

Reply to your comment (Referee #1).

Thank you very much for your valuable comments on our manuscript. We have responded to each of your comments and questions.

- > 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.
- > 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 5: Same question as for Figure 3.

The samples presented in this study were collected through a project (the Long-term Monitoring of Transboundary Air Pollution and Acid Deposition) promoted by the Ministry of the Environment in Japan. The flow rates of the streams and concentrations of nitrate and other constituents were determined through the project as well.

On the other hand, the measurements on the stable isotopes of nitrate were not included in the project, because we were unable to determine the stable isotopes of nitrate at the beginning of the project in 2003. The stable isotope analysis was done for the archived samples, in support of a different project in 2014.

Because the archived samples were precious and the measurements of the $\Delta^{17}\text{O}$ values of nitrate were costly and time consuming, the number of samples for stable isotopes were limited to 1/2 of the whole at site KJ. We will clarify this in the revised MS.

Despite this, 134 $\Delta^{17}\text{O}$ values are reported in this MS. We repeated the analysis for each sample at least three times to attain high precision (see section 2.5). We hope that our results, including these many data values, is worthy of publication.

We have addressed your concerns about snowmelt in a later reply.

- > A lengthy description of the results obtained for the catchments IJ1 and IJ2 is provided in the results section, but never discussed later on.
- > Page 15 This is a very long description of the results observed at IJ1 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?).

The data obtained at catchments IJ1 and IJ2 were integrated into Figure 8, the most important figure for discussion in this manuscript. We think the current length of this section is inevitable if the data obtained at catchments IJ1 and IJ2 are to be justified and the data is to be integrated into Figure 8.

Clarifying the reason for the sporadic increases detected at IJ1 and IJ2 was not the objective of this study. While the present results imply that the sporadic increases did not accompany significant changes in $\Delta^{17}\text{O}$ (see figure 6), a much higher time resolution of the samples is required to verify the results. Because the sampling interval was set to once a month under the project (Long-term Monitoring of Transboundary Air Pollution and Acid Deposition), an investigation of the reason for the sporadic increases was not possible in this study, and should be reserved for future study.

The reason for the differences between the data from IJ1 and that from IJ2 is discussed later, in section 4.3.

- > The Figure 4 presents a line without any caption, nor associated equation.
- > 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)

That is the regression line for both streams and soils. We will clarify this in the figure caption of the revised MS. We have added the p-value as well. Additionally, we will add the mixing line between the two end-members (atmospheric nitrate and remineralized nitrate) in the figure during the revision.

- > While the manuscript is understandable, a thorough English language editing will be needed, and should be favored before resubmitting the article.

The English of the manuscript was thoroughly edited by Editage English editing service (<http://www.editage.jp/>) prior to the submission. We intend to have them edit the English again prior to submission of the revised manuscript.

- > 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 than 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.

The sampling for nitrate concentrations was performed once per month, while the samples for isotopes were selected from archived samples that had previously been measured for concentrations. Due to this reason, the number of samples for stable isotopes was limited; we have clarified this in the manuscript.

While the total number of data points were 15 for nitrate isotopes during the 2 years of observation at site KJ, the most nitrate-enriched sample (Dec., 2013) and the second most nitrate-depleted sample (Oct., 2014) were included in the $\Delta^{17}\text{O}$ analysis. Nevertheless, the

nitrate isotopes showed little temporal variation with respect to the variation in nitrate concentration, and the variation range (1 sigma) was less than 0.4‰ for $\Delta^{17}\text{O}$. Without $\Delta^{17}\text{O}$ data it is difficult to assume sudden changes only in $\Delta^{17}\text{O}$ when there are no sudden changes in nitrate concentration during the period. Additionally, our results suggest that the seasonal variabilities in both atmospheric nitrate and soil nitrate were buffered by groundwater nitrate at the site, as discussed in section 4.1. We concluded that the total number of data points (15) was significant for determining the average isotopic compositions ($\Delta^{17}\text{O}$ of nitrate, especially) at the site.

> 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 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 NO_3^- 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.

> Page 20/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).

There have previously been many ecological and biogeochemical studies on the high elution rates of nitrate (site KJ: Kamisako et al., 2008, Sase et al., 2008; 2012, IJ1 site: Yamada et al., 2007; Nakahara et al., 2010). The possible factors that you suggested (topography, nature of the catchment soil/rock substrate, land-cover, percentage of forest cover, etc.) have been considered in previous studies as possible reasons for the high elution rates of nitrate. However, Kamisako et al. (2008) proposed that site KJ was at nitrogen saturation, probably due to the excess loading of nitrogen from the atmosphere. Nakahara et al. (2010) proposed that site IJ1 was at nitrogen saturation (stage 2) as well. While their studies served as important backgrounds of our research, we don't think it is worthwhile to repeat their discussions in our manuscript. Instead, we will emphasize that our conclusion regarding the nitrogen saturation at the studied sites agrees with those of these previous studies.

> Fourth, the main result of the manuscript, according to the authors, resides in using the Matm/Dmatm 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.

> Page 20/L.13-22: To me, you really fail to demonstrate here what your ratio (Matm/Datm) brings more in term of N saturation understanding than just the use of Matm, which was already described in previous studies. I don't see anything new here.

We did not indicate, in any part of this paper, that the high M_{atm}/D_{atm} (or M_{atm}) in an N saturated forest was a new finding of this study. Based on the results reported in previous studies, such as those that you pointed out (Durka et al. 1994; Rose et al., 2015), as well as those of our own previous studies (Tsunogai et al., 2010; 2014; 2016), we expected (1) that the biological metabolic processes of nitrate in forest soils primary will control the M_{atm}/D_{atm} ratios of nitrate, and (2) that the M_{atm}/D_{atm} ratios will increase with increase in the concentration of stream nitrate (i.e., elution rate of nitrate). We verified these expectations in this study.

The M_{atm}/D_{atm} ratio, the directly exported atmospheric nitrate flux relative to whole deposition flux of atmospheric nitrate in a catchment area, was used in our previous study as an index to evaluate the biological metabolic rate of nitrate in forest soils in a catchment (Fig. 9) (Tsunogai et al., 2014). Because the metabolic rates of nitrate (almost equal to the biological assimilation rates of nitrate) in forest soils primarily determine the $(D_{atm} - M_{atm})/D_{atm}$ ratio (removal ratio of atmospheric nitrate to the total atmospheric nitrate deposited in a catchment; Tsunogai et al., 2014), using M_{atm}/D_{atm} ratio as the index, instead of the M_{atm} , is essential in principle. Also, because D_{atm} is variable between the study sites (D_{atm} at site KJ is about twice as much as that at the site studied by Rose et al. (2015)), normalizing M_{atm} by D_{atm} is indispensable. We will emphasize this in the revised MS. Furthermore, we will present the relationship between average nitrate concentration and M_{atm} in the new version of Fig. 8.

> Specific Comments:

> Page 2/L.11: awkward use of the word “representative”. I think what you want to say is “most important”

We will make the suggested revision.

> Page 2/L.13: remove “receiving”.

We will make the suggested revision.

> Page 2/L.15-16: you need to remove “probably”. It is well-documented that N deposition is responsible for N saturation in forested ecosystems.

We will make the suggested revision.

> Page 2/L.23-25: Among the listed processes leading to nitrate removal should appear i) microbial immobilization (different from assimilation) and ii) nitrate leaching.

We are very sorry but we cannot understand the meaning of the phrase “microbial immobilization (of nitrate) different from assimilation”. Nonetheless, the aim of this sentence was to list the major processes in the catchment that control the nitrate concentration in the stream water, particularly those that influence the long-term changes in stream nitrate concentration. We think that most of the major processes were already included in the sentence.

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

We will make the suggested revision.

Kendall, C., E. M. Elliott, and S. D. Wankel (2007) Tracing anthropogenic inputs of nitrogen to ecosystems, in Stable Isotopes in Ecology and Environmental Science, 2nd edition, edited by R. H. Michener and K. Lajtha, pp. 375-449, Blackwell Publishing.

> Page 3/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.”.

We will make the suggested revision. The atmospheric nitrate involved in a part of the N cycle, however, no longer remained atmospheric nitrate; thus, the “full cycle” that you recommended is not necessary. We have changed the definition to “atmospheric nitrate that was supplied via atmospheric deposition and was not involved in the N cycle during the biological processing of nitrate, such as ...”.

> Page 3/L.12: This sentence should say “. . . we can quantify the proportion of unprocessed . . .”

The proportion of unprocessed atmospheric nitrate in total nitrate can be quantified only from $\Delta^{17}\text{O}$. What we wanted to emphasize here was that we can quantify unprocessed atmospheric nitrate (we can determine the absolute concentration of unprocessed atmospheric nitrate) from $\Delta^{17}\text{O}$ and the concentration of stream nitrate. So as not to mislead readers, we will revise this as mentioned.

> Page 4/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."

We will make the suggested revision.

> Page 4/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"

We will make the suggested revision.

> Page 4/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.

We will make the suggested revision.

> Page 4/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).

> Page 4/L.25: To use this equation, you must assume that D17O- NO₃-re = 0. This is not consistent with your statement line 12 that D17O- NO₃-re is "close to 0".

We would like to use 0‰ for $\Delta^{17}\text{O}$ of NO₃⁻_{re} while citing a reference.

> Page 4/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 D17ONO₃- atm is "almost constant" over time. Do you try to say the mean annual D17ONO₃- 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., 2009). This sentence needs to be much improved or utterly removed.

What we wanted to say was that the geographical difference in the annual average $\Delta^{17}\text{O}$ values of NO₃⁻_{atm} was less than a few ‰ in mid-latitude. We will revise this.

> Page 4/L.21: awkward use of "partial metabolism". Please rephrase.

We will rephrase this.

> Page 5/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 Catm, Fatm and Matm? I think this is an important, yet overlooked, piece that is missing in your manuscript.

The error in the $\Delta^{17}\text{O}$ value of $\text{NO}_3^-_{\text{atm}}$ ($\pm 3\%$), together with the error in the $\Delta^{17}\text{O}$ value of the sample nitrate in soils/stream ($\pm 0.1\%$) first translate into C_{atm} via Eq. (2), based on the general propagation law of errors, and then translate into F_{atm} followed by M_{atm} . Because the error in the $\Delta^{17}\text{O}$ value of $\text{NO}_3^-_{\text{atm}}$ (3%) corresponds to 12% of $\Delta^{17}\text{O}_{\text{atm}}$ (+26%) and the relative errors in the $\Delta^{17}\text{O}$ values of the sample nitrate were similar (around 10 %), the values of C_{atm} , F_{atm} , and M_{atm} showed errors of around 20% for each value. We did not overlook the errors but included them in the complete calculation processes presented in the text (e.g., page 19) and the figures (Fig. 8).

> Page 5/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).

We will make the suggested revision.

> Page 5/L.25: Do you know the respective contribution of summer/winter precipitation to the annual total? If yes, please specify it here.

We will make the suggested revision.

> Page 6/L. 1 and 14: Do you know the surface proportion of each watershed actually being covered by forests? If yes, please specify it.

Except for the stream surface, the entirety of the catchment areas were covered by forests. We have clarified this in the revised MS, in the first sentence of section 2.1. You can see the area covered by forests on Google maps as well (while you can see deforestation along the stream at site IJ2 on Google maps, the deforestation occurred in the winter of 2015 so this did not interfere with our results).

IJ1:

<https://www.google.co.jp/maps/@37.9960808,139.3904356,403m/data=!3m1!1e3>

RW1 and RW3:

<https://www.google.co.jp/maps/@35.5699514,136.6930194,4051m/data=!3m1!1e3>

> Page 6/L. 2: Since you are talking here of high loading rate, please provide the value.

We will make the suggested revision.

> Page 6/L. 3: the use of “enrichment” instead of “concentration” throughout the manuscript is very confusing and will need to be amended.

We will make the suggested revision.

> Page 6/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.

While Kamisako et al. (2008) proposed N-saturation at site KJ, we did not assume that the high nitrate concentrations in the studied streams were the result of N saturation, prior to obtaining the data. Because Japanese forests do not present seasonal variation in the elution rate of nitrate irrespective to the stage of N-saturation, it was difficult for us to assume that the site was N-saturated, according to the definition of N-saturation proposed by Aber et al. (1998). We studied site KJ because the stream showed high nitrate concentration while the catchment was fully covered by forest.

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

The stream water samples were collected manually in bottles which were rinsed at least twice with the sample itself. In this study, 1L or 2L polyethylene bottles, washed using chemical detergents, rinsed at least thrice using deionized water, and then dried in laboratory, were used for collecting samples. We will add this in the MS in response to your request.

> Page 7/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.

This was a mistype, sorry. There was only one outlet at the IJ1 catchment. We have revised this.

> Page 7/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.

Because these sites (IJ1 and IJ2) were located on the Pacific side of Japan (Monsoon area), the major rain (& snow) depositions were in summer. The deposition in summer (JJA) constituted 37% of the annual deposition, while that in winter (DJF) constituted 16% only. Thus, even if the actual winter aerial deposition rate (=snow deposition rate) at site IJ2 was half of that at site IJ1 due to the topographic difference, the difference between the annual aerial deposition rates (and thus annual discharge rates) at IJ1 and IJ2 would be less than 10%. Besides, the difference in water residence time have little influence on annual discharge rates under steady state condition. Because we allowed an error range of 10% in the discharge rates, we don't think this assumption is "pretty big".

Further, even if the actual annual discharge rate at IJ2 deviated from the annual discharge rate used in this study due to a smaller actual deposition rate than that used in this study (50% of that used in this study, for instance), the M_{atm} and the D_{atm} at IJ2 would become 50% of the present estimate, so that the M_{atm}/D_{atm} ratio (shown in Fig. 8) would remain constant. We therefore conclude that the present assumption regarding the discharge rate has little influence on the final conclusions of this study.

> Page 7/L.22: Please provide the proportion of samples collected during the winter period vs the rest of the year.

We will make the suggested revision.

> Page 8/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 NO₃-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 NO₃- 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).

While the progress of partial evaporation in the collecting bottle will bias nitrate concentrations as you point out, the deposition flux will be the same. If the volume is reduced to 50% due to partial evaporation, for instance, the nitrate concentration will become 200% of the original, while the water volume will become 50% of the original, so that the deposition flux of nitrate will remain the same.

Because the atmospheric observatory at site KJ was a simple on site observatory in the forested field, all the concerns you pointed out are possible. Thus, we estimated the possible range of errors due to the bias through comparison with data determined at a nearby national atmospheric observation site (Sado-seki National Acid Rain Monitoring station), where the deposition rates were determined based on the EANET protocol (EANET, 2014); we found that all these concerns are minor. (See section 3.1 for details)

In brief, the determined deposition rates at site KJ agree (< 10% difference) with those determined at the Sado-seki National Acid Rain Monitoring station. Thus, we used the results obtained through the observation at site KJ, allowing a moderate error range (20%) (see section 3.1).

While the differences between the $\Delta^{17}\text{O}$ values of nitrate in throughfall and rainfall could influence the identification of the places within the catchments where the major portions of nitrate metabolism and nitrification occurred, they had little impact on the final estimates of C_{atm} and $M_{\text{atm}}/D_{\text{atm}}$ ratio, when (1) the deposition rate of atmospheric nitrate on “the surface of catchment”, in which leaf surface and crown were included, was the same with D_{atm} used in this study within the error range ($\pm 20\%$), and (2) the average $\Delta^{17}\text{O}$ value of atmospheric nitrate prior to reaching “the surface of catchment”, in which leaf surface and crown were included, was the same with $\Delta^{17}\text{O}_{\text{atm}}$ used in this study within the error range ($\pm 3\%$). That is to say, the nitrate in throughfall showing a different $\Delta^{17}\text{O}$ value than $\Delta^{17}\text{O}_{\text{atm}}$ was no longer atmospheric nitrate as per the definition of atmospheric nitrate presented in section 1.2.

> Page 10/L.14: Does it mean that in the end, all samples were analyzed, and none rejected?

Yes.

> Page 10/L.15-21: So, the values given in the manuscript are the averages of these repeated analyses?

Yes, they are.

> Page 10/L.26: Please describe what would be the highest uncertainty caused by presence of nitrite in a sample on the $\Delta^{17}\text{O}$ value of nitrate (highest uncertainty would be for $\text{NO}_2^- = 0.049 \text{ umol.L}^{-1}$ 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.

We will make the suggested revision.

> Page 11/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 $\Delta^{17}\text{O}$ and their discrepancies.

Many studies have been reported regarding this; in those reports you can find the luculent figures you want (Bao et al., Ann. Rev. EPSL, 2016, etc). While the difference in definition will have little influence on the results presented in this study (see section 2.6 for the details), lengthy notes and citations will be required to explain the figure to “readers unfamiliar with the definition of $\Delta^{17}\text{O}$ ”. Thus, we don’t think the figure you requested is suitable for our paper.

> Page 12/L.6-12: A detail, but I don't think that M_{atm} , M_{re} , M_{tot} and D_{atm} can be classified as "fluxes", but more as "annual loads".

All the parameters (D_{atm} , M_{atm} , M_{re} , and M_{tot}) were certainly the "fluxes" per unit area of each catchment. While we also recognized that the term "loads" has often been used to refer to these parameters, using "loads" for those exported from the catchment (M_{atm} , M_{re} , and M_{tot}) will be misleading to readers not so familiar with forested catchment studies. Besides, we used the same term, "fluxes" in our previous papers (Tsunogai et al., 2014) without any trouble. We have, thus, not changed terminology in this case to avoid confusing readers.

> Page 12/L.13 Add "annual" before "deposition".

We will make the suggested revision.

> Page 12/L.23: I disagree, in 2014 the flux is still higher in spring than in December. You could probably replace "December" by "winter period".

Please note that we were talking about F_{total} , not F_{atm} , here. The highest F_{total} of 2014 was in December ($337.7 \mu\text{mol m}^{-2} \text{ day}^{-1}$). This F_{total} was larger than that in June 2014 ($336.0 \mu\text{mol m}^{-2} \text{ day}^{-1}$). The largest F_{total} of 2013 was found in December as well ($698.4 \mu\text{mol m}^{-2} \text{ day}^{-1}$).

> Page 12/L.25: In 2015, you also have a June-July maximum in F_{atm} that is noticeable.

As opposed to the winter maximum, we could not find reproducibility in the June-July maximum. When we estimated the periodic average F_{atm} for two months, the June-July maximum disappeared. We don't think this maximum is worth discussing.

> Page 13/L.5: If I understood correctly, you calculated a F_{atm} value for every D17O value measured in the stream. Which means 15 points over two years, according to Figure 3.

Yes, you understood correctly.

> Page 13/L.5: 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 here why such low sampling resolution is enough to describe the behavior of your catchment.

Here in the section we simply wrote "We could not find significant enrichment of F_{atm} in spring." We don't think this is a "strong statement". Because this section presents the results of our study, we don't want to include a detailed discussion here, as per your request.

As for your comment on the number of data points (i.e., whether 15 data in total was significant), please note that the residence time of water is longer than a few months for most

forested catchments in Japan with a humid temperate climate (Takimoto et al., 1994; Kabeya et al., 2007), as presented in the manuscript. That is to say, seasonal variation in the deposition rates of rain water and atmospheric nitrate in the forested catchments in Japan will be buffered by groundwater.

The almost stable $\Delta^{17}\text{O}$ values of stream nitrate also support the fact that the rain water (and atmospheric nitrate) deposited at site KJ was buffered by groundwater in the catchment. While the total number of data points were 15 for nitrate isotopes during the 2 years of observation at site KJ, the most nitrate-enriched sample (Dec., 2013) and the second most nitrate-depleted sample (Oct., 2014) were included in the dataset. Nevertheless, the 1 sigma variation range was less than 0.4‰ for $\Delta^{17}\text{O}$ values of stream nitrate. The “7 data per year” (=15 data in total) was significant to determine the average $\Delta^{17}\text{O}$ of nitrate in groundwater at the site and to characterize this catchment.

Additionally, while the stream atmospheric nitrate export was obtained from 15 data in total, the stream nitrate export, which can be estimated from nitrate concentration and flow rate, was obtained from 12 data per year. In addition to the data presented in this study, we have monthly data since 2002 (Kamisako et al., 2008; Sase et al., 2012). For instance, none of these data supported F_{total} enrichment in spring, while all supported F_{total} enrichment in winter. Because it is difficult to assume temporal changes only in $\Delta^{17}\text{O}$ without the export flux of nitrate, our observation (“We could not find significant enrichment of F_{atm} in spring.”) was valid.

> Page 13/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.

We will make the suggested revision.

> Page 13/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.

We will make the suggested revision.

> Page 13/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.

We will make the suggested revision.

> Page 14/L.4-18: It is more standard to present deposition fluxes in kg-N ha⁻¹ 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.

We are sorry, but we are not familiar with the unit kg-N ha^{-1} . While the unit seems to be traditionally used in the studies performed in forested catchments, the unit in weight will be inconvenient to compare the results with components other than N (such as C, P, S, etc.). We have used the same unit in our previous papers (Tsunogai et al., 2010; 2011; 2014; 2018) without facing any issues. We would like to use the same unit in this paper to avoid confusing readers. We have presented the values in the unit kg-N ha^{-1} together with the present unit ($\text{mmol m}^{-2} \text{yr}^{-1}$) where required.

> Page 14/L.17: Ok, so here is the error associated with your deposition estimation. Please refer to this section where appropriated earlier in your manuscript.

In the earlier sections where we talk about deposition rate estimation (such as section 2.4), we will mention that errors will be discussed in section 3.1.

> Page 14/L.21-22: Why don't you present also F_{atm} and F_{tot} 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.

We will add a new figure 3(e) in which F_{atm} and F_{total} for IJ2 are presented.

> Page 14/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?

The logic is simple. Please read carefully.

Nakahara et al. (2010) found a continuous increasing trend in the annual average stream nitrate concentration, from $22 \mu\text{mol L}^{-1}$ in 1989 to $42 \mu\text{mol L}^{-1}$ in 2002. On the other hand, we found the annual average nitrate concentration to be almost stable at $24.4 \mu\text{mol L}^{-1}$ from 2012 to 2014. To connect these different trends in the same stream (IJ1) continuously and smoothly, we needed to assume the turning point from increasing to decreasing trend. Thus, we wrote "the trend in stream nitrate concentration has changed from increasing to decreasing". We did not insist that the annual mean nitrate concentration at IJ1 was decreasing during our observation period (2012 to 2014).

Further, the turning point must have been between 2003 and 2011. If we assume the turning point to be immediately before our observation period (2010 or 2011), the trend would be discontinuous. Besides, it would be difficult to explain why the annual average nitrate concentration was almost stable from 2012 to 2014. Thus, we estimated that the turning point was in the 2000s, between 2003 and 2009, and wrote "probably since the 2000s".

> Page 16/L.10: Why not giving the corresponding proportions of nitrate for each source using D17O to calculate the percentages.

These are presented in section 4.3 as $M_{\text{atm}}/M_{\text{total}}$.

> Page 16/L.17-20: This sentence doesn't make sense. How can D17O of soil nitrate reflect the original value of nitrate in groundwater?

In L17-18 we write “the $\Delta^{17}\text{O}$ values of soil nitrate REPRESENTED the original $\Delta^{17}\text{O}$ values of nitrate in the groundwater”. Because all stream nitrate data were plotted at the central part of the region produced by soil nitrate in Fig. 4, this must be a reasonable explanation for the relation between stream nitrate (=groundwater nitrate) and soil nitrate.

> Page 16/L.17-20: 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.

We feel that your interpretation does not apply to the data presented. As clearly presented in Figs. 3(c) and 5, nitrification must be active in summer soil and inactive in winter soil. Without assuming nitrate in groundwater (i.e., as “buffer” we proposed), it is impossible to explain the much smaller temporal $\Delta^{17}\text{O}$ variation in stream nitrate than that in soil nitrate.

The soil nitrate in winter, for instance, always showed higher $\Delta^{17}\text{O}$ values than that of stream nitrate, irrespective of the location of sampling point and depths of catchment. That is to say, the proportion of nitrate produced through nitrification (i.e., the “buffer” you proposed) within soil nitrate in winter was smaller than that in stream nitrate in winter. Of course, the $\Delta^{17}\text{O}$ values of nitrate in rain/snow were higher than those in stream nitrate. Therefore, it is impossible to explain the lower $\Delta^{17}\text{O}$ values of stream nitrate in winter with your interpretation, where you did not assume the contribution of the nitrate in groundwater (i.e., as “buffer” we proposed).

> Page 17/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).

We used the relation presented in Buchwald et al. (2012). This was different from the equation you suggest. We will present the equation in the manuscript, in response to your request.

> Page 17/L.13: You should also try to plot $\Delta^{18}\text{O}$ vs $\Delta^{15}\text{N}$ and see how they correlate to confirm, or not, the absence of biological processes in your catchment.

> Page 18/L.9: Here you should provide a scatterplot of $\Delta^{18}\text{O}$ vs $\Delta^{15}\text{N}$ 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 than the recharge of new NO_3 -re is overprinting isotopic fractionation by assimilation (Granger and Winkel, 2016).

First of all, we did not intend to say that biological processes were absent in the catchment. What we wrote here was that “partial metabolism was MINOR (= not so active) in the catchment”. If “minor” is a misleading word, we will change it to a more appropriate expression.

We used a $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_{\text{re}}$) vs. $\delta^{18}\text{O}_{\text{re}}$ plot for stream nitrate eluted from a forested catchment in our previous paper (Tsunogai et al., 2014) to investigate the source and behaviour of remineralized nitrate. We also estimated $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{re}}$ in this study, but we could not find any significant correlation between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{re}}$ in stream nitrate at site KJ ($R^2 = 0.06$). However, we found significant variation in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{re}}$, around 5‰ in stream nitrate and more than 10‰ in soil nitrate.

Unlike in our previous study where nitrate metabolism simply controlled $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{re}}$, the controlling factor for $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_{\text{re}}$) of nitrate seems to be complicated at site KJ. To interpret the results accurately, however, many more pages and data would be needed. We are working towards this in a future article.

> Page 17/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.).

While we first estimated the average $\delta^{18}\text{O}_{\text{re}}$ in the catchment using the relationship between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Tsunogai et al., 2010), this work has often been ignored in many of the subsequent works (Dejwakh et al., 2012; Liu et al., 2013; Riha et al., 2014; etc.), which estimated $\delta^{18}\text{O}_{\text{re}}$ (or $\delta^{18}\text{O}_{\text{terr}}$ or $\delta^{18}\text{O}_{\text{bio}}$ in some cases) without citing our study. That is to say, Tsunogai et al. (2010) is still “new” (i.e., still not known) by many people studying $\Delta^{17}\text{O}$ of nitrate. We would like to emphasize the usability of this methodology again here, citing our previous work.

> Page 17/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).

That was a fact. You can find the evidence in the high flow rates of the stream in winter. We will make the suggested revision, by adding deposition rate data in section 2.1.

> Page 18/L.6: Add reference to Michalski et al. 2004 after the value of 0.

We will make the suggested revision.

> Page 18/L.18-19: Be more precise: you are talking about concentrations here.

Yes, we are.

> To say “stream nitrate shows a normal correlation with soil nitrate” doesn’t make any sense.

We will revise this to “stream nitrate concentration shows a normal correlation with soil nitrate concentration”.

> Also, I am a bit dubious of the strength of your correlation given the low number of samples presented in Figure 7 (n=11).

This was the reason we calculated the p-value.

> Page 18/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 F_{atm} 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.

We can find high Δ¹⁷O at the end of July (+1.5‰ in 2013 and +1.6‰ in 2014). The Δ¹⁷O value in 2013 was the 2nd highest Δ¹⁷O and the Δ¹⁷O value in 2014 was the 3rd highest Δ¹⁷O among the Δ¹⁷O data obtained each year studied (n=7, respectively). It was impossible to explain the higher Δ¹⁷O found at the end of July in both years by the “freeze/thaw events”, because all the snow disappeared by the end of April every year.

Further, we determined both δ¹⁸O and δ²H values of the samples of stream water. Both values in the stream water showed little seasonal variation (-9.1±0.3 ‰ and -48.6±3.0‰, respectively). The d-excess (=δ²H -8*δ¹⁸O) in the stream water showed little seasonal variation as well (+24.2±1.9‰). Because d-excess in rain (&snow) water in these regions (Japan sea side of eastern Japan) shows large seasonal variation every year (around +30‰ in winter and around +10‰ in summer; Tanoue et al., 2013), the water isotopes also supported our hypothesis, while the contribution of water from the “freeze/thaw events” was minor in the stream water.

We will make the suggested revision in 4.1 adding the reference (Tanoue et al., 2013). Additionally, we will present the data of water isotopes in supplement.

Tanoue, M., K. Ichiyangai, and J. Shimada (2013) Seasonal variation and spatial distribution of stable isotopes in precipitation over Japan, *J. Jpn. Assoc. Hydrol. Sci.*, 43(3), 73-91 (in Japanese with English abstract).

> Page 19/L.1-15: It would be nice here that you refer to a table where you list the annual mean values for Catm, Ctot, F_{atm}, F_{tot}, and M_{atm} 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.

We will make the suggested revision.

> Page 19/L.16: There is no Equation (9) in your manuscript

We are very sorry, but the numbering of the equations seems to have been removed while we were arranging the format for Biogeosciences Discuss. The equation (9) was the last equation presented in section 2.7. We will make these revisions.

> Page 19/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.

Twenty percent of the M_{atm}/D_{atm} ratio showing 9.4% ($=0.094$) corresponds to 1.9% ($=0.019$). Because M_{atm} also includes an error, the final error of the M_{atm}/D_{atm} ratio was 2.6%. These are simple calculations of error propagations that were beyond the scope of this study.

> Page 19/L.17: Also, I would be very curious on how you obtained your percentages. If I divide the Matm ($=8.8$, 5.7 , and 2.2 for KJ, IJ1 and IJ2 respectively) by Datm ($=45.6$, 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

We are very sorry, but the M_{atm} values presented here were total M_{atm} values during the observation (ca. 2 years) and the annual M_{atm} value was approximately 50% of the present. We will present the annual values for M_{total} and M_{atm} .

> Page 20/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^- leaching fluxes to stream/groundwater, and thus impact the $D_{17}O$ value of nitrate in stream (by dilution). This would impact Matm, and therefore the Matm/Datm ratio. So please clarify what you meant here.

Your statement "This would impact M_{atm} " does not apply. While different nitrification rates in soils lead to different NO_3^- leaching fluxes to stream/groundwater, and thus, impact the $\Delta^{17}O$ value of the nitrate in the streams (by dilution), different nitrification rates cannot impact M_{atm} , because M_{atm} is determined by the processes of (1) deposition rate of atmospheric nitrate (D_{atm}), and (2) metabolic rate of nitrate in the forested catchment. Under the same removal rate constants for nitrate metabolism, and the same residence time of water in the catchment, M_{atm} values are stable irrespective of the changes in the nitrification rates.

> Page 21/L.10-13: That is my point. Rose et al 2015 already showed the relationship between Matm 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.

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

The metabolic rates of nitrate in forest soils that determine the removal ratio of atmospheric nitrate from the total atmospheric nitrate deposited in a catchment ($(D_{atm} - M_{atm})/D_{atm}$ ratio; Tsunogai et al., 2014), not the M_{atm} . Because M_{atm} is a function of D_{atm} , using M_{atm}/D_{atm} ratio as the index, instead of M_{atm} , is essential in principle.

In response to your strong request, we will add a new figure 8(c) in which the relation between the nitrate concentrations and M_{atm} values is plotted. The correlation coefficient ($R^2 = 0.63$) was lower than those of the average nitrate concentration vs. M_{atm}/D_{atm} ratio ($R^2 = 0.92$) and average nitrate concentration vs. M_{atm}/M_{total} ratio ($R^2 = 0.80$).

We would like to thank you for the helpful comments and suggestions. We trust that our responses to your comments and questions are satisfactory.

Sincerely,
Urumu Tsunogai

Cc: Fumiko Nakagawa, Yusuke Obata, Kenta Ando, Naoyuki Yamashita, Tatsuyoshi Saito, Shigeki Uchiyama, Masayuki Morohashi, Hiroyuki Sase