchment area as converting factor.

Page 15 This is a very long description of the results observed at IJ 1 and 2 catchments, that are never discussed later in the discussion. Why is it so? The described patterns on this page look very interesting and to my opinion would deserve a thorough analysis later on! For instance, what causes the sporadic increase in nitrate concentrations in both streams (precipitation events?) and why is IJ1 more enriched in nitrate compared to IJ2 (more precipitation? Different percentage of land cover by forests?). L.23-26: This is very far stretched. Did you conduct a statistical test to verify the decreasing trend in concentration? Also, how can you say it started in 2000 when you report three years of data covering 2012-2014?

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L.10: Why not giving the corresponding proportions of nitrate for each source using D17O to calculate the percentages.

L.17-20: This sentence doesn't make sense. How can D17O of soil nitrate reflect the original value of nitrate in groundwater? I think that soil nitrate reflects atmospheric nitrate D17O value, that is buffered by nitrification in soils (as shown by the seasonal variation in figure 3). Soil nitrate isotopic composition is not related to groundwater nitrate isotopic composition.

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L.13: You need to indicate how you come up with this value. If you used the following equation: $\delta^{18}\text{O-NO}_3 = 1/3 (\delta^{18}\text{O-O}_2) + 2/3 (\delta^{18}\text{O-H}_2\text{O})$, then you must also comment on the limitations of its utilization (see Rose et al. 2015a and Snider et al. 2010). You should also try to plot d18O vs d15N and see how they correlate to confirm, or not, the absence of biological processes in your catchment.

L.17-19: This statement needs to be amended or removed. This is hardly new results, as the relationship between D17O and d18O have been used for almost a decade to understand biological processes in catchments (see previous work by Tsunogai et al.).

L.21-23: Is that an assumption or something you know for a fact? Please provide the data to justify that rain is responsible for Ftotal increase for winter (either the precipitation chart, or some data indicating that there is more precipitation in winter than I summer).

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L.6: Add reference to Michalski et al. 2004 after the value of 0.

L.9: Here you should provide a scatterplot of d18O vs d15N to discuss the presence, or not, of any correlation between these isotopic values throughout the year. And even if you don't find any correlation, it does not mean that no assimilation is taking place (it would be really surprising to have no assimilation anywhere in the catchment) but rather

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than the recharge of new NO₃-re is overprinting isotopic fractionation by assimilation (Granger and Wankel, 2016).

L.18-19: Be more precise: you are talking about concentrations here. To say "stream nitrate shows a normal correlation with soil nitrate" doesn't make any sense. Also, I am a bit dubious of the strength of your correlation given the low number of samples presented in Figure 7 (n=11).

L.20-25: Alternatively, the slightly higher D17O values in winter/spring compared to the rest of the year are due to freeze/thaw events leading to partial snowmelt, that is not well captured by your very coarse sampling resolution. How can you exclude that hypothesis, especially as you said that the KJ catchment is covered by snow from December to March, exactly when the Fatm is higher? This needs at least to be discussed. Didn't you measure water isotopes as well? Can't you tell from these measurements if the water comes from groundwater or from snowmelt (Hall et al., 2016; Liu et al., 2004)? That would be a very strong addition to your reasoning.

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L.1-15: It would be nice here that you refer to a table where you list the annual mean values for Catm, Ctot, Fatm, Ftot, and Matm for each watershed. It is hard to keep up with all you say because we are always looking for the values elsewhere in the manuscript.

L.16: There is no Equation (9) in your manuscript

L.17: You need to detail how you calculate your incertitude either in the Methods or in the SI: you stipulated earlier in the manuscript that you would assume a 20% error on the Datm at the KJ catchment (see Page 14, L.17). Can that result in the 2.6% error on the Matm/Datm ratio that you present here? Did you perform a formal error propagation calculation? Please expand more on this aspect. Also, I would be very curious on how you obtained your percentages. If I divide the Matm (=8.8, 5.7, and

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2.2 for KJ, IJ1 and IJ2 respectively) by D_{atm} (=45.6, 49.2, and 48.3 for KJ, IJ1 and IJ2 respectively), I obtain 19.3, 11.6 and 4.8%. Not at all what you calculated. Please explain

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L.1: That is something that bothers me in your manuscript: the link you draw between catchment N saturation and stream nitrate concentration seems very hazardous to me. Increase of stream nitrate concentration can be a symptom of a higher N saturation status, but N saturation is not per se the only reason that could explain higher N concentration in a stream (topology, geomorphology, land-cover are other very strong factors that can influence N exports in streams). You need to explain more why it is the N saturation status that drive higher nitrate export from the KJ site compared to the IJ catchments, and not the percentage of forest cover on the catchment for instance, or another parameter (like snow pack height).

L.7-8: I don't understand what in Figure 9 can lead to such conclusion: I am pretty sure that contrary to what you say, different nitrification rates in soils will lead to different NO_3 -re leaching fluxes to stream/groundwater, and thus impact the D_{17O} value of nitrate in stream (by dilution). This would impact M_{atm} , and therefore the M_{atm}/D_{atm} ratio. So please clarify what you meant here.

L.13-22: To me, you really fail to demonstrate here what your ratio (M_{atm}/D_{atm}) brings more in term of N saturation understanding than just the use of M_{atm} , which was already described in previous studies. I don't see anything new here.

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L.10-13: That is my point. Rose et al 2015 already showed the relationship between M_{atm} and N saturation? So, what is new here? What does your ratio bring more than just the use of M_{atm} ? Also, please try to plot the same correlation with M_{atm} instead of C_{atm} , and report the correlation strength.

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Figure 3: Why is there not the same number of samples for nitrate concentration and isotopic values for the stream? The temporal resolution of nitrate isotopes as presented in this graph is very low (one sample every two months) and not enough to capture seasonal events such as snowmelt. This needs to be clarified as it could substantially change the results interpretation and the overall study conclusion.

Figure 4: What is the line in black? Is it the regression line, and if yes, of what (only streams, streams + soils)? Add slope and p-value. If it is the mixing line, say it in the caption and show the two end-members (atmospheric nitrate and remineralized nitrate)

Figure 5: Same question as for Figure 3.

Figure 8: Please add a third panel to show M_{atm} vs C_{tot} .

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