Interactive comment on “Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica” by J. Savarino et al.

J. Savarino et al.

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We are delighted that referee# 2 found our dataset valuable. And after reading our manuscript again, we also felt that the structure of the MS was confusing and not well organized. In the hope to better express our ideas we have reorganized the MS following his/her suggestions. Unnecessary or redundant text has been removed. All technical parts are located in one section and discussion has been reorganized. We hope that referee# 2 will now found the MS more convincing and more pleasant to read.

Specific comments:

1. We have now used the column height of the atmosphere and the mass of the troposphere so budgets are calculated taking into account the pressure dependency. Regarding the mass balance calculation, we don’t understand the referee’s point. Let’s
take the simplest box model and ignoring in situ production and destruction.

\[
\frac{dC}{dt} = Fin - Fout \quad F: \text{flux and } Fout = C/\tau; \text{ with } \tau; \text{ the mean residence time}
\]
at steady state \( \frac{dc}{dt} = 0 \)

thus \( C = Fin \cdot \tau \); which is what we did, with the exception of the pressure correction, which has been applied now.

2. We hope that the new organization of the paper solves this confusion. What we originally wanted to say was that just based on PSC flux, the Nov-Dec concentration peak could be explained. However looking at the isotopic signatures, PSC appears to be incompatible with this nitrate peak.

3. Heaton et al. did not perform the integration calculation. Their reasoning is based only on the starting isotopic composition of N2O entering the stratosphere (our \((N2O)_0\)). We think that our calculation is more rigorous as it integrates the full denitrification column and therefore deserves to be here. Moreover, the same relation is used for snow emission. When it is possible to describe a physical process in a mathematically accurate fashion, we think that one should take advantage of this and use it to get the best possible estimate. The last sentence pointed out by the referee has been removed in the reorganized MS. No conclusions are now drawn before reviewing all characteristic sources. Conclusions for seasons are discussed in a specific section.

4. As suggested by other referees based on uncertainty, we have modified our discussion about the failure of the present O3 isotopic data to explain the highest nitrate oxygen anomaly. In addition, reasons why stratospheric nitrate should possess a higher isotopic anomaly are given.

5. Reorganization solves this confusion.

6. We don’t feel that we are in contradiction with Blunier’s conclusion. We are just saying that as snow loses its nitrate with depth and gets enriched in 15N, the emitted nitrogen species in the atmosphere will be depleted in 15N, independently of nature of
7. In his original paper Wolff et al, paragraph 4, bottom line wrote “The calculated photolysis rates would deplete the initially deposited nitrate content of snowpack in a very low snow accumulation rate region such as Dome C (27 kg m\(^{-2}\) yr\(^{-1}\)) by a maximum of about 40%.” Since almost 90% of the original nitrate contained in snow is lost and if 40% is due to photolysis according to Wolff et al., then we can reasonably deduce that the remaining 50% are due to other processes. Therefore saying that photolysis and evaporation “are quantitatively equivalent” is not contrary to Wolff et al. conclusions. If NOx is 40% and HONO is negligible, then only HNO\(_3\) evaporation remains. It is not an assumption it is a logical deduction which has more weight than an assumption.

8. We took in consideration this remark and took the average value of the photolytic zone (20cm) changing the value from 27.5 to 28 permill. It should be kept in mind that due to the low accumulation rate, the average of the photolytic zone is often the average of the annual mean.

9. Because the emitted NOy at South Pole is a mixture of deposited stratospheric nitrate with a high anomaly and reemitted NOx from snow that will attain a tropospheric isotopic signature during oxidation and transport. It is logical to find a higher summer anomaly than the one observed at lower latitudes. This is the reason why 28 permill is the mean summer value.

10. The reorganization of the paper should have solved that. a/ now the full range is given not only the XONO\(_2\) predicted oxygen anomaly b/ Added c/ The uncertainty is calculated according to the uncertainty propagation of this f coefficient which was varied between 10 and 50% (90% to 50% nitrate lost by the snow). Such range covers the field observations.

11. The text has been changed to include also long range transport from lower latitudes via PAN or alkyl nitrate.
12. As requested by the other referees, actually uncertainties are too high to clearly conclude that the mismatch is due only to the lack of stratospheric ozone isotopic composition in the vortex. In the rewording we have broadened the weakness points. If we trust the ozone data published so far, there is a significant statistical difference between tropospheric ozone and stratospheric even if their higher and lower limit respectively overlap.

13. Done

14. Done based on the manufacturer’s manual.

15. Section moved. As we stated, nobody actually really knows what a glass filter in this environment collects. Based on filter media evaluation, it seems to appear that glass filters collect only the particle phase as opposite to paper filters (Schaap, M., K. Muller, and H.M. ten Brink, Constructing the European aerosol nitrate concentration field from quality analysed data, Atmos. Env., 36 (8), 1323-1335, 2002). Regarding the effect of high ammonia content, we trust Legrand et al’s publications in which they have always interpreted their small filter nitrate collection as particulate nitrate and not as total nitrate.

16. Done

17. Now concentrations are P and T corrected, volume pumped was brought to STP.

Technical corrections

1. Corrected according the referee

2. Done

3. Clarified by referencing the section where this number was obtained

4. Kept the figure caption. We think it helps to understand the figure.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 8817, 2006.