

Reply to your comment (Referee #2).

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

> it is not clear to me how the “stable” “unprocessed” atmospheric nitrate can be used to evaluate nitrogen saturation in forested catchments.

Nakagawa et al. (2018) lately proposed that the $M_{\text{atm}}/D_{\text{atm}}$ ratio, the export flux of $\text{NO}_3^-_{\text{atm}}$ (M_{atm}) relative to the deposition flux of $\text{NO}_3^-_{\text{atm}}$ (D_{atm}), can be an alternative, more robust index to evaluate nitrogen saturation in each forested catchment, because the $M_{\text{atm}}/D_{\text{atm}}$ ratio directly reflect the demand on atmospheric nitrate deposited onto each forested catchments as a whole, and thus reflect the nitrogen saturation in each forested catchment. If the forested catchments under the nitrogen saturation, the demand on atmospheric nitrate of the forested catchments will decrease, and the export flux of $\text{NO}_3^-_{\text{atm}}$ (M_{atm}) will increase. Also, because D_{atm} is variable between the different forested catchments, normalizing M_{atm} by D_{atm} is necessary for compare M_{atm} between the different forested catchments. We would like to emphasize this in the revised MS.

> I’m also not able to follow why the conclusion of “the storm events have little impacts on the concentration of unprocessed atmospheric nitrate in the stream” is important and how the conclusion is arrived.

The concentrations of the unprocessed atmospheric nitrate ($[\text{NO}_3^-_{\text{atm}}]$) in rainwater (the $[\text{NO}_3^-_{\text{atm}}]$ in rainwater determined in Sado island, for example, was $27.2 \pm 18.5 \mu\text{M}$ from August to October in 2009, 2010, and 2011; Tsunogai et al., 2016) were much higher than those in stream water ($2.2 \pm 0.6 \mu\text{M}$ in this study). If significant portion of rainwater was added directly into the stream water during storm events, the $[\text{NO}_3^-_{\text{atm}}]$ in stream water should increase. The $[\text{NO}_3^-_{\text{atm}}]$ in stream water, however, was stable having no linear relationship with the precipitation or the total concentration of the stream nitrate during the storm events. As a result, we concluded that the directed input of the $[\text{NO}_3^-_{\text{atm}}]$ into the stream water was negligible even during the storm events. In addition, we also concluded that the $M_{\text{atm}}/D_{\text{atm}}$ ratio is controlled by the nitrogen saturation stage in each forest. Instead of direct input into the stream water during storm events, the $\text{NO}_3^-_{\text{atm}}$ experiences the metabolized processes (uptake or denitrification) in forested catchment subsequent to deposition, indicating that the $M_{\text{atm}}/D_{\text{atm}}$ ratio reflect the total demand on $\text{NO}_3^-_{\text{atm}}$ in each forested catchment and thus the nitrogen saturation status. We would like to clarify this in the revised MS.

> Overall, I'm not able to follow why "unprocessed atmospheric nitrate fraction" in river water is so important that the authors have to repeat and emphasize many times in the manuscript.

We mentioned the concentration of the unprocessed atmospheric nitrate ($[\text{NO}_3^-_{\text{atm}}]$) several times in the MS. The $M_{\text{atm}}/D_{\text{atm}}$ ratio can be controlled by two factors in forested catchments, (1) the hydrologic flow path, (2) nitrogen saturation stage. To verify the $M_{\text{atm}}/D_{\text{atm}}$ ratio can reflect the nitrogen saturation stage of the forested catchments, the amount of the direct input of the atmospheric nitrate in rainwater during storm events should be clarify. As a result, we discussed the amount of the direct input of the atmospheric nitrate in rainwater during storm events precisely and mentioned the $[\text{NO}_3^-_{\text{atm}}]$ in stream water many times.

> My understanding is that with finite fraction of atmospheric nitrate, one can utilize the unique triple oxygen isotope composition in atmospheric nitrate for riverine nitrogen dynamics study, which is what the group did in the past years. The fraction of "unprocessed atmospheric nitrate" represents a balance of release of soil nitrate and atmospheric deposition.

While the fraction of "unprocessed atmospheric nitrate" represents a balance of release of soil nitrate and atmospheric deposition in past studies (Nakagawa et al., 2018), it turns out that, while the concentration of stream nitrate increased, the $[\text{NO}_3^-_{\text{atm}}]$ in stream water remained almost stable during the storm events in this study indicating that the fraction of "unprocessed atmospheric nitrate" can't represent a balance of release of soil nitrate and atmospheric deposition. Thank you for your advice.

> Line 25-30: no flux estimation is provided, and so it is not clear how the statement of "the annual export flux of unprocessed atmospheric nitrate relative to the annual deposition flux" is obtained. Overall, from my understanding, the value of $\text{NO}_3^-_{\text{atm}}$ is quite stable. The values of the 3 storms are 1.6 ± 0.4 , 1.8 ± 0.4 , and 2.1 ± 0.4 μM , while that during non-storm time is 2.2 ± 0.6 μM . Isn't it more valuable to discuss storm and non-storm samples in the same context of nitrogen saturation and dynamics?

The annual export flux of unprocessed atmospheric nitrate relative to the annual deposition flux ($M_{\text{atm}}/D_{\text{atm}}$ ratio) was estimated from annual $[\text{NO}_3^-_{\text{atm}}]$ in the stream, annual flow rate of stream, and annual deposition flux of atmospheric nitrate. In the forested catchment, the annual flow rate of stream and annual deposition flux of atmospheric nitrate can be considered as constant. The $[\text{NO}_3^-_{\text{atm}}]$ in the stream was 1.6 ± 0.4 μM , 1.8 ± 0.4 μM , and 2.1 ± 0.4 μM during the storm events I, II, and III, respectively, which have no significant difference with the annual $[\text{NO}_3^-_{\text{atm}}]$ in the

stream ($2.2 \pm 0.6 \mu\text{M}$). Thus, the storm events have little impacts on the $M_{\text{atm}}/D_{\text{atm}}$ ratio. Thank you for your advising. We would like to clarify this in the revised MS.

> The term “enriched” may cause confusion. In isotope community, often the term is used for indicating an increase in isotope values, i.e., increase in the abundance of heavier isotopic compounds.

Thank you for your advising. We would like to revise the title as “Tracing the source of nitrate in a forested stream showing elevated concentrations during storm events” in the revised manuscript.

> Line 121: M_{atm} , D_{atm} are not defined till much later in section 4.3. Even in section 4.3, the two variables are not clearly defined and explained. Instead, the authors referred to their earlier paper (Nakagawa et al., 2018). The authors are fine to have the details in their previous paper but the authors have to at least explain the meaning of the two.

Thank you for your advising. We would like to revise as suggested.

> M_{atm} (or NO_3_{atm}) is obtained by assuming a certain number of $\text{D}_17\text{O}_{\text{atm}}$, which is not measured in this work. And so, D_{atm} is not known. Please elaborate and explain why $M_{\text{atm}}/D_{\text{atm}}$ is little affected by storms and how this conclusion is arrived.

We have mentioned that above.

> Line 163: Please discuss whether 1-2 weeks of storage would affect the sample nitrate concentration and isotope compositions.

We think the microbial alteration of the stream water samples during the storage period can be negligible.

(1) The sampler was set on the riverbank near a weir surrounded by ferns and other understory vegetation avoiding sunlight during the observation. In addition, the bottles are stored in a shaded space to minimize the microbial alteration of the samples. Besides, the automatic sampler (SIGMA 900, Hach, USA) has equipped with refrigerator to keep the samples in 4°C . (2) Kotlash and Chessman (1998) have assessed the storage effects of freezing, acidification, refrigeration and extended storage without refrigeration (6 days) on measured concentrations of nitrogen of different stream water samples, and found there was little difference in concentration of oxidized nitrogen ($\text{NO}_3^- + \text{NO}_2^-$) according to different treatment. (3) The concentrations of stream nitrate showed temporal variation in accordance with the variation in the stream flow rate during storm events (Figs. 3 and S1). As a result, the

variation of the stream nitrate concentrations was primarily controlled by the flow rate instead of the microbial process. (4) The $\Delta^{17}\text{O}$ of stream nitrate is stable during the progress of such microbial processes (e.g., denitrification or assimilation). While the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of stream nitrate can be altered by the progress of partial removal through microbial process, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of stream nitrate showed strong linear relationship between the reciprocal of concentrations, implying that the primary process controlling both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ was mixing. Thank you for your advising. We would like to emphasize this in the revised manuscript.

> Line 428, enhancement of D17O on 2019/1/31: I did a simple estimate by assuming that the snow nitrate has the same D17O value as the atmospheric at 26 per mil and took 2018/12/28 as an initial state before snow melting. From 2018/12/28 to 2019/1/31, the D17O value increases by 7 per mil, implying ~30% (=7 per mil/26 per mil) of stream nitrate is from snow melting. This increase however is not reflected in the water flow rate (from 110.0 to 117.3 L/min only). Please elaborate and provide a more quantitative explanation.

From 2018/12/28 to 2019/1/31, the $\Delta^{17}\text{O}$ value doesn't increase by 7 ‰, by +2.73 ‰ instead (Table S1). The flow rate, concentration of stream nitrate, and $\Delta^{17}\text{O}$ was 110.0 L/min, 70.0 μM , and +1.17 ‰ on 2018/12/28, respectively, and 117.3 L/min, 62.4 μM , and +2.73 ‰ on 2019/1/31, respectively. The $[\text{NO}_3^-]_{\text{atm}}$ in stream water was estimated to be 3.1 μM on 2018/12/28 and 6.5 μM on 2019/1/31. Assuming the $[\text{NO}_3^-]_{\text{atm}}$ in snow melt to be the same with that in rainwater (87.8 μM in the $[\text{NO}_3^-]_{\text{atm}}$ in rainwater at Sado island in January from 2009 to 2011; Tsunogai et al., 2016), we can estimate the amount of melting snow water into the stream water to be 4.8 L/min by using the mass balance law ($[\text{NO}_3^-]_{\text{atm}}]_{2019/1/31} * \text{flow}_{2019/1/31} = [\text{NO}_3^-]_{\text{atm}}]_{2018/12/28} * \text{flow}_{2018/12/28} + [\text{NO}_3^-]_{\text{atm}}]_{\text{snowmelt}} * \text{flow}_{\text{snowmelt}}$). As a result, the estimated amount of melting snow water into the stream water (4.8 L/min) less than the increase of flow rate (7.3 L/min; 117.3 L/min - 110.0 L/min), proved that the increased $\Delta^{17}\text{O}$ on 2019/1/31 can be caused by the snow melting. Thank you for your advising. We would like to emphasize this in the revised MS.

> To be more complete, for routine sampling analysis and discussion, please include precipitation and do the same analysis as the storm events.

Thank you for your advising. We would like to add the data and discuss the data as suggested.

> Fig 4: it seems there are two groups (one having smaller slope and one steeper) of D17O vs. $1/[\text{NO}_3^-]$ in the storm event II. Any reason for that?

The increase of $\Delta^{17}\text{O}$ (steeper groups) could be caused by the input of the small amount of the $\text{NO}_3^-_{\text{atm}}$ in rainwater during the storm event II. Anyway, in the storm event II, the $\Delta^{17}\text{O}$ of stream nitrate showed strong linear relationship ($R^2=0.81$; $P<0.0001$) between the reciprocal of concentrations as whole, further, the $\Delta^{17}\text{O}$ of the riparian soil nitrate were plotted on the extension line indicated the primarily source of stream nitrate increased during storm event II was also riparian soil nitrate instead of the $\text{NO}_3^-_{\text{atm}}$ in rainwater. Thank you for your advising.

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,
Weitian Ding

Reference

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