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Atmospheric Chemistry and Physics Discussions

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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General comments As stated in the replies to referees 1 and 2, we have reorganized the structure of the manuscript and used this opportunity to address referee # 3's comments about the general tone of our manuscript. We hope that the referee will find now our text more sober and less "showy".

Specific comments -Abstract We have followed the referee's advise and removed the sentence on the size-segregated samples

Regarding the "failure" of the currently available isotopic composition of stratospheric ozone to explain the Antarctic nitrate oxygen isotopic anomaly, we agree with the referee that this is not the main conclusion of our work. Consequently, in the abstract we removed the incriminated sentence. We changed our body text in away that this

specific point becomes just one source of uncertainty among others. This point was also raised by referee 1 and after reviewing our MS we also think that many uncertainties remain that should be addressed first. Taking all uncertainties into account, our observations could in fact be explained by the available isotopic measurements for stratospheric O3.

-Sampling issues The blank issue is now resolved by clearly stating that only one blank was collected at the beginning of the sampling

In their study Wagenbach et al. carefully evaluated the potential contamination by the station activity and the penguin population. Their work seems to be very convincing and we found no reason to believe that they erred in their analysis of the contamination issue. This is now clearly stated in the text. Bird faeces (as it should be said!) and feathers were disregarded not because of possible risk of nitrate contamination but because we did not want to clog the centricon filter unit and introduce unnecessary organic matter. This is also clearly stated in the text now. A small portion of bird faeces were also found on the second stage of the impactor unit, we never observed outlier data or systematic offset for these samples. And last but not least, neither concentration nor isotopic profile seem to indicate a contamination issue. The consistency of a dataset is often a good criterion to identify contamination issues. With the goal to clarify our manuscript and following referee 2 advices, we have merged all technical parts under just one section.

-Equation 2 This point has already been discussed in our reply to the other referee comments. We agreed to switch for the linear approximation and a slope of 0.52 to be consistent and thus easy to compare with previous publications on the same topic. 0.52 is chosen because it reflects a mean value as no specific value can be assigned for atmospheric nitrate. This issue is now clearly explained in the text body

-Estimation of 15N stratospheric nitrate Clarification has been made following referee advice.

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-Laboratory experiment It is a very difficult issue. When you have unpublished data that influence your current work, what should a scientist do? In our case, our scientific ethic forces us to take into account such a result. This experiment was done in an atmospheric chamber. All traceable species by FTIR were followed. We did not detect any interference and the experiment was done in the dark just by mixing NO + O3 with known starting isotopic composition of reactants and collecting produced NO2. Slightly excess NO conditions were used so all O3 react only with NO. No NO3, N2O5 N2O4 etc were observed at dl. In one experiment O3 was introduced with a slight excess, NO3 and N2O5 were readily detected. If the referee asks for, we can provide the experimental results. The manuscript is in preparation but as a matter of objectivity we want first to reproduce the experiment. Unfortunately, the chamber schedule is very busy and time slots are difficult to find. Regarding the stratospheric ozone issue, we have addressed this issue as stated before.

-Denitrification and dehydration We have clarified this point. PSC I and II are thermodynamically stable only in the stratosphere. When PSCs I (HNO3.3H2O or 2H2O) penetrate the troposphere, pHNO3 in this region is too low to maintain the equilibrium with the ice phase and HNO3 should diffuse out, but the real limiting factor is that the lifetime of any ice particle in the atmosphere barely exceeds a couple of day. The water cycle in the atmosphere is very dynamic and the lifetime of a droplet/ice crystal is roughly the lifetime of any atmospheric cloud, pretty short and definitely shorter than transfer to the ground level. We are not aware of any cloud that can survive for days. So, yes, PSCs evaporate in the troposphere especially considering the warm troposphere (220 K) compared to the cold stratosphere (190 K).

-estimation vs evaluation Changed.

-Terminology and simultaneity of THO and nitrate The terminology has been adjusted to be less categorical. Also we hope to have clarified the THO and nitrate simultaneity. Wagenbach et al. already recognized the difficulty to claim nitrate PSCs as the cause of the Nov-Dec nitrate peak when THO peaks two months earlier. We are suggesting

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that PSC nitrate is responsible for the Sep-Oct peak based on isotopic composition which alternatively solves the inconsistency picked out by Wagenbach et al.

-terminology for periods We opted for the solution 2 advocated by the referee. We used the month or range of months.

-Figure 1 We have added the tritium profile to figure 1 as suggested

-Figure 5 We decided to remove this figure as actually we agree with the referee it doesn't bring any thing new. Instead we used the Konig-Langlo et al., 1998 which is a really excellent work of DDU meteorology

-Technical corrections. All proposed corrections have been included.

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