Atmos. Chem. Phys. Discuss., 10, C12027–C12037, 2011
www.atmos-chem-phys-discuss.net/10/C12027/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China" *by* Y. T. Fang et al.

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Received and published: 6 January 2011

Answer to Referee #2

General comments:

Fang et al present an impressive dataset of two air pollution. atmospheric cycling of NOx. Overall the manuscript is well written, well organized and clearly presented. The data seem to be of sound quality and the interpretations are, for the most part, well justiïňĄed, within the bounds of our ability to characterize N sources and understand chemical cycling.

My primary criticism of this work, presented below, involves the invocation of the inïňĆuence of a poorly characterized isotopic inïňĆuence by a peroxyl radical pathway for explaining 'anomalous' δ18O composition as well as only minimal attention given to the potential inïňĆuence of other mechanisms that might be controlling variability of δ15N in NO3$-$ found in rain.

Answer: Thank you very much for your thorough, thought-provoking and detailed comments to our manuscript. All comments you raised, particularly the specific comments, have been carefully considered when we revised the manuscript.

SpeciïňĄc Comments:

1 The role of a peroxyl radical associated pathway of NOx oxidation on NO3 isotopic composition is intriguing. However, I feel that, particularly because this may be a relatively new idea and/or novel to this type of highly polluted environment, there needs to be more support, references and discussion. Is this complete speculation? What is known about reactions involving peroxyl radicals and their transfer of O atoms (and isotopic composition) to a NOx pool? Is there any other evidence that supports this as a potentially important player in the NOx cycle for this environment or any others? Again I feel that this may be an important ïňĄnding/discussion point for the paper and the manuscript would beneïňĄt (and readers too!) from a more thorough discussion of the potential inïňĆuence of this pathway.

Answer: Thank you for this concern. To some extent, we agree with you that it may be a relative new idea to this type of highly polluted environment. However, we hesitate to address this issue too much. One reason is that the reaction of NO with peroxy radical remains poorly understood, especially in southern China, to our knowledge. We just think that this reaction is likely occurring, to explain in part the low δ18O values of nitrate. The other reason is that just as criticized by reviewer #1, "interpreting δ18O of nitrate for the contribution of various NOx oxidation pathways featuring different "δ18O signatures" is not entirely correct", because "unlike Δ17O, isotopic fractionation oc-

curring at each step of any chemical mechanism can induce large variations between δ18O values of the reactants and the products" (see the comments from reviewer #1). Therefore, we would like to have some general discussion. In order to make clear that the potential isotopic fractionation during each chemical pathway, we have added a sentence in the revised manuscript "However, before we attempt to separate the contribution of each formation pathway of atmospheric NO3- using δ18O signatures, we'd better to be aware of that unlike 17O, isotopic fractionation can occur at each step of chemical reactions, which can induce large variations between δ18O values of the reactants and the products (see e.g. Chakraborty and Chakraborty, 2003) as suggested by Reviewer #1.

Additionally, requested by reviewer #3, in the revised version we have calculated the expected δ18O minimum of formed NO3- if we assume that NO exchanges O atom with peroxy radicals to convert to NO2 and the expected minimum will be between +11‰ and 28‰ depending on the oxidants in the following interactions to form NO3-. More details please refer to the reply to reviewer #3 and the text of the revised manuscript (Discussion 4.4).

2 What about other factors that might control δ15N of NO3-/HNO3 deposition and also then the potential for seasonality of these controls (e.g., temperature, humidity, etc.) for exercising some power over the seasonality observed in δ15N of NO3-. For example,

a. Higher ozone in polluted areas promotes higher NO2 concentrations and lower δ15N of NO3$-$ (Freyer et al., 1993). Thus, could seasonal variation in the δ15N of NO3-be related to changes in the relative sizes of the NO and NO2 pools as it relates to O3?

Answer: This was similarly concerned in the comments from Prof. Savarino and by the reviewer #1. To address this issue, we have greatly modified the discussion in the revised manuscript (Discussion 4.2). In the revised version, we have presented the seasonal variations of concentration of O3, NO and NO2 during the study period, and we concluded that N isotopic exchange can not fully explain the observed pattern of

δ15N in precipitation NO3- in the study city. More details please see the reply to short comments and reviewer #1, or the text of the revised manuscript.

b. Changes in temperature and/or humidity can inïňĆuence interactions between HNO3 vapor and aerosol NO3$-$. Could seasonal changes in temperature be inïňĆuencing the partitioning of N between these two forms and hence inïňĆuence the isotopic composition of the component in rain?

Answer: We found that temperature was correlated with δ15N of precipitation NO3- in 2009 but not in 2008 (Fig. 4). Thus, temperature cannot fully explain the seasonal pattern of δ15N-NO3-, which was different between in 2008 and 2009. We do not have data on humidity, which can be indicated by the distribution of precipitation throughout the year. In the manuscript, we had made a figure showing the relationship between temperature and δ15N-NO3- (Fig. 4) and discussed the seasonal pattern of precipitation on seasonal pattern of δ15N-NO3- in comparison with other studies (Discussion 4.2).

c. How high is the particulate load? Is the NO3$-$ particle associated? Particles can be important reactive surfaces – any insight into variability of the particulate composition and/or seasonality or concentrations?

Answer: We are sorry for that the information on particulate load is scarce for our study region.

d. The precipitation samples contained substantial NH4+ . Therefore, I wonder about the dynamic equilibrium between NH4NO3 and HNO3 and the implications for isotopic exchange? Under conditions of high temperatures and high humidity the model of Morino et al. 2006 would predict that most of the NO3$-$ would be in the form of particulate NO3$-$ (vs HNO3 vapor). The isotopic discrepancy between these two pools could have important implication for measured NO3$-$ in rain as several studies have shown (Baker et al., 2007; Elliott et al., 2009; Freyer 1991).

Answer: It is a good point. And we wish we can make further research on this topic. We plan to measure 15N abundance for precipitation NH4+. But this work has not been started yet.

3. There seems to be a lot of attention and comparison with other studies of atmospheric NO3− found in precipitation. However, I feel that there was more attention given to high latitude studies than needed. In fact, reference to the studies of arctic NOx cycling may not be pertinent to your study at all. There are data available from similar latitudes (Morin et al., 2009 -wide range of latitudes; Hastings et al., 2003, Bermuda 32N; Wankel et al., 2010, Israel 29N) that might provide a better basis for comparison in your discussion.

Answer: Initially we would like to put our study in a world-wide context, since very limited studies come out from low latitude regions. Just mentioned here and by reviewer #1, the setting in polar region and thereby NOx cycling is very different in polar region particularly in some seasons, we limited our comparison more with similar latitudes in the main text, but the information for polar regions remained in this paper. We have modified our discussion in the revised version. First, regarding 15N, we remind the readers of the potential difference between aerosol and rainwater nitrate δ15N, because particulate has been usually collected for the polar sites (Table 4 in the original manuscript, Appendix B in the revised manuscript). Secondly, when we compare our results with coastal Antarctica, we have excluded the austral later winter and early spring because during that period NO3- sedimentation from polar stratospheric clouds results in particular high δ18O values which is very different from the situation in other seasons. Finally, we have changed Table 4 to be an appendix in the revised manuscript to minimize confusion. For more details please go to the revised manuscript.

Technical Corrections:

P21440, L4: Don't need to mention the use of the denitriïňĄer method here.

Answer: Good. We have removed it.

P21440, L17: Should this be "altitude" or "latitude?"

Answer: Corrected to be "latitude" now.

P21441, L6: You deïňĄne NOx as a 'sum of NO and NO2 ' as is traditionally done. However, a sum is a singular object and should be used grammatically so throughout the paper. "NOx contributes", "NOx is", "NOx dominates" – and so on.

Answer: Done.

P21441, L7: "...and are thus important factors..."

Answer: Done.

P21441, L17: Awkward sentence. Rephrase "The dominant source of NOx emissions is expected to have shifted..."

Answer: Here it means the growth rate instead of dominant source. We changed the sentence "The growth rate in NOx emissions is expected to have shifted. . .".

P21441, L19: "...due to increased vehicle usage and power plant emissions."

Answer: Done.

P21441, L23: Not sure the Figure 1 is needed.

Answer: We think that it is necessary to demonstrate the importance of HNO3- in acid rain for the study region and maybe other sites in China as well. But we put it as an appendix in the revised version.

P21441, L24: Not clear how you can expect to control anthropogenic production of NOx from natural processes such as lightning?

Answer: "control" has been changed to be "separate"

P21442, L2: "NOx is..."

Answer: Done.

P21442, L5: “NOx is...”

Answer: Done.

P21442, L22: “Nitrogen stable isotopic composition of atmospheric deposition...”

Answer: Done.

P21443, L2: “vehicular NOx emissions measured from tailpipe...”

Answer: Done.

P21443, L29: “This explains the higher δ18O ...”

Answer: Done.

P21444, L1: “in winter than in summer in previous studies”

Answer: Done.

P21444, L7: “and proximity of stationary source...”

Answer: Done.

P21444, L9: Elliott et al did not use ‘dual’ isotopes – only δ15N.

Answer: “dual” has been removed.

P21447, L20: “Annual N load from precipitation is the sum...”

Answer: Done. Thanks.

P21448, L16: falling

Answer: Done.

P21448, L18: falling

Answer: Done.

P21450, L7: Is this mean a ïňĆux weighted value?

Answer: No. it is an arithmetic mean. We make it clear now as “. . .with a total arithmetic mean of. . .”

P21450, L26: “...was also found to signiïňĄcantly inïňĆuence...”

Answer: Done.

P21452, L22: “Partitioning of NOx sources using...”

Answer: Done.

P21453, L14: “using a simple two end-member mixing model.”

Answer: Done.

P21543, L14: Were ïňĆux-weighted average used for this mixing analysis?

Answer: No. They were the averages of all sampling events in each year. To make it clear, “on average” was added before the percentages. If we use flux-weight average to calculate the anthropogenic contribution, the percentages are slightly higher.

P21453, L28: “may be higher than our assumed value...”

Answer: here we mean that the assumed value may be higher than actual one.

P21455, L9: “donates fewer O atoms”

Answer: Corrected.

P21455, L22: “When the air temperature...”

Answer: Corrected.

P21456, L12: provide reference for this statement.

Answer: Alexander et al., 2009 has been provided.

P21456, L15: provide reference for statement.

Answer: Alexander et al., 2009 has been provided.

P21456, L17: provide reference for this statement. Please explain why the DMS/HC pathway would necessarily lead to higher δ18O than the N2O5 pathway.

Answer: Alexander et al., 2009 has been provided in the new version. Alexander et al. quantified atmospheric NO3- formation pathways based on a global model of the Δ17O of atmospheric. We can infer the possible involvement with O3 for each main formation channel in that paper. We wrote it now "Atmospheric NO3- induced via the NO3-+DMS/HC pathway will probably have higher δ18O values than those induced via the OH pathway and the N2O5 pathway due to its more involvement with O3 during formation (Alexander et al., 2009).".

P21457, L4-11: Invoking a peroxyl radical pathway is a potentially important explanation/ïňĄnding/conclusion – but there needs to be more discussion about the supporting work done on the inïňĆuence of this pathway on the isotopic composition of NO3$-$.

Answer: See the response to specific comments above.

Table 1, 2, and 3: No need to report arithmetic mean. Should be using ïňĆux-weighted means for all calculations involving δ15N – in particular the mixing model calculations. There also appears to be some slight disagreement among Tables 1, 2, and 3 regarding weighted δ15N values.

Answer: We have explained why we presented arithmetic means in our responses to reviewer #1. The reasons are: 1) we can compare the difference between arithmetic and NO3–flux-weighted (mass-weighted) means. In the present study, we did not observed big difference between these two means (Table 1); 2) we need arithmetic means when we examine the season difference and source difference (Table 2 and Table 3); and 3) finally in many previous studied arithmetic means were presented rather than mass-weighted average. Thus the presentation on NO3- data remained unchanged in the revised version. We don't think there are slight disagreements among three tables.

In Table 1 both arithmetic and NO3–flux-weighted values were listed. In Table 2 and 3, only arithmetic means were presented for different seasons and different sources, respectively.

Table 4: Not sure if this is needed. Table excludes Michalski et al., 2003, 2004; Hastings et al., 2004; Jarvis et al., 2008; Wankel et al., 2010. Savarino is misspelled.

Answer: We think it is good to have this table, so the readers can see the differences in 15N signature among the different study regions. But we put it as an appendix in the revised version. The result from Wankel et al. 2010 has been included in this table. In the papers of Michalshi et al. 2003, 2004, only 18O and 17O were presented, thus were taken. For Hastings et al., 2004, 15N were reported for snow pack and surface snow, which have been included. Jarvis et al., 2008 used the same data as in Hastings et al. 2004 (two snow pits), which has not been included in the table. Spelling errors have been corrected.

Fig 1: Not sure if this is needed.

Answer: We think it is good to have it. But we put it as an appendix in the revised version.

Fig 2: Recommend using shading for warm vs cool seasons.

Answer: Agree. The warm seasons have been shaded.

Fig 3: Maybe also provide a map of the region?

Answer: We think the purpose of figure 3 was to show air mass backward trajectories for the sampling events.

Fig 6: When looking at this ïňĄgure, I wondered whether this spread of data could be thought of as mixing? While recognizing a general lack of knowledge of isotope effects from the various oxidation reactions (which greatly limits our understanding of Δ17O of atmospheric NO3$-$ in general), if this were to be plotted against inverse concentration

(e.g. a Keeling plot) could this be used to help bracket the end ember composition for a mixing model? I also recognize that the concentration of $NO3^-$ in precipitation results from more complex processes than simple mixing of two end embers, but perhaps this could be a point off of which to build some discussion (just a thought).

Answer: We considered such a correlation as a coincidence; the samples characterized with high 15N and 18O abundance had higher concentration, and those with low isotopic abundance had low concentration. The purpose to make this figure was to show that high NO3- concentration was associated with high 15N/14N ratio, which indicated anthropogenic influence.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 21439, 2010.