Atmospheric Chemistry and Physics Discussions

Interactive Comment

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

S. Morin et al.

Received and published: 4 October 2006

Before formally addressing the points raised by Referee 1 and Referee 2, the authors want to thank both referees for the extensive review they carried out on our article. Taking into account these comments resulted -to us- in substantial improvements of the manuscript.

Since both referees have raised quite similar points (with a few notable exceptions), this letter aims at answering to both of them. Some specific comments are addressed separately. Technical details and modifications affecting the revised version will be sent to the Editor separately.

1 - General remarks

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

These remarks were first introduced by the Referee 1, but were also endorsed by the Referee 2 a few days later. These consist in :

* The criticism of our (rather short) discussion of existing data on the isotopic composition of tropospheric ozone, and the consequences on the conclusions of our manuscript (see below).

* A discussion on the the potential for OH radicals to bear a non-zero isotope anomaly due to a slower equilibration process in Arctic conditions than at mid-latitudes. We agree that the original sentence was ambiguous. We show below that this issue does not affect at all the conclusions of our paper, since what should be compared is the reaction of OH with H2O (isotopic equilibration) vs. the reaction of OH with NO2. Other OH sinks are not relevant to this discussion.

Several technical points were raised by both referees (length of sentences, structure of the discussion section, wording of the title, estimation of uncertainties, definition of mean back trajectories ...). The answers to each of them are described below. Constructive remarks dealing with grammar and literature references were included in the revised manuscript. These changes are visible in the modified manuscript attached to the letter for the Editor (not online).

2 - Specific comments

1. Δ17O of tropospheric ozone

It was stated in our manuscript that Δ17O(O3) was a crucial variable for our analysis. The value of 35 ^{o}/oo was chosen because of the similarity of our approach with the work by Michalski et al. (2003). They relied on mass-balance calculations to derive main oxidation routes leading to the formation of atmospheric nitrate assuming a Δ17O(O3) value of 35 ^{o}/oo . This value is consistent with the ad hoc calculation by Lyons (2001). In addition, our goal in this paper, maybe not clearly-enough stated, was not quantitative modeling as interpreted by the Referee 1. It was rather an exploration

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

of the reasons why $\Delta 17O$ in atmospheric nitrate is much higher in the Arctic springtime than at lower latitudes at the same period of year, and why it covaries with the mixing ratio of ozone during ozone depletion events (ODEs). Therefore the Monte-Carlo approach developed at the end of our manuscript was meant to be a simple and crude modeling of the observed range and variability in $\Delta 17O(NO3-)$ and not an attempt to quantitatively reproduce the observed variations at a very fine scale. The latter objective would require an extensive modeling effort. It is currently beyond our capabilities and possibly not worth the effort given the uncertainties carried by some of the terms of the isotopic equations considered here.

We accept that the value of 35 ^{o}/oo is biased towards a specific research group (Michalski et al.), and that the apparent absence of uncertainty attached to this value (in previously published papers as well as in ours) gives the false impression that this value is robust throughout the troposphere. We show below that it is likely not to be the case so far.

We include in our revised article, as a figure, the data reported in the two only papers ever published on the triple isotopic composition of tropospheric ozone (i.e. Krankowsky et al. (1995) (hereafter K95) and Johnston and Thiemens (1997) (hereafter JT97)) (see revised version of the manuscript, figure 6). For this, we first digitized the figures published in these articles in terms of $\delta 18O$ and $\delta 17O$. We then calculated the corresponding $\Delta 17O$ using the same definition as the one used in our article ($\Delta 17O = \delta 17O - 0.52\ \delta 18O$). Finally we calculated statistical moments on these isotopic data distributions. This procedure allows for a quantitative comparison between these datasets and our measurements.

The data published by these authors were obtained in samples collected in a variety of environments (urban : Pasadena (JT97) and K95, semi-urban : La Jolla (JT97) and in a desertic environment (White Sand, JT97)). As demonstrated by the figure we produced, in all cases $\Delta 17O(O3)$ exhibits a considerable scatter. For instance, $\Delta 17O(O3)$ measurements by K95 range between 6 ^{o}/oo and 54 ^{o}/oo , with an average

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

of 25°/oo and a standard deviation (1 sigma) of 12 ^{o}/oo . The data published by JT97 also exhibit a large variability (1 sigma = 5 ^{o}/oo for the La Jolla dataset). Fewer data points were obtained at the White Sand and Pasadena sites by JT97, but a large scatter is also reported (4 ^{o}/oo and 2 ^{o}/oo , respectively).

In addition, each dataset has a different mean, with values as low as 21 ^{o}/oo (Pasadena, JT97) and as high as 32°/oo (White Sand, JT97). The La Jolla site (JT97) and the unidentified urban site (K95) have average values of 26 ^{o}/oo and 25 ^{o}/oo , respectively.

Contrary to the predictions of Morton et al. (1990), K95 rule out the possibility that Δ17O(O3) depend on the temperature in a simple manner in the atmosphere, since no correlation was observed between their measurements and the temperature recorded at the sampling site. The large difference between the data from different sites considered in JT97 can also not be related to temperature changes only (see revised manuscript). What can be reasonably drawn from K95 and JT97 is that tropospheric ozone exhibits a significant isotopic anomaly, of the order of 20-35 ^{o}/oo .

We compare ozone isotopes measurements in the troposphere (K95 and JT97) to the isotopic composition of atmospheric nitrate published by Michalski et al. (2003, hereafter M03) and to our dataset from Alert, Nunavut. M03 carried out a year-round survey of atmospheric nitrate in La Jolla, California. From the whole dataset we calculated an average isotopic anomaly of 24 ^{o}/oo (+/- 3 ^{o}/oo , 1 sigma). On our dataset from Alert, we calculated an average isotopic anomaly of 32 ^{o}/oo (+/- 2 ^{o}/oo , 1 sigma). It appears from this analysis that the variability in ozone isotope measurements, among each sampling site for the K95 and the JT97 study, is larger than for the nitrate isotopic surveys carried out by M03 and ourselves.

Since Δ17O(NO3-) exhibits a strong seasonal cycle (M03) and correlates well with an external parameter in certain cases (e.g. the ozone mixing ratio in our study), a first approach to account for this behavior is simply to explore the relationship theoretically,

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

fixing a certain number of variables, among which the isotopic composition of ozone. Indeed, the processes governing the variations of $\Delta17O(O3)$ in the troposphere are not clearly understood. M03 (as well as subsequent papers by his research group) made the hypothesis, just a starting point, that $\Delta17O(O3,$ troposphere) is more or less constant. This empirical approach has lead M03 to account for the changes in $\Delta17O(NO3\text{-})$ over the year in a satisfying manner (given the uncertainties carried by each of the variable considered, the first of which being $\Delta17O(O3)$ itself, as shown above). In the present study, we decided to follow the same approach. We found that $\Delta17O(NO3\text{-})$ is correlated with the ozone mixing ratio. In addition, $\Delta17O(O3)$ does not appear to be correlated with the mixing ratio of ozone (see K95 or JT97). Given that transport processes should not result in major variations of $\Delta17O(O3)$, it is reasonable to explore the correlation between $\Delta17O(NO3\text{-})$ and the ozone mixing ratio in terms of a kinetic effect best described by the dilution equation that we derived. We chose to use the value used by M03 because $\Delta17O(O3)$ has never been measured in polar environments. It seems to us that our interpretation in terms of oxidation pathways and our ability to reproduce, even broadly, the variations in the $\Delta17O(NO3\text{-})$ signal over a period of a few weeks, corroborates the idea that $\Delta17O(O3)$ is not the driving variable in the system.

Having said that, we accept that that the value of 35 ^{o}/oo may not be fully justified. Hence the quantitative estimation of parameters (Monte Carlo calculations) may make an abusive use of this particular value in this context.

As a consequence, we decided to modify the structure and the content of the article, as follows : We make a better (critical) description of existing data on tropospheric ozone, using the new figure described above. We base our reasoning on a range of $\Delta17O(O3)$ values, spanning from 25 to 35 ^{o}/oo , thus overlapping most of the measurements and/or estimations available in the literature. From this $\Delta17O(O3)$ range we calculate, using mass balance equations, the predicted range in $\Delta17O(NO3\text{-})$ in arctic conditions. Our measurements being 9 ^{o}/oo higher than M03's measurements for the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

same period of the year, a specific process (namely the formation and hydrolysis of BrONO2) is appropriately invoked. The plausible mechanism behind the correlation between $\Delta 17O(NO3-)$ and the ozone mixing ratio is still discussed. However, given the broad range of $\Delta 17O(O3)$ value in the literature, the estimation of parameters based on Monte-Carlo calculations has been dropped. Note that our goal, contrary to what is stated in the report by Referee 1, is not quantitative modeling, but rather the description and the qualitatitive interpretation of a new phenomenon dealing with nitrate isotopes chemistry and ozone depletion events. A more detailed analysis, supported by new data from more recent field campaigns in the Arctic, will be carried out by our team in a near future.

2.Equilibration of OH with H2O

We incorrectly stated that : "In all meteorological conditions found in the Arctic basin, the equilibration between H2O and OH is always the fastest process, compared to other sink reactions for OH". The end of this sentence should have read "[...], compared to the reaction rate for the oxidation of NO2 by OH". Indeed, when computing the isotope anomaly of oxygen in HONO2, the two rates to be compared are the rate of the isotopic exchange reaction (OH+H2O) and the reaction rate for the transfer of the OH isotopic anomaly to HONO2 (OH+NO2). We note $x=k(OH+NO2)/k(OH+H2O)$, and take the rate constant for the kinetic equilibration of OH with H2O from Dubey et al. (1997). For the typical meteorological conditions at Alert from January to May 2004, the temperature varies between $-40°C$ and $-12°C$ (i.e. between 232 and 261 K). Assuming RH = 70

What would be the isotopic composition of OH in the absence of any isotopic-fractioning sink reactions and equilibration processes? This depends on the reactions that forms OH :

OH can be formed by reaction of ozone with water (through the formation of O(1D) oxygen atoms) : O3+H2O ? O2 + 2OH. In this reaction, half of the OH formed bears the isotopic anomaly of ozone (between 20 and 40 ^{o}/oo , see above ...). The other

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

half bears the isotopic anomaly of atmospheric H_2O, i.e. 0 ^{o}/oo . So in the absence of any equilibration/sink process, Δ17O(OH) = 0.5 Δ17O(O3-asym) 10-20 ^{o}/oo . OH can be formed by photolysis of CH2O and HONO (Dominé and Shepson (2002)). Both species are emitted by the snowpack after recycling of organic matter and nitrogen oxides, in quantities such that they account for most of the OH production in the High Arctic in springtime. In both cases, the isotope anomaly of the OH produced should lie between 0 ^{o}/oo (full equilibration with atmospheric water) and 35 ^{o}/oo (in the extreme case where nitrogen oxides recycled within the snowpack keep the isotopic anomaly of nitrate after its deposition onto the snowpack ...)

A mass-balance calculation shows that, during the reaction OH+NO2, one third of the isotopic anomaly of OH is transferred to HNO3 (the remaining 2/3 being derived from NO2). A reasonable maximum for 1/3Δ17O(OH) is 10 ^{o}/oo . Then, one has to take into account the competition between the NO2 oxidation and the OH-H2O equilibration (see above). In the most extreme case (x = 0.024), one finds that up to 0.2-0.3 ^{o}/oo in the nitrate isotope anomaly would originate from OH. Even in this extreme case (not likely), this cannot be a significant part of the isotopic anomaly measured in nitrate. It is also not significant with respect to the variability of this variable (standard deviation of 2 ^{o}/oo). Finally, it is also lower than the estimated uncertainty affecting Δ17O(NO3-) measurements (see below).

The fact that the potential for OH to transfer a non-zero Δ17O to nitrate is not significant, is better explained in the revised version of the manuscript (see above). However, in relation to the point raised by Referee 1, it is possible for OH to transfer a significant non-zero Δ17O to species such as CO or CH4, given the rates of the oxidation. However, the reaction of OH with CH4 yields H2O and CH3, so it has no implication on the isotopic budget of water vapour given that this anomaly is buffered by the large reservoir of water vapour in the troposphere. The oxidation of CO by OH represents a minor source for CO2, hence the isotope anomaly induced by the reaction with OH is most likely undetectable in the troposphere.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

3.Discussion part

We agree with both referees that the discussion section deserved some improvements in its layout, formulation and content. The clarification of the goals and limitations of our approach led to improve this section, which is now organized as follow, taking into account the constructive remarks by both Referees.

4.1 Chemical mechanisms, including ODEs-specific mechanisms

4.2 Isotopic signatures of products and precursors. This part also includes the important question of the isotopic signature of tropospheric ozone (see above).

4.3 Derivation of Δ17O(NO2)

4.4 Nitrate formation

4.5 Comparison of predicted values with measured values

To answer the final remark by Referee 1 (and also Minor Comment 15 by Referee 2) on the absence of error estimates on the Monte Carlo method, we would like to state that, given the large uncertainty on many crucial variables in our equations (e.g. Δ17O(O3) or Δ17O(BrO), due to inconsistent literature on the intramolecular distribution of Δ17O among the ozone molecule ...), an estimation of the errors would be very uncertain. As a consequence of this and for also the reasons exposed above, we decided to drop this part.

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

EGU