

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

**Anonymous Referee #2**

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Tsunogai et al present measurements of nitrate D17O from precipitation and ground water in an island in Japan in order to trace the fate of atmospherically-deposited nitrate within the ecosystem. This is a very nice study. I have several comments below that the authors should address before publication in ACP.

In the abstract and throughout the text, the authors say that the measured value of 34.5‰ for precipitation nitrate is “extraordinarily large”. I don’t think that this is unusually large. There are examples in the literature of similar or larger values measured in aerosol and ice core samples (values up to 41‰ [McCabe et al., 2007; Morin et al., 2009; Savarino et al., 2007], and are similar to values predicted by a global atmo-

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spheric model of nitrate D17O in the winter at this location [Alexander et al., 2009]. The authors should not use this language to describe this one value, but just state the range of observations.

I also think that the authors’ conclusion that these “large” nitrate D17O values are due to the reaction of the nitrate radical with hydrocarbons is highly speculative. Values of up to 40‰ can be explained solely from nitrate formation via  $\text{N}_2\text{O}_5$  hydrolysis, assuming  $\text{D}^{17}\text{O}(\text{O}_3) = 35\text{\textperthousand}$  and using the [Savarino et al., 2007] transfer function (an assumption in a global model that produced the best agreement with worldwide observations [Alexander et al., 2009]). Also, nitrate formation via  $\text{N}_2\text{O}_5$  hydrolysis is thought to be much more important (especially in the northern hemisphere) than the reaction of  $\text{NO}_3$  with HC. Most of the atmospheric nitrate formed through H-abstraction reactions with  $\text{NO}_3$  is thought to occur with DMS over the oceans. Indeed, [Alexander et al., 2009] calculate D17O nitrate values of similar magnitude to the observations presented here with the  $\text{NO}_3 + \text{HC}$  reaction contributing minimally to total nitrate formation.

I agree with the previous reviewer that the linear equation for calculating nitrate D17O should be used for Equation 1.

Since you report d15N values from measurements of  $\text{N}_2\text{O}$ , are you using your d17O measurements to correct for  $14\text{N}^{17}\text{O}$ ?

On page 23084 lines 24-27, wouldn’t enhanced aerosol surface area point to increased  $\text{N}_2\text{O}_5$  hydrolysis more than the  $\text{NO}_3 + \text{HC}$  reaction? The rate of  $\text{N}_2\text{O}_5$  hydrolysis depends strongly on aerosol surface area. Again, I am totally unconvinced that nitrate formation via  $\text{NO}_3 + \text{HC}$  is significant compared to  $\text{N}_2\text{O}_5$  hydrolysis.

Page 23087 lines 2-3: I don’t understand what the last sentence of this paragraph means.

Page 23087 line 19: “...we can evaluate the extent...” The “extent” of what?

I agree with the first reviewer that the authors should give a range of the amount of

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atmospheric nitrate to total nitrate (instead of just 7%) that reflects the uncertainty in their calculations.

References: Alexander, B., M. G. Hastings, D. J. Allman, J. Dachs, J. A. Thornton, and S. A. Kunasek (2009), Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition (D17O) of atmospheric nitrate, *Atmos. Chem. Phys.*, 9, 5043-5056. McCabe, J. R., M. H. Thiemens, and J. Savarino (2007), A record of ozone variability in South Pole Antarctic snow: Role of nitrate oxygen isotopes, *J. Geophys. Res.*, 112, D12303. 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 65S to 79N, *J. Geophys. Res.*, 114, D05303. 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, *Atmos. Chem. Phys.*, 7, 1925-1945.

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