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Atmospheric
Chemistry
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Discussions

Interactive comment on “Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition (Δ^{17}O) of atmospheric nitrate” *by* B. Alexander et al.

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1 General comments

Alexander et al. (2009a) have carried out the first global-scale simulation of the isotope anomaly (Δ^{17}O) of atmospheric nitrate. Following-up several box-model assessments of the causes of the variations of Δ^{17}O in atmospheric nitrate (e.g. Michalski et al., 2003; Morin et al., 2008), this work at the global scale represents a landmark in this rapidly growing scientific field, and is most likely to set the stage for subsequent studies on this topic. Δ^{17}O of atmospheric nitrate is believed to be a powerful tracer of

NO_x oxidation pathways, with potential for use as a diagnostic variable in atmospheric chemistry models. The authors have to be commended for such an effort, which ultimately will definitely deserve publication in *Atmos. Chem. Phys.*. **Prior to this, several hypotheses of the present work deserve a firmer assessment and discussion**. **Scientific issues highlighted below aim at making this paper less prone to future reconsideration, given the fast rate of scientific advances in this field**.

I’m afraid the review is quite long and detailed, which I hope the authors will understand as a proof of interest for their work, if needed.

2 Specific comments

2.1 Structure and content

The paper follows a classical structure. My only problem with the content is in the "Observations" section, where I think analytical details are not useful for the scope of this study.

Perhaps sections 1 (introduction) and 2 could be merged, and the discussion on the Δ^{17}O of tropospheric ozone found there moved further down the paper in the results/discussion section, where the same discussion is almost carried out again in the present state (in section 5.1). Along the same line, the second paragraph of page 11190 (description of NOx and nitrate chemistry) is introductory in nature (together with Figure 1), and should be moved to the introduction.

The model description is long as it ought to be, as this is the very first time such a model is described in detail for Δ^{17}O of atmospheric nitrate (see below for specific comments on the model description).

The observation section summarizes presently available measurements of Δ^{17}O of atmospheric nitrate, with which model results can be compared. A table summarizing the measurements used for the study would be highly desirable, showing in particular the range in annual cycle of Δ^{17}O, the nature of the nitrate samples (fog water, aerosol etc.) and the analytical method employed, with a link to the primary publication describing them.

While most of the measurements presented in this article derive from peer-reviewed articles, two new data sets are introduced, namely Δ^{17}O data from a cruise in the Atlantic Ocean (the "COCA" cruise, whatever this stands for) and from the tropical forest in Ecuador (Brothers et al., unpublished). While it is clear that measurements at mid-latitude are scarce, which poses a problem for model evaluation (see below), I don't think that it makes any good to this manuscript to introduce in detail the analytical approach used for measuring a few samples (the "COCA" dataset), that are included in the comparison analysis with model results, but not discussed specifically. For instance, analytical details for this given dataset would require a more detailed description than given here: for instance, it is not clear what is the effect of the addition of H_2O_2 to the sample, both chemically and isotopically. **What I recommend is leaving the results of this analysis as "unpublished"** (or possibly "in preparation", if the authors plan on using these data for a more specific assessment warranting future publication of these data), just like the authors have done for the Brothers et al. data. **The intrusion of analytical details into a paper focussed on modeling makes it hard to follow and diverts the reader's attention from the main purpose of the article**.

2.2 Model description

This section is well written and clear for most of it. As suggested above, the paragraph describing Figure 1 should be moved into the introduction, as it contains no information relevant to the model, but rather general information on lifetime of species and

atmospheric chemical reactions.

I have a major problem with the way $\Delta^{17}O(NO_2)$ is calculated (see in Scientific issues, below).

Equations (3a) to (3d) should be made more compact. It will then become obvious that these are the same exact equations already described in Michalski et al. (2003), Kunasek et al. (2008) and Morin et al. (2007,2008,2009).

The formulation of equations (4a) to (4c) is a little unclear, as it doesn't explicitly says that this only applies to nitrate formed locally, which has then to be added to nitrate already present in each grid cell, and nitrate resulting from transport, minus the fraction of nitrate that is deposited or lost to the other grid cells. As written, it gives the false impression that Δ^{17}O of nitrate is fixed at each time step in each grid cell using this set of equations, which clearly is not the case because it is said that the model includes transport and deposition. **I suggest rephrasing this part by introducing a differential equation of $\Delta^{17}O(NO_3^-)\times[NO_3^-]$**, like in Morin et al. (2008, supplementary material) modified to include transport into and from adjacent grid cells. This would clarify thinks a lot. Similar ways of presenting isotopic mass-balance within each grid cell can be found in Hoag et al. (2005), which the authors can use as a source of inspiration for rephrasing this part of the Model section.

One missing information appears to be the time step of the resolution of the photochemical equations.

2.3 Scientific issues

2.3.1 Bias due to available data

Alexander et al. (2009a) sort of "assimilate" atmospheric measurements of Δ^{17}O into their tropospheric model, to obtain estimates of the isotopic variables that have so far not been reliably measured in the troposphere. This includes mostly Δ^{17}O(O_3) and the rate of transfer of Δ^{17}O into NO_x and nitrate. The goal is thus to optimize these isotopic variables so that the model output fits observed data and can be used to discuss global maps of Δ^{17}O at different seasons. Until actual measurements of Δ^{17}O(O_3) and more isotopic transfer rates (Savarino et al., 2008) are available, this approach is OK.

The major issue of this work is due to the discrepancy between the locations where Δ^{17}O measurements were carried out, and the ability of the model to represent atmospheric processes accurately in these locations: as far as I understand, GEOS-CHEM was built to study atmospheric chemistry at the global scale with a focus on mid-latitude Northern Hemisphere. It's virtually impossible to count how many successful uses of the model have been reported in the peer-reviewed literature over such areas (including tropics and mid-latitudes in the Southern Hemisphere), but it was likewise nearly impossible for me to find an assessment of the performance of the model to simulate NO_x-NO_y chemistry in polar regions. Very unfortunately, polar regions appear to be the place where most measurements of Δ^{17}O have been performed so far, due to the specific relevance of studying Δ^{17}O close to ice coring sites (McCabe et al., 2007; Savarino et al., 2007; Kunasek et al., 2008; Frey et al. 2009) or within a scope on reactive halogen chemistry, which is most pronounced in the polar marine boundary layer (Morin et al., 2007, 2008, 2009). Key processes occurring in polar areas and impacting the measurements, such as Antarctic stratospheric denitrification (as seen in Savarino et al. (2007) at the coast and in the interior by McCabe et al. (2007) and Frey et al. (2009), are not described by GEOS-CHEM. The same applies for halogen chemistry in the Arctic, although Morin et al. (2008) have found its effect on Δ^{17}O to be confined to the spring period. **Given the strongly higher Δ^{17}O assumed to characterize stratospheric nitrate (Savarino et al., 2007; Alexander et al., 200a), ignoring this contribution in GEOS-CHEM makes questionable the predictions of the model in early austral spring in Antarctica.**

In contrast, there are only few measurements in mid-latitudes. Besides the "historical" study on atmospheric nitrate by Michalski et al. (2003), the authors used measurements ranging from rain water from Princeton (Kaiser et al., 2007) and Bermuda (Hastings et al., 2003) (although the latter are in no way direct Δ^{17}O measurements but rather an estimate with no seasonal variations, as indicated in the original publication) to fog water from Ecuador and passive atmospheric nitrate samples from Atacama (also no seasonal variations given). More germane to the focus of this study, Alexander et al. (2009a) could also have included the data from Patris et al. (2007), and the recent work by our group (Morin et al., 2009) which provides latitudinal variations of Δ^{17}O across the Atlantic Ocean, which would be useful to compare with the output of the model for a given month (April-May).

From this point on, two approaches are possible: either assuming the model is "chemically" correct everywhere and all the time, and the isotopic parameterization has to be adjusted to fit the model output with the measured data, or the other way around. In their work, Alexander et al. (2009a) definitely chose the first approach, which I disagree with. **Because GEOS-CHEM does not reproduce phenomena occurring in the Antarctic stratosphere (particularly in springtime), field data from Antarctica during spring should have been excluded from the comparison exercise**. This includes the data from Savarino et al. (2007), Frey et al. (2009) and McCabe et al. (2007). All of them report Δ^{17}O data in the high range of tropospheric measurements (above 40 ‰). In the present work, Alexander et al. (2009a) have included such high data in their analysis, have chosen the set of isotopic variables able to match them, and then a little "naively" state that "[their] results suggest that Δ^{17}O(nitrate) values on the order of 40 ‰ can be explained by a dominant source of tropospheric nitrate" in Antarctica (page 11199, line 11). This is no surprise, has they have chosen a set of isotopic variables able to match such high Δ^{17}O values, even in the troposphere. Note that, having chosen this set of variables makes their model over-estimate Δ^{17}O of atmospheric nitrate in mid-latitudes by as much as 5 to 7 ‰ in Princeton !

This bias in the data used for discussing the isotopic variables used in the model is strong, and should be discussed in a more objective manner in the revised manuscript. **The main discrepancy stems from using Antarctic data, which in the present state of the model (lack of denitrification in the stratosphere) CANNOT be directly compared with the model output**. This is thus no surprise that if the model reproduces Δ^{17}O of nitrate in Antarctica (for the wrong reason, and with the wrong timing as evidenced from the DDU model/data comparison), it does not match data produced at mid-latitudes (La Jolla, Princeton), where the model is supposed to be able to reproduce tropospheric processes more accurately.

I see at least two ways how the calculation could be improved:

2.3.2 Δ^{17}O(O_3) and transfer

Over the last few years, considerable progress has been made in our understanding of the transfer of Δ^{17}O from ozone to NO_x, then to nitrate. In their early work, Michalski et al. (2003) used the simple assumption that Δ^{17}O of ozone is constant (with a value of 35 ‰) and transferred as is to NO_x through the NO + O_3 reaction. Recent work by Savarino et al. (2008) have shown that the transfer of isotope anomaly does operate mostly from the terminal atom of ozone. The same authors, based on a discussion of available data for Δ^{17}O in the troposphere, showed that the average value for Δ^{17}O(O_3) measured in on the order of 25 ‰.

I agree there is considerable debate around the absolute value for Δ^{17}O of ozone in the troposphere. The two most "popular" values in the literature are 25 ‰ and 35 ‰. Based on work by Savarino et al. (2000) and modelling with GEOS-CHEM (e.g. Alexander et al., 2009b), it is accepted that the value of 35 ‰ makes it easier to reconcile measured and predicted Δ^{17}O of tropospheric sulfate. A lower value for Δ^{17}O(O_3) (25 ‰) is apparently not consistent with our understanding of Δ^{17}O of sulfate, although **this should be investigated quantitatively in the near future**.

This leaves two different scenarios, i.e. either Δ^{17}O(O_3) = 25 or 35 ‰. Alexander et al. (2009a) have mentioned the recent actual measurement of the isotopic transfer rate of Δ^{17}O from ozone to NO_2, during the NO+O_3 reaction (Savarino et al., 2008). I want to point out here, that using this transfer rate for the NO+O_3 reaction implies using the same transfer rate for NO_2+O_3 as well. **It is not consistent to use this transfer reaction rate for NO+O_3 (which implies that ozone is isotopically not symmetric and not stochastic and that the transferred O atom to NO_2 preferentially stems from the terminal position of ozone), and not for NO_2+O_3, which is done in the present manuscript in the results in Figures 2b and 2c**. Indeed, these two reactions share very similar characteristics, as shown by Peiro-Garcia et Nebot-Gil (2002,2003) for the NO+O_3 and NO_2+O_3 reactions, respectively. I thus strongly advise the authors to replot Figure 2 with a different selection of variables. Figure 2a can remain as it (as it would directly compare with the study of Michalski et al., 2003). Figure 2b,c,d could be the results of the runs with Δ^{17}O(O_3) = 25 and 35 ‰, with and without the Savarino et al. (2008) transfer rate applied to both the NO+O_3 and NO_2 + O_3 reactions. This will be much more useful and consistent than at present.

2.3.3 Δ^{17}O(NO_2) calculation

I have a major problem with the way Δ^{17}O(NO_2) is calculated in the model. During the day (i.e., as long as the photolysis of NO_2 makes the lifetime of this compound shorter than a few minutes), I agree that Δ^{17}O(NO_2) is given by Δ^{17}O(NO_2)= $\alpha\times$ Δ^{17}O($O_3^\star$), where α is given by equation (2b), and Δ^{17}O($O_3^\star$) is the transferred anomaly from ozone (i.e., either incorporating or not the measurements of Savarino et al. (2008). At present, equation (2a) does not incorporate this effect and is likely to confuse the reader (see Morin et al., 2009, for a way to introduce this). This set of equation is only valid when photochemical steady state occurs (see Morin et al., 2007, for a thorough demonstration ...). At night, the question is to know whether the Δ^{17}O(NO_2) calculated at steady-state during the day still holds. In their manuscript, Alexander et al.

(2009a) clearly assume this is the case, which I disagree with. Indeed, towards dusk, the photolysis of NO_2 (requiring visible sunlight) still occurs long after the RO_2 start to disappear (because they stem from UV-photolysis, which stops earlier than visible photolysis). Thus **the NO_2 formed during the day with a $\Delta^{17}O(NO_2)$ fixed by the α valid during the day does not survive dusk, and is progressively replaced with NO_2 only produced through the $NO+O_3$ reaction, thus featuring a much higher $\Delta^{17}O$**. This issue has first been pointed out in Morin et al. (2009, page 13), where α was suggested to be extended at night with a value close to 1. The attached figure shows the result of a box model run (model similar to Morin et al., 2008), run at 40°N on March 14 (doy 73) with standard atmospheric concentrations of trace species. The upper panel displays production and destruction rates of NO_2 throughout the day. The lower panel shows the value for the photochemical α. I arbitrarily assume it to be valid as long as the photolytical lifetime of NO_2 is lower than 10 minutes. It clearly shows that at dusk, when the lifetime of NO_2 is still lower than 10 min, the value of α is extremely close to 1.0. This confirms our previous qualitative assertion. Thus I believe allowing diurnal variations of $\Delta^{17}O(NO_2)$ in GEOS-CHEM would have a very significant impact on the results, in particular in tropical areas, where at present a very small value of α is used throughout the day, although night-time reaction pathways should operate with a much higher than calculated $\Delta^{17}O(NO_2)$. **In short, the approach used so far is fine for day-time pathways ($OH+NO_2$ etc.) but should be modified for night-time pathways (involving the NO_3 radical) with an α value close to 1**. We leave it to the authors to find a way to cope with dawn and dusk, especially in a context of variable daytime duration in midlatitudes. **The net effect of this modification will be to further increase the value of $\Delta^{17}O$ of atmospheric nitrate predicted by the model, which will be found even further off the measurements at mid-latitudes, and will require a reassessment of the isotopic variables used (in particular $\Delta^{17}O(O_3)$), which I believed are wrong because they are biased by the available set of measurements in polar regions (see above) and the wrong $\Delta^{17}O(NO_2)$ scheme, as demonstrated above**. Note that this long-neglected issue will be discussed in more

details in an article currently in preparation in our group, dealing with the sensitivity of $\Delta^{17}O$ of atmospheric nitrate to atmospheric conditions.

2.3.4 $\Delta^{17}O$ of OH

While this issue was recognized in Kunasek et al. (2008), I find surprising to not see this discussed in this paper, although many areas could be impacted by the fact that $\Delta^{17}O$ of OH is not necessarily 0 ‰, in particular in the cold and dry polar regions (Morin et al., 2007). Why is this not considered at all in this manuscript ?

2.3.5 Analytical techniques

To rationalize the discrepancy between observed and modeled $\Delta^{17}O$ values, especially at low latitudes, Alexander et al. (2009a) invoke analytical biases that could originate from the fact that the bacteria used for the isotopic analyses could consume organic nitrate in addition to inorganic nitrate and nitrite (the latter is generally totally ignored for atmospheric applications). In doing so, they question the reliability of the denitrifier method for samples containing organic nitrates. While **Alexander et al. (2009a) do not provide any scientific argument to support their claim**, I have several arguments against it.

First of all, atmospheric nitrate sampling by pumping through filtering material is believed to suffer little interferences with organic nitrate, and in particular PAN (Sirois and Barrie, 1999). If this is true, then atmospheric nitrate samples should be unaffected by this issue (this applies to Michalski et al. (2003), which shows little difference from the Princeton rainwater data ...). Second, my own experience is that the ratio between N_2 (or O_2) peak areas deriving from the N_2O produced by the bacteria (Kaiser et al., 2007) and the concentration of nitrate in the samples (measured with either IC or colorimetric methods, that are both insensitive to organic nitrate) is constant throughout a given analytical run. It is the same for isotopic standards (USGS34, USGS 35 and USGS 32), which do not contain any organic nitrate, and for samples such as snow, air, well- and river-water analyzed so far in our laboratory. If organic nitrate was to be consumed by the denitrifying bacteria and used to produce N_2O, this would lead to higher than expected the N_2 (or O_2) peak areas, based on the nitrate concentrations measured before. This simple observation makes the claim of Alexander et al. (2009a) hard to believe. In addition, such an issue was never brought up by the soil science community (Morkved et al., 2007), where the organic nitrate component could be significant. In conclusion, if no microbiological evidence is provided in the revised manuscript (or results from new experiments that could support it), I see no reason why the authors could leave this unsupported claim in their article. There are many other things to discuss in the model output before starting to question the quality of the measurements carried out previously.

Of course, the same applies to the "penguins" discussion at the end of the discussion section (page 11203, lines 25 to the end). As even recognized by the authors, it has no relevance to the problem raised before and should be removed from the revised manuscript. In addition, it may be useful to point out that photolysis does not occur significantly during winter in DDU, and thermal decomposition should be quite slow at the temperature prevailing there in winter ...

2.4 Update to Kunasek et al., 2008

Given that Kunasek et al. (2008) have used the same model for an application at Summit, Greenland, it would be good that the authors provide here an update to their results, taking into account the results of the modification performed to the analytical framework in light of the issues raised in this review. This applies, for instance, to the calculation of Δ^{17}O of NO_2.

3 Technical corrections

References: the style for all references throughout the text is incorrect. When an author name is used within a sentence, only the year has to be put between brackets. I believe this has to be performed by the ACP editorial staff, i.e. replacing the LaTeX command `\citep` by `\citet` whenever a formulation like Name et al. (yyyy) is required. I'm not listing all the occurrences here, as this happens throughout the whole manuscript. The first example I found is on page 11188, line 17: pleace replace "(Michalski and Bhattacharya, 2009)" with "Michalski and Bhattacharya (2009)" and so on.

Running title: here again I believe the proof-reading has been done quickly, as the running-title reads only "Δ^{17}O", which of course is a good summary of the central topic of the paper, although detailing it with a few words would not be useless ... In contrast, the title of the paper is very long and could be shortened. A suggestion is "Global modeling of the isotope anomaly Δ^{17}O of atmospheric nitrate and implications for NO_x oxidation pathways" (or "implications for nitrate formation pathways"). Also note that the current title is somewhat misleading, as the "oxygen isotopic composition" comprises also δ^{18}O, which is not dealt with in the paper.

In the text:

Page 11188, line 10: the range of Δ^{17}O measurements of tropospheric ozone is actually much wider than 25 to 35 ‰. See the discussion in Morin et al. (2007).

Page 11188, line 21: Lyon (2001) simulates highly unrealistic Δ^{17}O distributions in ozone. It would be more accurate to refer to the more recent study by Zahn et al. (2006) to support the fact that ozone is isotopically non-stochastic.

Page 11189, line 4: the reason why $BrONO_2$ induces a higher Δ^{17}O than other pathways is not only because O_3 reacts with its terminal atom with Br (the same is true for NO+O_3 and NO+NO_2 so this can't be the right reason), but because during the hydrolysis all O atoms in the nitrate produced originate from $BrONO_2$ (contrary to what happens during the N_2O_5 hydrolysis, for example). In this regard, the $BrONO_2$ hydrolysis reaction is isotopically equivalent to the NO_3 + DMS/HC reaction.

Page 11189, line 9: GEOS CHEM does not simulate observations. It simulates $\Delta^{17}O$ of atmospheric nitrate, which is compared with observation.

Page 11194, line 23: the longitude of Alert is about 62°W.

Page 11200, line 6: I assume you wanted to mention BrO radicals, not "Bromine radicals".

Page 11201, line 16: this definition of NOX is inconsistent with the standard NO_x-NO_y definition.

Figures:

Fig 5: along with isotopic measurements and predictions, it would be informative to show a time series of the predicted and measured atmospheric concentrations of nitrate. While at first order nitrate concentrations are not directly linked with $\Delta^{17}O$, which only depends on the proportion between reaction pathways, it is clear that if the model is not able to reproduce seasonal variations of the concentrations of nitrate it is useless to use its output to constrain and assimilate the isotopic data. This will be particularly useful in polar regions.

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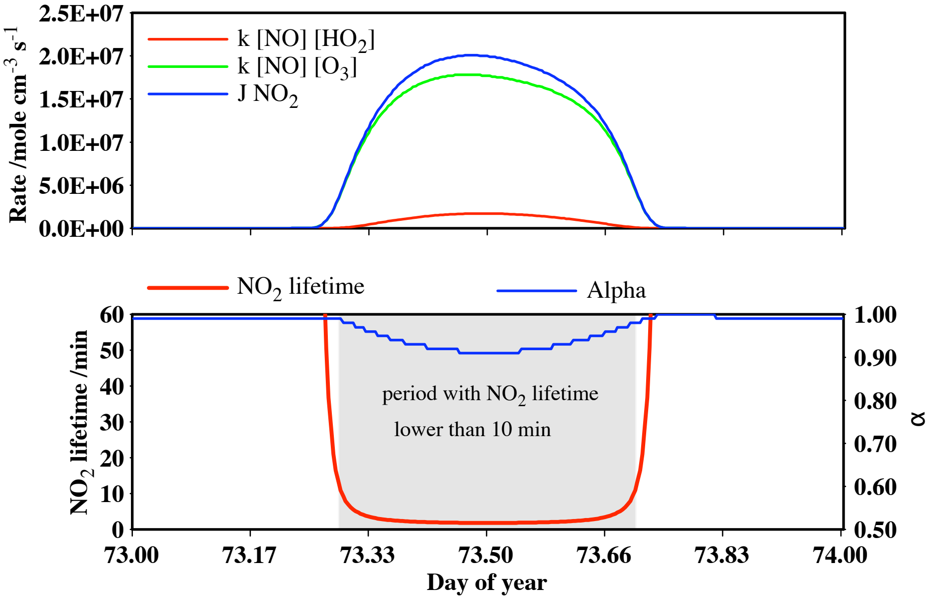
Rate /mole cm^{-3} s^{-1}
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
k [NO] [HO$_2$]
k [NO] [O$_3$]
J NO$_2$
NO$_2$ lifetime
Alpha
NO$_2$ lifetime /min
60
50
40
30
20
10
0
period with NO$_2$ lifetime
lower than 10 min
1.00
0.90
0.80
0.70
0.60
0.50
α
73.00
73.17
73.33
73.50
73.66
73.83
74.00
Day of year

Fig. 1.