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Atmospheric
Chemistry
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Discussions

Interactive comment on “Pronounced signature of arctic surface ozone depletion events after polar sunrise on Δ^{17}O in atmospheric nitrate” *by* S. Morin et al.

S. Morin et al.

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This author comment only refers to specific comments raised by the Referee 2. Main issues raised by both referees are addressed in a separate, extensive, author comment.

1. Title of the paper. We agree with Referee 2 that “after polar sunrise” is unnecessary. Also, we capitalised “arctic” into “Arctic” everywhere in the paper as suggested by the Referee 2. However, even if this represents four standard deviations around the mean, we estimate that the variation in Δ17O(NO3-) values are significant and pronounced. Δ17O(NO3-) usually does not vary so much within short periods of time, and variations of up to 6 ^{o}/oo within the same week are strongly significant in an atmospheric context.

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As a consequence, we propose the following title for the revised manuscript : “Pronounced signature of Arctic surface ozone depletion in the isotope anomaly (Δ17O) of atmospheric nitrate”

2. We respectfully disagree with the Δ17O data reported by Referee 2 (which were also reported by Brenninkmeijer et al., 2003), supposed to be representative of the datasets reported by Krankowsky et al. (1995) and Johnston and Thiemens (1997). Indeed, it seems to us that the Referee 2 calculated Δ17O using averaged δ18O and δ17O values, which gives a surprisingly low standard deviation (for instance 1.7 ^{o}/oo for K95 instead of 12^{o}/oo with our explicit method, see above). The average values are similar, due to the linearity with δ18O and δ17O of the Δ17O definition that we adopted. However, these calculations give the false impression that the standard deviation of these values is low, which is not true, by far (see above). Δ17O(O3) measurements are indeed strongly variable, and this information is lost when summing up measurements taken in different locations (for instance, in JT97 the Pasadena and White Sand data set tend to cancel out to 25 ^{o}/oo average, even if their respective averages are 10 ^{o}/oo apart (ca. 20 ^{o}/oo and 30 ^{o}/oo , respectively)).

3. The collection efficiencies of our sampling device has been evaluated to be over 95 % (Sirois and Barrie, 1999). It is true that some particulate nitrate might not be captured by this sampling device, and thus if nitrate from this size fraction has a different isotopic composition, then our results are biased towards a particular size fraction for nitrate. It is therefore not absolutely true that the value of the collection efficiency has no effect on the measurement of Δ17O(NO3-). A more specific way to answer in detail to the point raised by the Referee 2 is to use a cascade impactor, that would allow for a discrimination of Δ17O(NO3-) with respect to several particles size fractions. In the revised version of our manuscript, we do not explicitly state that the collection efficiency has no effect on the isotopic composition of nitrate. We just interpret the evolution in the isotopic composition of TIN sampled by the high volume sampler which is in operation at Alert for over twenty years.

4. See point 16. of Referee 1

5. Estimation of uncertainty : the authors certainly agree with Referee 2 that a good estimation of the measurements uncertainty is crucial for a reasonable interpretation of the obtained data. The point raised by Referee 2 is that, if the blank correction applied to each of the samples is kept constant (i.e. constant contribution of 0.14 umol of O2), then this should only introduce an offset in the data, but no increase in the uncertainty. We first acknowledge that, using the linear definition for Δ17O(NO3-), the isotope anomalies of the standards are different from what was stated in our manuscript (Δ17O(USGS34) = -0.1 ^{o}/oo and Δ17O(USGS35) = 21.6 ^{o}/oo , and Δ17O(O2) = -0.3 ^{o}/oo). This was changed, and the updated blank contribution was estimated to be about 0.16 umol of O2. This quantity is derived from measurements of Δ17O(USGS 35 - NO3-) for different sample sizes. The curvature in the plot of Δ17O(NO3-) as a function of the sample size is related to the magnitude of the blank term (Michalski et al. 2002). During our analysis, we determined that this blank represents (0.16 +/- 0.05) umol O2. When derivating the mass-balance derived by Michalski et al. (2002) to compute the uncertainty term, one finds indeed that this 0.05 umol uncertainty causes the 1^{o}/oo uncertainty that we state in the manuscript. All samples were indeed between 1 and 2 umol, in terms of molecular O2. This has been clarified in the revised version of the manuscript.

6. In our manuscript, we do not state that “sources of uncertainty are inversely related to the size” of the sample, contrary to what is stated by the Referee 2 in his comment. We simply wrote that “the sources of uncertainty are correlated to the size of the O2 samples”. Regarding the mass-spectrometric uncertainty, this does not specify any particular shape for this correlation function. This sentence was changed into “the sources of uncertainty vary with the size of the samples”.

7. and 8. See Referee 1 point 3.

9. The method to calculate the mean of N back-trajectories is the following: each mean

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position is calculated as the mean of the N positions, i.e mean of N longitude and latitude. The only possible ambiguity with this definition is the extreme case described by the reviewer, when positions are just opposite in longitude. But our back-trajectories never diverge in such a way.

10. We agree with the Referee 2, that the rate of transfer of Δ17O from ozone to NO2 is not the most crucial parameter, given the large uncertainty carried by almost each term in the equations. However, we wish to make it clear that this rate is currently surestimated, partly because existing mechanistical evidence is not taken into account in several articles (e.g. Lyons (2001), Zahn et al. (2006)). Indeed, Δ17O(NO2) in both articles mimics the calculated isotopic composition of terminal atoms in ozone (see e.g. Figure 1 a) in Zahn et al. (2006), in the case of the lower stratopshere), as if NO2 was influenced by terminal O-atoms from ozone only. The crossed molecular beam experiments by van den Ende et al. (1982) show that the reaction probability of NO with a central atom of ozone is far from zero.

As a consequence, we chose to use the parameterization by M03 to account for this transfer, since to date it is not clear what the rate of transfer exactly is. In this parameterization, ozone transfers its bulk isotopic signature, regardless of the position of the atoms involved in this transfer.

11. We agree with the Referee 2 that the terminal atom isotopic composition calculated by Lyons (2001) is an upper limit. At the time when our manuscript was written and submitted, the recent article by Zahn et al. (2006) was just being published. We are pleased to reference this work, which, together with Janssen (2005) and the recent thesis by Tuzson (2006), form a more consistent analysis of the intramolecular distribution of the three O isotopes in ozone.

12. As stated above, the temperature dependency of the Δ17O(O3) alone does not explain the variations in the measured Δ17O(NO3-), since the temperature dependency of Δ17O(O3) is a second order effect with respect to the large uncertainty which affect

these measurements. However, we performed a sensitivity calculation which was not initially in our manuscript, to check the influence of several values of Δ17O(O3) in our results (see revised manuscript for more details).

13.,14., 15. and 16. These remarks are linked to the Monte Carlo approach we initially developped. As discussed above, these calculations have been dropped.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 6255, 2006.