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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.

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Thank you very much for your comments on our manuscript. We have carefully studied your comments and revised the manuscript accordingly.

Responses to your comments are as follows:

1) Definition of Delta17O: While you requested to present our Delta17O data based on the linear approximation to keep the entire dataset of the so far published results coherent between them, we don't want to revise our definition based on the power law (eq.(1)) to keep our internal calculation coherence with the Delta17O data of N2O from which we calculated those of nitrate, otherwise we have to use different formula

between natural N2O and nitrate derived N2O. As there have not been any international recommendations on this quantity, we would like to present the data based on the power law. Instead of changing the definition, however, we would like to add sentences to notify the difference in the definition in section 2.3 in the revised MS. Besides, we would like to present the approximate extent of differences in Delta17O when we change to the linear approximation. Furthermore, we would like to add one reference for the calculation.

Michalski, G., Savarino, J., Bohlke, J. K., and Thiemens, M.: Determination of the total oxygen isotopic composition of nitrate and the calibration of a Delta17O nitrate reference material, Anal. Chem., 74, 4989-4993, 2002.

2) The input flux of N: While you surmised that we had ignored the contribution of dry deposition in the flux calculation in section 3.4, we included the dry deposition in our calculation, by adopting the data of total deposition rate for the flux calculation. We just used the isotopic compositions of wet deposition representing those of total deposition, because (1) the dry deposition in Rishiri occupied only 16 % of the total deposition in 2006 (Ministry of the Environment, 2009), and (2) the differences between dry and wet deposition were small for Delta17O of nitrate (unpublished). The approximation could have little impact on the mass balance calculation. To avoid similar misleading, we added a sentence to clarify the ratio of dry deposition within total deposition in the Rishiri observatory at the end of section 2.2. Besides, we would like to add one reference for the data source.

Ministry of the Environment: Report on Long-term Acid Deposition Monitoring (FY2003-2007), Ministry of the Environment, 2009 (in Japanese).

3) Analysis: We would like to clarify the nitrate quantities used for our analyses (from 4 to 10 nmol for d15N/d18O and from 20 to 100 nmol for Delta17O) in section 2.3 in the revised MS, as requested.

The word "clean" means that the vial had been washed by acid to remove residual Cd.

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We would like to clarify this in section 2.3 in the revised MS.

We would like to comment on both the concentrations of nitrite in our samples and the possible extent of the interference in section 2.3 in the revised MS, as requested.

We would like to correct for the molecule that is responsible for exchanging reaction of the oxygen isotopes, from nitrate to "some reaction intermediates" in section 2.3 in the revised MS, as suggested.

4) Calibration: The standards (USGS-34 and -35) are the "primary" standards in our laboratory, as noted in the original MS. The "primary" means that they are the standards to define the values of nitrate in our lab so that we only notified the two as our standards. Because the standards are limited and not so easy to obtain in Japan, we used the other internal secondary standards (including their mixtures) for our routine calibration, to which we used the mixture of the international standards to calibrate as in Morin et al. (2009) or Kaiser et al. (2007). Except for using the secondary internal standards instead of the primary international standards, our calibration processes were much the same with the past methods so that we did not explain the detail.

All the errors were estimated from the reproducibility analyzing same solution having similar matrix compositions and similar nitrate concentrations with the samples analyzed. While the chemical conversion process from nitrate to N2O was responsible for the errors of d15N and d18O, the thermal decomposition process from N2O to O2 was responsible for the errors of Delta17O. We would like to clarify this in section 2.3 in the revised MS, as requested.

5) Atmospheric nitrate: The word "extraordinary" means the value (+34.5 permille) exceeded the 2 sigma variation range of the atmospheric nitrate observed in this study. We would like to clarify this in the revised MS.

6) The event on 23-24 February: The daily averaged concentrations in February 23 were the second largest concentration for NO2 and the third largest concentration for

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SO2 and PM10 among all the daily averaged concentrations within the days from April 2006 to March 2007. Besides, among all the episodic contribution events of similar highly polluted air-mass, the event was the only one accompanying precipitation on Rishiri. We would like to clarify this in section 3.1 in the revised MS.

Concerning to the reaction to produce nitrate with high Delta17O, our interpretation in the original MS (section 3.1) included some misleading sentences, as pointed out by you. We would like to correct for them in the revised MS. We also approve of the significance of bromine chemistry even in mid latitude region. However, it is unrealistic to assume for the nitrate production process in such highly polluted air mass derived from megacities around 40 degreeN.

7) Proportion of atmospheric nitrate: We certainly approve that much more studies are needed to determine the mixing ratio of atmospheric nitrate in natural nitrate eluted from forest ecosystem in general. We would like to use softer phrases in section 3.2 in the revised MS, as suggested.

8) Fig 5: While you requested to rephrase the text related to this figure, we could not find anything wrong or misleading in the original MS. To attain observed small and uniform mixing ratio of NO3-(atm) within the groundwater samples, NO3-(atm) concentrations must be uniformly small in groundwater in Rishiri since being recharged.

The weak correlation in the figure might be produced through mixing of two slightly different hydrological components in the island. To prove this, however, detailed discussions must be needed for the hydrology of the island adding much more data and much more references. The slight hydrological difference could not be a major factor to determine NO3-(atm) and total NO3- in groundwater. Besides, hydrology of the island could not be the major interests for the readers of ACP. Thus, we did not discuss the detail in the text.

9) Removal flux: We would like to revise the 3rd paragraph in section 3.4 (concerning to the increasing depositional flux in eastern Asia) in the revised MS, as suggested.

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10) Table 1 Note #c: We would like to remove the note.

We trust that the revision is satisfactory response to your comments. Please find the revised pdf files of our manuscript attached. Thank you for your consideration.

Sincerely, Urumu

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/9/C10319/2010/acpd-9-C10319-2010-supplement.pdf

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