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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Tracing the fate of atmospheric nitrate deposited onto a forest ecosystem in eastern Asia using $Delta^{17}$O" *by* U. Tsunogai et al.

Anonymous Referee #1

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This is a long-awaited paper. I found the manuscript well presented and clear in its aims. It is a concrete application of the 17O anomaly of atmospheric to the field of N cycle of forest ecosystem. The conclusions are robust and should open a new area in this field. The authors' data are very convincing. They cleverly show how efficiency the 17O anomaly of atmospheric nitrate can be applied to the nitrogen cycle. Using this new tracer there are able to quantify the input and output of N in a small untouched and preserved Japanese island. I don't have major comments, just few little remarks that I will appreciate if the authors can answer and correct accordingly.

Definition of cap17: The authors are using the power law. If I agree that this is a more

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precise and correct quantification of 17O excess, the common rule with the nitrate anomaly has been to use the linear approximation. Here, with nitrate, we are not dealing with minute variations of cap17O and the power brings little improvement. I will suggest the author to present the power law but then use the linear formula to keep the entire dataset of the so far published results coherent between them. The linear form allow easier math too.

The input flux of N Authors quantified the input flux of nitrogen based on wet deposition. There are not taking into account the dry deposition of nitrate. Is there any reason to ignore such deposition? Could it change their mass balance?

Analysis Please give the amount of nitrate used for the analysis, 50 nmol or more? What the authors mean by “clean screw-cap vials”? Can they be more precise about what is behind “clean”? is there any special washing procedure?

Nowhere in the paper they mention the concentration of nitrite in their sample? Do theyv have reason to ignore this potential interference?

Middle of page 7 they’re mentioning the isotopic exchange between nitrate and water (ca 20%), correct as the isotopic exchange is between nitrite or some intermediates and water.

Calibration Why using only two standards to calibrate the procedure and not also some mixture of both international standards (See eg Morin et al., 2009)? This will give better and more robust calibration lines and could allow a direct quantification of the uncertainties using the sum of the residue between the mean regression lines and the actual measurements. Corollary, how they calculate their errors? Can they give more details here how the errors are calculated?

Atmospheric nitrate Can the authors remove, whenever they use it, the word “extraordinary”, having nitrate at 34.5 permil has nothing extraordinary, Savarino et al. (acp 2007) and the recent Frey et al (acpd) present values well above this hypothetic tropo-

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spheric upper limit.

The event 23-24 February I wonder if along the monitoring year, this event was the only polluted event experienced at the site. If not, why they did not find high cap17? The authors propose the NO3 + RH reaction to explain their high anomaly. Well first I want to bring to the attention of the authors that this reaction is a gas phase homogeneous reaction that has no connection with surface area of aerosols. OK to quote that high aerosol loading is a good tracer of a pollution event but please don't link the reactivity of nitrate radical with aerosol. Another possibility of increasing the cap17O is to invoke the halogen chemistry and specially BrO. Did the authors explore this possibility? There is more and more signs showing that bromine chemistry is also active in coastal mid latitude region (see eg Mahajan et al. 2009) which could also be invoked to explain the high cap17 of nitrate.

Proportion of atmospheric nitrate I think it is too early to claim that $\sim$ 7% represent the atmospheric nitrate in natural nitrate eluted from the forest ecosystem. There are simply not enough studies so far to claim that. Use a softer phrase.

Fig 5: Authors claim that NO3- atmospheric is almost uniform giving its small range. Well this is a direct consequence of the small fraction of atmospheric nitrate found in water. If this range seems to be small compared to the total nitrate, still its relative range varies almost identically as the total nitrate. Please, rephrase the according section in the text. Also looking at the fig 5, it appears to me that there is quite a good correlation between the two quantities, at least as well as fig 6 that they comment. Can the authors comment also this correlation?

Removal flux; The last paragraph of page 13 (talking about the increasing depositional flux in eastern Asia) is very confusing and I barely understand what the author want to say.

Table 1 Note #: I don't understand why cap17O has been calculated using delta15N and dalta18O, Cap17O is not directly quantified, even for this event? Please clarify.

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references that I cite Morin, S., J. Savarino, M. M. Frey, F. Domine, H. W. Jacobi, L. Kaleschke, and J. M. F. Martins (2009), Comprehensive isotopic composition of atmospheric nitrate in the Atlantic Ocean boundary layer from 65°S to 79°N, J. Geophys. Res., 114, D05303, doi:10.1029/2008JD010696.

Savarino, J., J. Kaiser, S. Morin, D. M. Sigman, and M. H. Thiemens (2007), Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, Atmospheric Chemistry and Physics, 7, 1925-1945.

M. M. Frey, J. Savarino, S. Morin, J. Erbland, and J. M. F. Martins Photolytic control of the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling Atmos. Chem. Phys. Discuss., 9, 12559-12596, 2009

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23073, 2009.