

October 26, 2022

Dr. Perran Cook  
Editor of Biogeosciences

Title: Stable isotopic evidence for the excess leaching of unprocessed atmospheric nitrate from forested catchments under high nitrogen saturation

Authors: Weitian Ding et al.

MS No.: egusphere-2022-717

Dear Dr. Cook:

Thank you very much for handling our manuscript. We would like to thank the referees as well for the constructive comments on our manuscript. We have carefully studied the comments and revised the manuscript accordingly. We include below point-by-point responses to the comments, and detailed descriptions of the modifications we made to the manuscript. Besides, we also uploaded the revised manuscript in MS Word, in which all the revisions from BGD version were recorded. We hope that with these changes you will find our revised manuscript appropriate for publication in your journal.

Sincerely yours,  
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**Response to the handing associate editor:**

**>Your abstract starts quite abruptly. Please start with 1-2 sentences of context.**

Thank you for the comment and the advising. “Owing to the elevated loading of nitrogen through atmospheric deposition, some forested ecosystems become nitrogen saturated, from which elevated levels of nitrate are exported.” We added the sentence in abstract of the revised MS (P2/L4-6).

**>As noted by reviewer 2, do not use abbreviations especially undefined in the abstract.**

Thank you for the advising. We added the full name of the forested catchments (Kasuya Research forested catchments for FK catchments and Shiiba Research forested catchment for MY catchment) in abstract of the revised MS (P2/L6-7 and P2/L16).

**>Figure 2. As I suggested in your previous manuscript, I am not familiar with the ‘1000’ before the delta values and suggest removing and replace with the ‘per mil’ symbol at the end.**

Thank you for the suggestion. We revised that in Figure 2 in the revised MS.

## Response to the referee #1:

**>We definitely can observed low  $M_{atm}/D_{atm}$  ratio if a forest is N limited and almost all precipitation nitrate is biologically processed. However, there are two exceptions. One is high precipitation may cause high  $M_{atm}/D_{atm}$  ratio due to limited contact time of precipitation nitrate with soil microbes and roots.**

Our conclusion was derived from FK, MY, and the past data ever reported in forested streams through continuous monitoring on  $\Delta^{17}O$  (Table 3 in the revised Manuscript), where the data of precipitation up to 3837 mm per year, average  $[NO_3^-]$ , and  $M_{atm}/D_{atm}$  ratio were included. While the stream nitrate concentration showed the strong linear relationship ( $R^2 = 0.76$ ;  $P < 0.0001$ ) with the  $M_{atm}/D_{atm}$  ratio (Fig. 3d in the revised MS), the amount of precipitation showed no linear relationship ( $R^2 = 0.06$ ;  $P = 0.47$ ) with the  $M_{atm}/D_{atm}$  ratio (Fig. 4a in the revised MS).

Besides, the differences in the number of storm events could affect the  $M_{atm}/D_{atm}$  ratio as well, because  $NO_3^-_{atm}$  could be injected into the stream water directly, along with the storm water (Inamdar and Mitchell, 2006). In recent study, however, we found that the storm events have little impacts on the  $M_{atm}/D_{atm}$  ratio, based on monitoring temporal variation of  $[NO_3^-_{atm}]$  in a stream water during storm events (Ding et al., 2022).

As a result, we concluded that the  $M_{atm}/D_{atm}$  ratio was mainly controlled by the progress of nitrogen saturation, rather than the differences in the number of storm events, the amount of precipitation. We mentioned these in the revised MS (P23-24/L450-L468).

Inamdar, S. P. and Mitchell, M. J.: Hydrologic and topographic controls on storm-event exports of dissolved organic carbon (BOC) and nitrate across catchment scales, *Water Resour. Res.*, 42(3), 1–16, doi:10.1029/2005WR004212, 2006.

Ding, W., Tsunogai, U., Nakagawa, F., Sambuichi, T., Sase, H., Morohashi, M., and Yotsuyanagi, H.: Tracing the source of nitrate in a forested stream showing elevated concentrations during storm events, *Biogeosciences*, 19, 3247–3261, <https://doi.org/10.5194/bg-19-3247-2022>, 2022.

**>The other is high soil nitrate production (gross nitrification rate), which can dilute of 17O of precipitation nitrate that reaches the soil.**

For the aspect of calculating, the high or low gross nitrification rate (GNR) does not influence the annual export flux of  $NO_3^-_{atm}$  ( $M_{atm}$ ), and thus the the  $M_{atm}/D_{atm}$  ratio. For the aspect of the GNR influence the nitrogen saturation of forest and thus the  $M_{atm}/D_{atm}$  ratio, we would like to discuss.

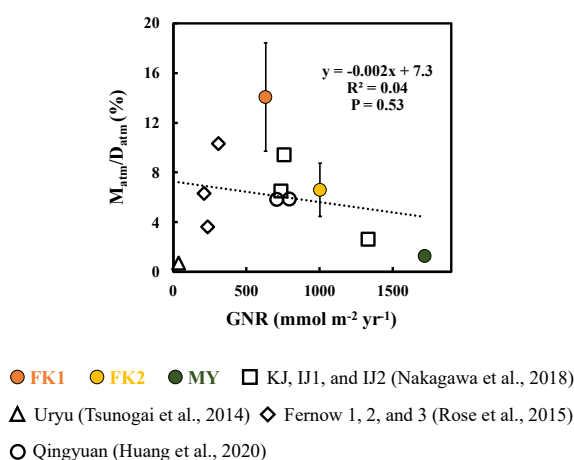
Past studies determined the gross nitrification rate (GNR) in the forested catchments based on the elution flux of unprocessed atmospheric nitrate and

remineralized nitrate via stream, determined from the  $\Delta^{17}\text{O}$  values of  $\text{NO}_3^-$  in stream water eluted from the catchment, and deposition flux of atmospheric nitrate into the catchment (Riha et al., 2014; Fang et al., 2015; Hattori et al., 2019; Huang et al., 2020).

$$\text{GNR} = D_{\text{atm}} \times (\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{atm}} - \Delta^{17}\text{O}(\text{NO}_3^-)_{\text{stream}}) / \Delta^{17}\text{O}(\text{NO}_3^-)_{\text{stream}} \quad (1)$$

where  $D_{\text{atm}}$  denote the deposition flux of nitrate into the catchments,  $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{atm}}$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{stream}}$  denote the  $\Delta^{17}\text{O}$  value of atmospheric nitrate and stream nitrate, respectively.

The GNR showed no linear relationship ( $R^2 = 0.04$ ;  $P = 0.53$ ; Fig. 1) with the  $M_{\text{atm}}/D_{\text{atm}}$  ratio in all forested catchments. As a result, the GNR have no influence with the  $M_{\text{atm}}/D_{\text{atm}}$  ratio.



**Figure 1.** the  $M_{\text{atm}}/D_{\text{atm}}$  ratio plotted as a function of the gross nitrification rate (GNR).

Fang, Y., Koba, K., Makabe, A., Takahashi, C., Zhu, W., Hayashi, T., Hokari, A. A., Urakawa, R., Bai, E., Houlton, B. Z., Xi, D., Zhang, S., Matsushita, K., Tu, Y., Liu, D., Zhu, F., Wang, Z., Zhou, G., Chen, D., Makita, T., Toda, H., Liu, X., Chen, Q., Zhang, D., Li, Y. and Yoh, M.: Microbial denitrification dominates nitrate losses from forest ecosystems, Proc. Natl. Acad. Sci. U. S. A., 112(5), 1470–1474, doi:10.1073/pnas.1416776112, 2015.

Hattori, S., Nuñez Palma, Y., Itoh, Y., Kawasaki, M., Fujihara, Y., Takase, K. and Yoshida, N.: Isotopic evidence for seasonality of microbial internal nitrogen cycles in a temperate forested catchment with heavy snowfall, Sci. Total Environ., 690, 290–299, doi:10.1016/j.scitotenv.2019.06.507, 2019.

Huang, S., Wang, F., Elliott, E. M., Zhu, F., Zhu, W., Koba, K., Yu, Z., Hobbie, E. A., Michalski, G., Kang, R., Wang, A., Zhu, J., Fu, S. and Fang, Y.: Multiyear Measurements on  $\Delta^{17}\text{O}$  of Stream Nitrate Indicate High Nitrate Production in a Temperate Forest, Environ. Sci. Technol., 54(7), 4231–4239, doi:10.1021/acs.est.9b07839, 2020.

Riha, K. M., Michalski, G., Gallo, E. L., Lohse, K. A., Brooks, P. D. and Meixner, T.: High Atmospheric Nitrate Inputs and Nitrogen Turnover in Semi-arid Urban

Catchments, Ecosystems, 17(8), 1309–1325, doi:10.1007/s10021-014-9797-x, 2014.

**>The streamwater samples for the three forested catchments were collected in 2019 to 2021, while  $\delta^{17}\text{O}$  of precipitation nitrate used in the calculation was from the site Sado island in central Japan during 2009 to 2012. So the space and time both were mismatched between stream water sampling sites and precipitation sites. So it is better that authors justified the mismatch. In addition, the average of  $\delta^{17}\text{O}$  in precipitation nitrate were used. However, there are a number of studies reporting highly seasonal variation of  $\delta^{17}\text{O}$  in precipitation nitrate.**

We estimated the uncertainty derived from the difference in the locality as 1 ‰ (Nakagawa et al., 2018). This was based on the standard deviation between the annual average  $\Delta^{17}\text{O}$  values determined in four different monitoring stations located in the same mid-latitudes, in the past studies such as La Jolla (33° N; Michalski et al., 2003), Princeton (40° N; Kaiser et al., 2007), Rishiri (45° N; Tsunogai et al., 2010), and Sado (38° N; Tsunogai et al., 2016). Besides, we estimated the uncertainty derived from the seasonal difference in the  $\Delta^{17}\text{O}$  values of atmospheric nitrate as 1.8 ‰, based on the standard deviation of six-month moving averages of atmospheric nitrate determined at the Sado monitoring station. Adding an additional 0.2 ‰ as a margin, we adopted 3 ‰ as the possible error for  $\Delta^{17}\text{O}$  atm in the streams (we mentioned that in Line 258–261 of manuscript). Additionally, the residence time of groundwater 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 a result, seasonal variation of the  $\Delta^{17}\text{O}$  values of atmospheric nitrate in the forested catchments in Japan will be buffered by groundwater and the uncertainty of 1.8 ‰ is enough for the seasonal difference in the  $\Delta^{17}\text{O}$  values of atmospheric nitrate. In addition, Tsunogai et al. (2010) reported the  $\Delta^{17}\text{O}$  values of atmospheric nitrate in Rishiri as +26.2 ‰ for 2006 to 2007. Tsunogai et al. (2016) reported the the  $\Delta^{17}\text{O}$  values of atmospheric nitrate in Sado island as +25.5 ‰ for 2009, +27.2 ‰ for 2010 and +25.7 ‰ for 2011. As a result, the temporal variation of the  $\Delta^{17}\text{O}$  values of atmospheric nitrate can be negligible.

Kabeya, N., Katsuyama, M., Kawasaki, M., Ohte, N., and Sugimoto, A.: Estimation of mean residence times of subsurface waters using seasonal variation in deuterium excess in a small head-water catchment in Japan, *Hydrol. Process.*, 21, 308–322, 2007.

Kaiser, J., Hastings, M. G., Houlton, B. Z., Röckmann, T. and Sigman, D. M.: Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of  $\text{N}_2\text{O}$ , *Anal. Chem.*, 79(2), 599–607, doi:10.1021/ac061022s, 2007.

Michalski, G., Scott, Z., Kabling, M. and Thiemens, M. H.: First measurements and modeling of  $\Delta^{17}\text{O}$  in atmospheric nitrate, *Geophys. Res. Lett.*, 30(16), 3–6, doi:10.1029/2003GL017015, 2003.

Nakagawa, F., Tsunogai, U., Obata, Y., Ando, K., Yamashita, N., Saito, T., Uchiyama, S., Morohashi, M. and Sase, H.: Export flux of unprocessed atmospheric nitrate from temperate forested catchments: A possible new index for nitrogen saturation, *Biogeosciences*, 15(22), 7025–7042, doi:10.5194/bg-15-7025-2018, 2018.

Tsunogai, U., Komatsu, D. D., Daita, S., Kazemi, G. A., Nakagawa, F., Noguchi, I. and Zhang, J.: Tracing the fate of atmospheric nitrate deposited onto a forest ecosystem in Eastern Asia using  $\Delta^{17}\text{O}$ , *Atmos. Chem. Phys.*, 10(4), 1809–1820, doi:10.5194/acp-10-1809-2010, 2010.

Tsunogai, U., Miyauchi, T., Ohyama, T., Komatsu, D. D., Nakagawa, F., Obata, Y., Sato, K. and Ohizumi, T.: Accurate and precise quantification of atmospheric nitrate in streams draining land of various uses by using triple oxygen isotopes as tracers, *Biogeosciences*, 13(11), 3441–3459, doi:10.5194/bg-13-3441-2016, 2016.

Takimoto, H., Tanaka, T., and Horino, H.: Does forest conserve runoff discharge during drought?, *Transactions of The Japanese Society of Irrigation, Drainage and Reclamation Engineering*, 170, 75–81, [https://doi.org/10.11408/jsidre1965.1994.170\\_75](https://doi.org/10.11408/jsidre1965.1994.170_75), 1994 (in Japanese with English abstract)

## **Response to the referee #2:**

**>It is difficult to identify a single driver for the differences in the proportion of atmospheric NO<sub>3</sub><sup>-</sup> export between the two sites given that they differ both in terms of the amount of N deposition and their climate (the low deposition site receives significantly less rainfall and is significantly cooler than the high deposition site; L120-121). Differences in hydrology are not accounted for, but should be (e.g., both surface water – groundwater interactions and slope, both of which could impact N attenuation and the degree of stream water mixing with microbial NO<sub>3</sub><sup>-</sup> sources).**

Our conclusion was derived from FK, MY, and the past data ever reported in forested streams through continuous monitoring on  $\Delta^{17}\text{O}$ , where the data of amount of precipitation, average  $[\text{NO}_3^-]$ , temperature, amount of discharge, and the  $M_{\text{atm}}/D_{\text{atm}}$  ratio were included (Table S1 in the revised supplement). While the stream nitrate concentration showed the strong linear relationship ( $R^2 = 0.76$ ;  $P < 0.0001$ ) with the  $M_{\text{atm}}/D_{\text{atm}}$  ratio (Fig. 3d in the revised MS), the amount of precipitation, temperature, and amount of discharge showed no significant relationship with the  $M_{\text{atm}}/D_{\text{atm}}$  ratio ( $P > 0.14$ ; Fig. 4 in the revised MS). As a result, we concluded the  $M_{\text{atm}}/D_{\text{atm}}$  ratio was mainly controlled by the progress of the nitrogen saturation, rather than the amount of precipitation, temperature, and hydrology. We mentioned these in the revised MS (P23-24/L459-L468).

**>These also led to differences in vegetation between the two sites (L114-119).**

By compare the type and the age of plantations in FK1, FK2, and MY catchments, we concluded that the age and type of plantations caused the reduction in N uptake rates and thus increased of the nitrogen saturation and the  $M_{\text{atm}}/D_{\text{atm}}$  ratio in 4.2 section of MS.

**>The fact that FK has lower concentrations of atmospheric NO<sub>3</sub><sup>-</sup> at the upstream site than the downstream does indicate that there is unaccounted for hydrologic mixing (or loss) occurring along the stream, which could significantly bias M/D estimates based on a single sampling point (as in the MY catchment).**

FK catchments have higher concentrations of atmospheric nitrate at the upstream site than the downstream, insteadly (Table 3 in MS). The higher concentrations of atmospheric nitrate (or higher  $M_{\text{atm}}/D_{\text{atm}}$  ratio) in FK1 catchment than FK2 catchment indicated that progress of the nitrogen saturation was heterogeneities, even in a small area ( $< 100$  ha). As a result, we only discussed the  $M_{\text{atm}}/D_{\text{atm}}$  ratio that the area can be covered by the ridgeline and sampling points in MY catchment (43 ha) and other forested catchments.

**>The atmospheric deposition info used to calculate M/D (the crux of the study) were collected over 10 years, but these measurements ended prior to the stream water sampling that is the primary data here. This is a major limitation, given how much atmospheric N deposition can vary month to month and year to year. A robust approach to constrain the uncertainty created by relying on this ‘mean’ data is required.**

Chiwa (2020) reported the bulk deposition rate of atmospheric nitrate ( $D_{\text{atm}}$ ) as 4.7 and 3.4 kg ha<sup>-1</sup> yr<sup>-1</sup> for 2009 to 2018 in FK and MY catchments, respectively, which all the  $D_{\text{atm}}$  showed no temporal variation (decreased or increased trend during 2009 to 2018). The standard deviation (SD) and coefficient of variation (CV) were 0.9 kg ha<sup>-1</sup> yr<sup>-1</sup> and 16 % for FK catchments, 0.5 kg ha<sup>-1</sup> yr<sup>-1</sup> and 15% for MY catchment, respectively. Besides, the residence time of groundwater 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). Thus, seasonal variation of  $D_{\text{atm}}$  in the forested catchments in Japan will be buffered by groundwater. In this study, we assumed the uncertainty of the  $D_{\text{atm}}$  as 20% (large than 16 % and 15 %) in FK and MY catchments, which is enough for the temporal variation in each forested catchment.

Kabeya, N., Katsuyama, M., Kawasaki, M., Ohte, N., and Sugimoto, A.: Estimation of mean residence times of subsurface waters using seasonal variation in deuterium excess in a small head-water catchment in Japan, *Hydrol. Process.*, 21, 308–322, 2007.

Takimoto, H., Tanaka, T., and Horino, H.: Does forest conserve runoff discharge during drought?, *Transactions of The Japanese Society of Irrigation, Drainage and Reclamation Engineering*, 170, 75–81, [https://doi.org/10.11408/jsidre1965.1994.170\\_75](https://doi.org/10.11408/jsidre1965.1994.170_75), 1994 (in Japanese with English abstract)

**>Information is also needed on the exact location of the atmospheric sample collection relative to the streamwater collection sites (in particular for helping to assess whether there might be differences in atmospheric inputs at sites FK1 v FK2)**

The distances between the monitoring sites of bulk deposition in the FK1, FK2, and MY forested catchments and the stations of stream water sampling were 3.9, 2.9, and 4.5 km, respectively (Calculated from google map). We mentioned this in the revised MS (P11/L209-211).



**>L4: The abstract should be revised to start with establishing the ‘big picture’ issue addressed and aim of the study, rather than jumping straight in to site differences.**

“Owing to the elevated loading of nitrogen through atmospheric deposition, some forested ecosystems become nitrogen saturated, from which elevated levels of nitrate are exported.” We added the sentence in abstract of the revised MS (P2/L4-6).

**>L4-6: Here and elsewhere, I suggest referring to the sites by name rather than using acronyms, as this will make it easier to connect this to other work on the sites and more intuitive to follow within the manuscript.**

We added the full name of the forested catchments (Kasuya Research forested catchments for FK catchments and Shiiba Research forested catchment for MY catchment) in abstract of the revised MS (P2/L6-7 and P2/L16).

**>L50: This line suggests that groundwater inputs are greater in humid temperate forests than other biomes, which is as far as I know not true.**

We revised this in the revised MS (P4/L53-56).  
“seasonal variation of soil nitrate can be buffered by groundwater with long residence time, so that the seasonal variation is unclear in stream nitrate concentration in Japan, even in normal forests under the nitrogen saturation stage of 0 (Mitchell et al., 1997)”

**>L66: Word missing after ‘recent’**

We revised this in the revised MS (P5/L70).

**>L93-95: How could the validity of the approach be tested with the collected data?**

Past studies have reported that the forested catchments under the nitrogen saturated exported the elevated levels of nitrate, together with the high concentration of nitrate (Aber et al., 1989; Mitchell et al., 1997; Peterjohn et al., 1996). The higher concentration of nitrate and export flux of nitrate ( $M_{\text{total}}$ ) in FK catchments compare to the KJ forested catchment, the maximum value of the  $M_{\text{atm}}/D_{\text{atm}}$  ratio before this study, implied progress of nitrogen saturation in FK catchments were severe. The higher  $M_{\text{atm}}/D_{\text{atm}}$  ratio in FK catchments supported the implication.

Aber, J. D.: Nitrogen cycling and nitrogen saturation in temperate forest ecosystems, Trends Ecol. Evol., 7(7), 220–224, doi:10.1016/0169-5347(92)90048-G, 1992.  
Aber, J. D., Nadelhoffer, K. J., Steudler, P. and Melillo, J. M.: Nitrogen Saturation in

Northern Forest Ecosystems, *Bioscience*, 39(6), 378–386, doi:10.2307/1311067, 1989.

Mitchell, M. J., Iwatsubo, G., Ohnishi, K. and Nakagawa, Y.: Nitrogen saturation in Japanese forests: An evaluation, *For. Ecol. Manage.*, 97(1), 39–51, doi:10.1016/S0378-1127(97)00047-9, 1997.

Peterjohn, W. T., Adams, M. B. and Gilliam, F. S.: Symptoms of nitrogen saturation in two central Appalachian hardwood forest ecosystems, *Biogeochemistry*, 35(3), 507–522, doi:10.1007/BF02183038, 1996.

**>Why is there reason to think that this method wouldn't work in catchments with higher rates of N deposition?**

Because concentration of nitrate and export flux of nitrate of FK forested catchments higher than the KJ forested catchment, where the  $M_{\text{atm}}/D_{\text{atm}}$  ratio was the highest prior to this study. While we expected high  $M_{\text{atm}}/D_{\text{atm}}$  ratio in FK forested catchments, we conducted this study to verify this.

**>A clear hypothesis about how and why catchment retain v export atmospheric NO<sub>3</sub>- will be important for setting up a stronger discussion section.**

We added this in revised manuscript (P6/L98-100).

“Whether the index of the  $M_{\text{atm}}/D_{\text{atm}}$  ratio can be applied to forested catchments, where the leaching of stream nitrate is much higher than the KJ forested catchment, remained unclarified. Besides, the advantages of the  $M_{\text{atm}}/D_{\text{atm}}$  ratio within the past indexes of nitrogen saturation have not been discussed.”

**>L96: Word missing after ‘recent’**

We revised this in the revised MS (P6/L101).

**>L105-107: As above, it is not clear how the reliability of the M/D ratio can be evaluated using these methods. What results would show that it's unreliable?**

If the  $M_{\text{atm}}/D_{\text{atm}}$  ratio would be lower in FK catchments than the other low export flux of nitrate ( $M_{\text{total}}$ ) catchments, it was difficult to conclude that the  $M_{\text{atm}}/D_{\text{atm}}$  ratio is reliable as an index of nitrogen saturation.

**>L161-163: More information on internal standards needed (number, delta values, etc). Information on calibration for  $\delta^{17}\text{O}$  also needed.**

In this study, we used three kinds of the local laboratory nitrate standards, which were named to be GG01 ( $\delta^{15}\text{N} = -3.07\text{‰}$ ,  $\delta^{18}\text{O} = +1.10\text{‰}$ , and  $\Delta^{17}\text{O} = 0\text{‰}$ ),

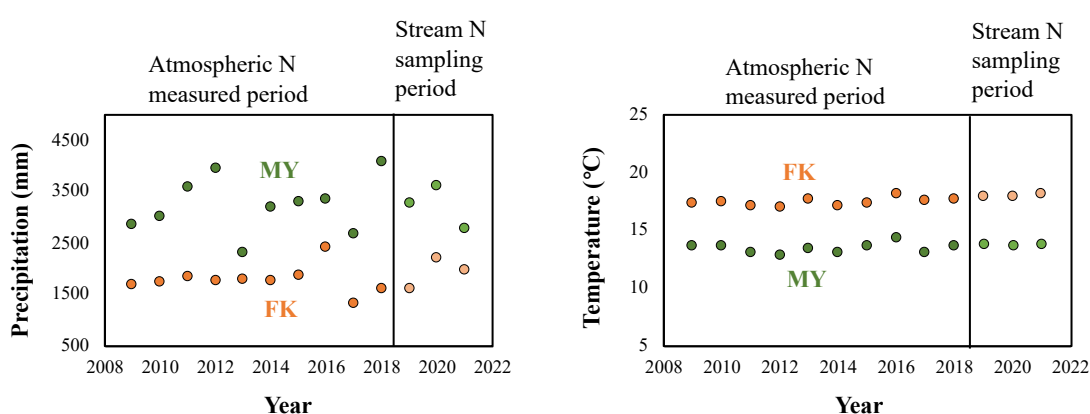
HDLW02 ( $\delta^{15}\text{N} = +8.94 \text{ ‰}$ ,  $\delta^{18}\text{O} = +24.07 \text{ ‰}$ ), and NF ( $\Delta^{17}\text{O} = +19.16 \text{ ‰}$ ), which the GG01 and the HDLW02 were used to determine the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of stream nitrate, and the GG01 and the NF was used to determine the  $\Delta^{17}\text{O}$  of stream nitrate. The oxygen exchange rate between nitrate and water during the chemical conversion was calculated through Eq. (1):

$$\text{Oxygen exchange rate (\%)} = \Delta^{17}\text{O}(\text{N}_2\text{O})_{\text{NF}} / \Delta^{17}\text{O}(\text{NO}_3^-)_{\text{NF}} \quad (1)$$

where the  $\Delta^{17}\text{O}(\text{N}_2\text{O})_{\text{NF}}$  denote the  $\Delta^{17}\text{O}$  value of  $\text{N}_2\text{O}$  that convert from the NF nitrate, the  $\Delta^{17}\text{O}(\text{NO}_3^-)_{\text{NF}}$  denote the  $\Delta^{17}\text{O}$  value of NF nitrate ( $\Delta^{17}\text{O} = +19.16 \text{ ‰}$ ). We mentioned these in the revised MS (P9-10/L163-174).

**>L226-229: Were climate conditions (rainfall, stream flow, temperature) significantly different between the years where atmospheric N was measured v the years where stream N was measured?**

We could not find significant differences in both rainfall and temperature between 2009-2018 (the years when atmospheric N was measured) and 2019-2021 (the years when stream N was measured). We compiled the rainfall and temperature during 2009 to 2021 based on the Japan Meteorological Agency at the nearest Fukuoka station ( $33^\circ 34'\text{N}$ ,  $130^\circ 22'\text{E}$ ) and Miyazaki station ( $31^\circ 56'\text{N}$ ,  $131^\circ 24'\text{E}$ ) (Fig. 2). There are no significant different of rainfall and temperature between 2009-2018 and 2019-2021 (t-test; all the  $P > 0.21$ ). Because the stream flow was mainly controlled by the rainfall and temperature, we think the stream flow also have no significant different between 2009-2018 and 2019-2021. We used the average value of them during 2009-2021 in the revised manuscript (P13/L240-241).



**Figure 2.** Temporal variations in the precipitation and temperature during 2009 to 2021 at Fukuoka province (orange) and Miyazaki province (green).

**>L234: Is this a reasonable explanation for the two sites? Some geologic / hydrologic information is needed to support this.**

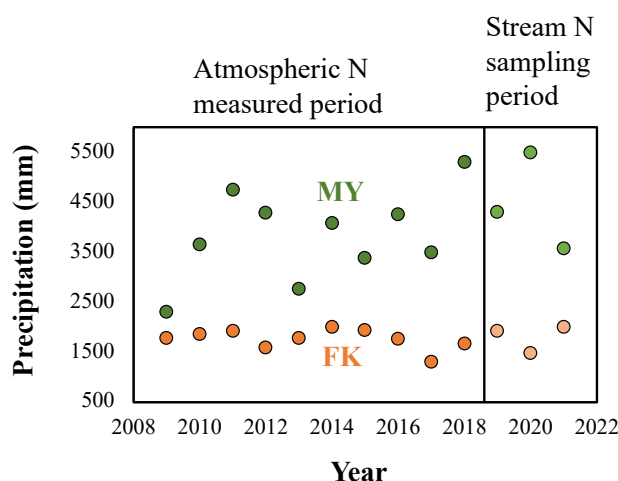
Yes. By using the water balance method ( $E \text{ (mm)} = 31.4T_{avg} \text{ (}^{\circ}\text{C)} + 376$ ), Komatsu et al. (2008) estimated the flux of stream water ( $F_{stream}$ ) of three forested catchments in Japan for ten years. They found the estimated year-to-year  $F_{stream}$  were well corresponded to year-to-year observed  $F_{stream}$  variations in three forested catchments. The estimated errors were less than 6%, and  $R^2$  values were higher than 0.91. Thus, the water balance method was reasonable.

**>L236: Given how important this value is for estimated M/D (L264), it would be illustrative to calculate stream flow based on a range rather than a single average value.**

Komatsu et al. (2008) proposed the standard error when use the method to estimate the flux of stream water ( $F_{stream}$ ). The standard error (range) was included in the calculated  $M_{atm}/D_{atm}$  ratio.

**>L273-275: Did rainfall differ between the two stream water sampled years? This would be useful information for helping interpret differences in NO<sub>3</sub>- over time.**

No. We also could not find significant difference in rainfall of FK and MY catchments between 2009-2018 and 2019-2021 (Fig. 3) (t-test; all the  $P > 0.16$ ). We used the average value of rainfall during 2009-2021 in the revised MS (P16/L314-316).



**Figure 3.** Temporal variations in the precipitation during 2009 to 2021 at FK catchments (orange) and MY catchment (green).

**>L290: Report in more quantitative terms (what is ‘little’ variation?)**

We added the relationship information of the concentrations of stream nitrate and the time (month), together with the standard deviation (SD) and the coefficient of

variation (CV) of them in the revised MS (P17/L334-336). We also revised this in the revised MS (P17/L336-337).

“All catchments showed no clear seasonal variation during the observation periods.”

**>L302-305: Move to Discussion.**

We revised this as suggestion (P17/L388-391).

**>L325-329: What is the likely source of the 20% discrepancy? Is this due to differences in method (and if so how / what?) or genuine inter-annual differences in either N inputs or N retention? These points should be expanded on here.**

We think the environmental difference of observation site is likely source of the 20% discrepancy. The assumption should be verified by the observation. However, this is not the target in this study.

**>L336-343: The collected data would need to be combined with more detailed meteorological information and/or isotopic modelling in order to determine the source of atmospheric N to the two sites. Consequently this explanation for the differences between the two sites is mostly speculation and does not have much bearing on the overall aim of the study (to understand forest N saturation dynamics), so I suggest removing altogether or moving to the site description as part of the explanation for the known difference in N deposition rates between the two locations.**

We removed the sentence of “As a result, the local emission in the Fukuoka metropolitan area should be responsible for the high  $D_{\text{atm}}$  at the FK catchments” in the revised MS.

**>L349: But how many locations has this been reported for? Given the relatively small dataset shown in Table 3 I wonder how surprising the relatively high M/D ratio is.**

The average  $[\text{NO}_3^-]_{\text{atm}}$  of forested stream have reported by many past studies ((Bostic et al., 2021; Bourgeois et al., 2018b, 2018a; Hattori et al., 2019; Huang et al., 2020; Nakagawa et al., 2018; Rose et al., 2015; Sabo et al., 2016; Tsunogai et al., 2014, 2016). However, for calculating the  $M_{\text{atm}}/D_{\text{atm}}$  ratio, not only the average  $[\text{NO}_3^-]_{\text{atm}}$  was needed, the  $D_{\text{atm}}$  (deposition rate of atmospheric nitrate) and the flux of stream water were also needed. Some past studies have not reported the  $D_{\text{atm}}$  or the flux of stream water. Thus, the number of the forested catchments we compiled in the

Table 3 of manuscript were smaller than the number of the forested catchments that reported the average  $[\text{NO}_3^-]_{\text{atm}}$  data we listed.

**>Is it likely that other sites around the world will have similar (or even higher!) ratios?**

Yes. We expect the  $M_{\text{atm}}/D_{\text{atm}}$  ratios higher than the FK catchments in forested catchments where the progress of nitrogen saturation is more severe than the FK catchments. We would like to conduct the further observations in the future, when the COVID-19 become stable.

**>L353: What else besides  $D_{\text{atm}}$  could cause the high concentration of  $\text{NO}_3(\text{atm})$  in the stream water? Alternative explanations (if they exist) should be discussed.**

We assumed the happening of the storm or snowmelt could also cause the high concentration of atmospheric nitrate in the stream water, because  $\text{NO}_3^-$  could be injected into the stream water directly, along with the storm / snowmelt water (Tsunogai et al., 2014; Ding et al., 2022; Inamdar and Mitchell, 2006). In recent study, however, we found that the storm events have little impacts on the  $M_{\text{atm}}/D_{\text{atm}}$  ratio, based on monitoring temporal variation of  $[\text{NO}_3^-]_{\text{atm}}$  in a stream water during storm events (Ding et al., 2022). Besides, the number of happening of snowmelt in the FK and MY forested catchments can be negligible. In addition, the amount of the snowmelt is smaller than the amount of the precipitation significantly. We added the information as suggested in the revised MS (P23/L450-458).

Besides, the only concern on using the  $M_{\text{atm}}/D_{\text{atm}}$  ratio as the index of nitrogen saturation is the impact of the differences in the residence time of water in each catchment. The residence time of water varies from 1 month to more than 1 year in forested catchments (Asano et al., 2002; Farrick and Branfireun, 2015; Kabeya et al., 2008; Rodgers et al., 2005; Soulsby et al., 2006; Tetzlaff et al., 2007). The  $M_{\text{atm}}/D_{\text{atm}}$  ratio could be higher in catchments with shorter residence time of water. We would like to clarify this in future studies by adding much more data of stream nitrate eluted from various forested catchments. We mentioned this in the revised MS (P25/L492-499).

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Tetzlaff, D., Malcolm, I. A. and Soulsby, C.: Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments, *J. Hydrol.*, 346(3–4), 93–111, doi:10.1016/j.jhydrol.2007.08.016, 2007.

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**>L370-388: Beyond forest N uptake, what could cause catchment retention of N deposition? E.g., retention in soils or groundwater?**

In this study, the retention is included in uptake.

**>L415-418: How does this finding compare to other parts of the world where precipitation is low but N deposition is high (e.g., parts of the southwestern US)?**

We compiled all past data ever reported in forested streams through continuous monitoring in Table 3, where the data of average  $[\text{NO}_3^-]$ , average  $[\text{NO}_3^-]_{\text{atm}}$ ,  $M_{\text{atm}}$ ,  $M_{\text{total}}$ ,  $D_{\text{atm}}$ , and  $M_{\text{atm}}/D_{\text{atm}}$  ratio were included.

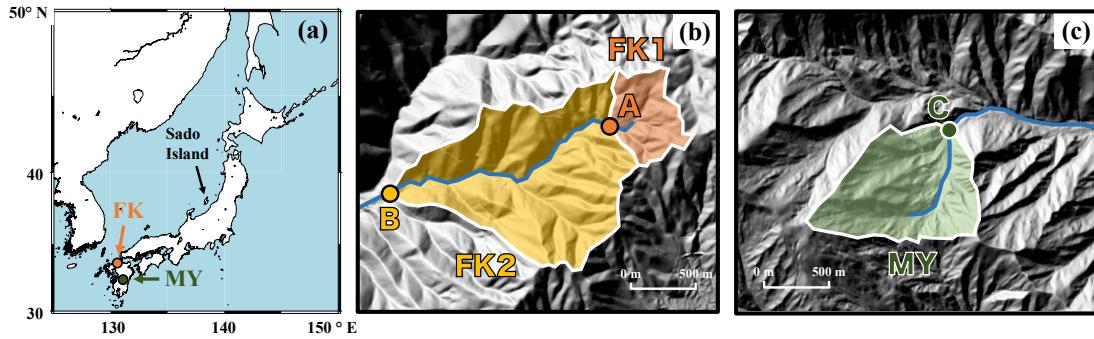
**>L421-422: The relationship between precipitation and N losses really cannot be evaluated here given that the stream and precipitation data is decoupled (stream**

data collected after the precipitation sampling was concluded), and that dynamics are consequently evaluated only at a very broad timescale based on mean average annual precipitation and evapotranspiration for the two sites.

There was no significant difference in precipitation between 2009-2018 and 2019-2021 (t-test;  $P > 0.16$ ) (Fig. 3). We used the average value of precipitation during 2009-2021 in the revised MS. Besides, the uncertainty in  $D_{\text{atm}}$ , uncertainty in stream water flux, and uncertainty in concentration of unprocessed nitrate in the streams were included in the calculated  $M_{\text{atm}}/D_{\text{atm}}$  ratios. Because the  $M_{\text{atm}}/D_{\text{atm}}$  ratios in FK1 forested catchment was significantly large, even account for the uncertainties, the  $M_{\text{atm}}/D_{\text{atm}}$  ratios can be an index for evaluating nitrogen saturation.

**>Fig. 1: This indicates that sites FK1 and FK2 are just two points along the same stream, meaning that they represent the same catchment. Some clarification is needed in the Methods and here to describe the hydrologic connection between the two locations and whether they should be considered upstream/downstream or two different sub-catchment (in which case this map should be updated to clearly show the catchments).**

We updated the map as follow as suggested in the revised MS (Fig.1 in the revised MS):



In addition, we added a new section of 2.7 as fellow to update the data that relation to FK2 catchment (P15-16/L282-310).

## 2.7 Concentration and isotopic compositions of stream nitrate eluted only from the FK2 catchment

The concentration and isotopic compositions ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$ ) of stream nitrate determined at the station B were the mixture of those eluted from FK1 and FK2 catchments (Fig. 1b of MS). Assuming that the stream nitrate eluted from FK1 catchment was stable during the flow path from station A to station B. The concentration of stream nitrate eluted from the FK2 catchment was determined by applying Eq. (9):

$$[\text{NO}_3^-]_{\text{FK2}} = ([\text{NO}_3^-]_{\text{FK1+FK2}} * F_{\text{FK1+FK2}} - [\text{NO}_3^-]_{\text{FK1}} * F_{\text{FK1}}) / F_{\text{FK2}} \quad (9)$$

where  $F_{\text{FK1}}$ ,  $F_{\text{FK2}}$ , and  $F_{\text{FK1+FK2}}$  denote the flux of stream water eluted from the FK1, FK2 (only), and FK1+FK2 catchment, respectively.  $[\text{NO}_3^-]_{\text{FK1}}$ ,  $[\text{NO}_3^-]_{\text{FK2}}$ , and



$[\text{NO}_3^-]_{\text{FK1+FK2}}$  denote the concentration of stream nitrate eluted from the FK1, FK2 (only), and FK1+FK2 catchment, respectively. In this study, the flow rates measured at stations A and B on 2021/01/15 by using the salt dilution method (Sappa et al., 2015) was used for  $F_{\text{FK1}}$  (0.85 L/s) and  $F_{\text{FK1+FK2}}$  (4.75 L/s), respectively, and the measured  $[\text{NO}_3^-]$  at stations A and B was used for  $[\text{NO}_3^-]_{\text{FK1}}$  and  $[\text{NO}_3^-]_{\text{FK1+FK2}}$ , respectively. Because the relation between the measured flow rates was comparable with the relation between the catchment area of FK1 (14 ha) and that of FK1+FK2 (76 ha), we concluded that the measured flow rates of 0.85 L/s and 4.75 L/s were reasonable as for those representing the  $F_{\text{FK1}}$  and  $F_{\text{FK1+FK2}}$ , respectively. According to the mass balance of water, we can estimate the  $F_{\text{FK2}}$  eluted from the FK2 catchment only to be 3.90 L/s.

Assuming that the stream nitrate eluted from FK1 catchment was stable during the flow path from station A to station B, the  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  values of stream nitrate eluted from the FK2 catchment only were determined by applying Eq. (10):

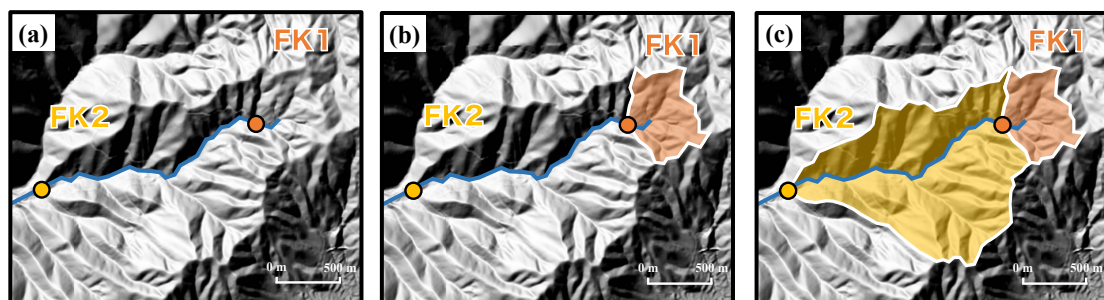
$$\delta_{\text{FK2}} = (\delta_{\text{FK1+FK2}} * [\text{NO}_3^-]_{\text{FK1+FK2}} * F_{\text{FK1+FK2}} - \delta_{\text{FK1}} * [\text{NO}_3^-]_{\text{FK1}} * F_{\text{FK1}}) / ([\text{NO}_3^-]_{\text{FK2}} * F_{\text{FK2}}) \quad (10)$$

where  $\delta_{\text{FK1}}$ ,  $\delta_{\text{FK2}}$ , and  $\delta_{\text{FK1+FK2}}$  denote the  $\delta^{15}\text{N}$  (or  $\delta^{18}\text{O}$  or  $\Delta^{17}\text{O}$ ) of stream nitrate eluted from the FK1, FK2, and FK1+FK2 catchment, respectively. The  $\delta^{15}\text{N}$  (or  $\delta^{18}\text{O}$  or  $\Delta^{17}\text{O}$ ) values of stream nitrate measured at stations A and B were used for  $\delta_{\text{FK1}}$  and  $\delta_{\text{FK1+FK2}}$ , respectively.

Sappa, G., Ferranti, F. and Pecchia, G. M.: Validation Of Salt Dilution Method For Discharge Measurements In The Upper Valley Of Aniene River (Central Italy), Recent Adv. Environ. Ecosyst. Dev., (October 2015), 42–48, 2015.

**>L126: How were the boundaries between the FK1 and FK2 catchments determined? Fig. 1 indicates that these sites are both located along the same stream in the same catchment.**

Firstly, we determined the sampling point in the map by using the GPS data (33.39.31.2689, 130.32.55.0910 for FK1; 33.39.20.9586, 130.32.18.8808 for FK2) (Fig. 4a). Then, we connected the ridge line and the upstream sampling point, which the area (orange) is the FK1 catchment (Fig. 4b). Lastly, by using the same method, the FK2 catchment area was drawn in Fig 4c.



**Figure 4.** The maps showing how we determined the boundary line of the FK1 and FK2 forested catchments.