

## ***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 #3

The discussion paper “Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China,” by Y.T. Fang represents a well-written manuscript with interesting results that are of relevance to the scope of ACP. The authors present measurements of the isotopic composition of nitrate in precipitation samples collected over two years in a polluted area of the Pearl River Delta region. The authors interpret their data in the context of previous work on relating the isotopic composition of nitrate to sources and chemistry of nitrogen oxides

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(NO<sub>x</sub>), the precursor of atmospheric nitrate. As such, they conclude that the nitrogen isotopic composition of nitrate shows an impact of anthropogenic emissions of NO<sub>x</sub>, particularly from coal combustion, while the oxygen isotopic composition is explained by reaction of NO with oxidants, in particular peroxy radicals. The manuscript presents a more complete dataset than previously published from this region of the world. Some weaknesses are apparent in the discussion and interpretation, and while these should be addressed in a revised manuscript, overall they are relatively minor issues.

Two main areas of concern are raised below. First, I believe the authors should take some further steps in calculating the influence of different oxidation pathways on their observed d18O of nitrate. Second, because rainfall varies significantly seasonally the authors should focus their reporting on volume weighted data rather than numerical averages. It should also be reported in the methods section how volume weighted (and/or flux-weighted) calculations are done.

Answer: Thank you very much for your thorough, thought-provoking and detailed comments to our manuscript. All comments you raised, particularly the major comments, have been seriously taken into account in the revised manuscript.

Major Comments:

The authors present a very certain quantitative interpretation of their d18O data. I would caution the authors be more careful. For instance on p 21443 (lines 23-27), the authors specify that the isotopic composition of HNO<sub>3</sub> reflects 2/3 ozone and 1/3 OH for the OH pathway. This language should be referenced to Hastings et al. (2003) who first suggested this. However, my read of the Hastings et al work is that it is clear that UP TO 2/3 oxygens can come from ozone in the OH pathway case and UP TO 5/6 of the oxygens in the N<sub>2</sub>O<sub>5</sub> pathway case. This is important since these pathways have not been specifically quantified in terms of isotopic fractionation and exchange. Therefore, this is a good working framework for estimating the influence of oxidants on the formation of HNO<sub>3</sub>, since, for example, Jarvis et al. 2008 were able

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to explain their entire range of observation of  $\delta^{18}\text{O}$  of nitrate based on photochemistry alone. Still, this framework should be treated as such and not as concretely quantitative. The authors must quantify the impact of the presence of nitrite on their data and/or identify which samples had the greatest nitrite concentrations. This is mentioned below in more detail, but a several per mil impact could bring their data much closer to the range they calculate. On page 21456 the authors use the above mentioned framework to calculate the expected range of  $\delta^{18}\text{O}$  for comparison with their observations, and conclude that a minimum of 50 per mil should be expected while they observe values lower than this. While I agree with the authors that the role of peroxy radicals would lower this calculated minimum. The authors should complete a calculation based on the scenario they present (i.e. using 23.5 per mil as a value for the oxygens from peroxy radical) to update their expected range and see if their observations do indeed match with this. Alternatively, they could quantify how much this pathway must impact their estimated minimum in order to explain their observations (e.g., we need 20% of the  $\text{HNO}_3$  to be produced by this pathway compared to OH). This would give much more interesting information and something to be tested in the future, rather than presenting the peroxy radical idea as speculation. Further, I suggest the authors look at the availability of water isotope data in their region for making better assumptions regarding the values of OH that might be expected (a good source for precip water isotopes (need to calculate expected values for water vapor in region) -[http://wateriso.eas.purdue.edu/waterisotopes/pages/data\\_access/](http://wateriso.eas.purdue.edu/waterisotopes/pages/data_access/) Agures.html). Finally, the authors reference the Alexander et al. 2009 D17O model to back up their claim of lower values expected from peroxy radical impacts on  $\text{HNO}_3$  formation. Can they not look at the results from this model to see if the model predicts a strong influence of peroxy radicals on D17O of  $\text{HNO}_3$  in the region?

Answer: 1) Thank you. Basically, we agree with you. Thus in the revised version, first of all, we have re-worded those sentences; we put "up to" before 2/3 and 5/6. And the work of Hastings et al., 2003 has been cited there.

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2) With regard to the influence induced from the presence of nitrite, please see the response below.

3) In the revised version, we have calculated the expected  $\delta^{18}\text{O}$  of formed  $\text{NO}_3^-$  if we assume that NO exchanges O atom with peroxy radicals to convert to  $\text{NO}_2$  and the expected minimum will be between +11‰ and +28‰ depending on the oxidants in the following interactions to form  $\text{NO}_3^-$ . In the revised manuscript, we have added: "The  $\delta^{18}\text{O}$  of peroxy radicals is expected to be much lower than that of  $\text{O}_3$  as the O atoms should come from atmospheric  $\text{O}_2$  ( $\delta^{18}\text{O} = +23.5\text{‰}$  see Barkan and Luz, 2003). If we assume that NO exchanges O atom to form  $\text{NO}_2$  completely with peroxy radicals instead of  $\text{O}_3$ , then we can expect that the minimum  $\delta^{18}\text{O}$  value of formed  $\text{NO}_3^-$  will be +11‰ followed by the reaction R3 (up to 2/3 of the O atoms from atmospheric  $\text{O}_2$  and 1/3 from OH) and +28‰ followed by the reactions R4 to R6 (up to 4/6 of the O atom from atmospheric  $\text{O}_2$ , 1/6 from  $\text{O}_3$  and 1/6 O from  $\text{H}_2\text{O}$ ), respectively. We observed the lowest value of +33‰ in the study city, which is just slightly higher than the calculated minimum of +28‰ suggesting that peroxy radicals may be an important oxidant in the conversion of NO to  $\text{NO}_2$  and thereby  $\text{NO}_3^-$  formation in the atmosphere.". However, we are not able to simply quantify how much this pathway must impact the estimated minimum in order to explain the observations, since there are more than two pathways of  $\text{HNO}_3$  formation now and there are multiple oxidants involved.

4) When revising the manuscript, we have used water isotope data (from -15‰ to 0‰ in the study region (over the Asian continent) for making better assumptions regarding the values of OH that might be expected, following the suggestion. And we found the calculated minimum would be +55‰. As a consequence, more samples (16% of the samples) have values being lower than this minimum. More details please see the text of revised manuscript.

5) In Alexander et al. work, the relative importance of peroxy radicals on NO oxidation has been considered when quantifying atmospheric  $\text{NO}_3^-$  formation pathways, but based on our reading, it has not presented clearly.

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P 21446-21447 – The authors should make the calculation of how much they expect the presence of NO<sub>2</sub>-to impact their results. While the amount of NO<sub>2</sub>-relative to NO<sub>3</sub> may be small, the impact is partially based on the exchange of NO<sub>2</sub>-oxygen isotopes with water isotopes and if the water isotopes are significantly different than those found in the Wankel et al. study then the quantitative effect of the NO<sub>2</sub>-could be very different.

Answer: A good concern. In the revised manuscript, we have attempted to calculate the NO<sub>2</sub>- inference. In our case, our isotope analysis was performed in the laboratory (Tokyo, Japan). In the method section of revised manuscript, we have added “Assuming that  $\delta^{18}\text{O}$  of NO<sub>2</sub>- is the same as  $\delta^{18}\text{O}$  of water (-15 to + 0‰, NO<sub>2</sub>- contributes 1.6‰ to (NO<sub>2</sub>-+NO<sub>3</sub>-) and we can apply the calibration curve for NO<sub>2</sub>- with denitrifier reported by Casciotti et al. (2007), the NO<sub>2</sub>- will drop the values of  $\delta^{18}\text{O}$ -NO<sub>3</sub>- by 1.1-1.3‰”. Additionally, in the discussion (4.4) we corrected the NO<sub>2</sub>- interference, and then looked at how many values will be lower the expected minimum of +55‰. We found that the NO<sub>2</sub>- interference is not sufficient to drop observed values to be lower than the minimum. More please see the text of the revised manuscript.

P 21448 line 13-15 – The authors should justify the separation of cool and warm season data. The figures imply a significant amount of temperature variability in October – March, so it is not clear to me why this season is clearly the “cool” season.

Answer: It is true that there is a big variability in temperature during the period from October to March. However, we separated the season to cool and warm for study region following the traditional way (e.g., Tang et al. Global Change Biology), to avoid more confusion.

Tang XL, Liu SG, Zhou GY, Zhang DQ, Zhou CY (2006) Soil-atmospheric exchange of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O in three subtropical forest ecosystems in southern China. *Glob Change Biol* 12:546-560 doi:10.1111/j.1365-2486.2006.01109.x.

P 21448 – The authors should focus their reporting of results on volume weighed data.

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This is most appropriate given the significant difference in rainfall over the course of the year. Further, the authors should define the difference between volume weighted and flux-weighted means (ie Table 1) in their methods section.

Answer: In this paper, we reported the volume weighted mean for nitrate concentration. However, we think that NO<sub>3</sub>-flux-weighted mean make more sense to isotopic compositions, because isotopic signature is determined by not only volume but NO<sub>3</sub>-concentration. In the method, we have clarified it.

Technical Comments:

P 21441, line 8 and line 27 – The reference of Morin et al., 2008 is not appropriate here; there is extensive literature on how NO<sub>x</sub> impacts air quality and radiative balance and the importance of distinguishing the contribution of different sources. These statements are not specifically addressed by the Morin study, rather they are part of the motivation/background for their study. Please find a more appropriate reference; you might for example look in the most recent IPCC report, or references by H. Levy II (GFDL) or J. Logan (Harvard).

Answer: Replaced with Ehhalt et al. 2001 (IPCC).

P 21442 line 20 – this is an equilibrium reaction.

Answer: OK. Corrected now.

P 21444 lines 3-13 – Elliott et al., 2009 should be referenced here as well; the Elliott et al., 2007 study that is discussed does NOT present dual isotopes, only d<sup>15</sup>N of nitrate.

Answer: Elliott et al., 2009 has been added in the revised manuscript and “dual nitrate isotope...” changed to be “nitrate isotope...”

P 21446 line 21 – “lowing” should be “lowering”

Answer: Have been corrected.

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P 21447 – The authors should mention what meteorological dataset is used with HYSPLIT to calculate the back trajectories.

Answer: We added a sentence: “In this case, terrain height, ambient temperature, rainfall and relative humidity were used with HYSPLIT to calculate the back trajectories.”

P 21452 line 9-10 – I don’t understand the phrase “blown N-bearing pollutants over the city away...” in the context of a significant precipitation events. A larger amount of precipitation typically dilutes nitrate concentrations because of “scrubbing” or “washing” of the atmospheric column that comes into contact with the precipitation event. I don’t see how there is a clear link between precipitation and the “blowing” of air masses in and out of an area.

Answer: The study city Guangzhou, is located in the center of a large economic area (Pearl River Delta), which consists of many big cities, like Guangzhou, Shenzhen, Zhuhai and Dongguan. It is an area of  $4.2 \times 10^4$  km<sup>2</sup>, where there are more than 0.4 billion habitants. During the strong precipitation events, especially typhoons, there is obvious air mass transportation from east to west in warm season (see air mass backward trajectories, Fig. 3 in Discussion paper). This air transportation can blow N-bearing pollutants away from the study city. In the revised manuscript, we added this information to show the link between precipitation and the blowing of air masses in and out of the study area.

P 21453 line 23 – A more appropriate reference to changes in anthropogenic emissions with time related to the isotopes of nitrate is Hastings et al., Science, 2009 rather than Hastings et al., 2003.

Answer: Hastings et al., 2003 and 2009 have been cited here in the revised manuscript, since Hastings et al. 2003 addressed seasonal variation and Hastings et al. 2009 addressed the change across three hundred years.

P 21455 line 12 – Define  $\Delta 17\text{O}$ . Line 20 – “higher” should be “lower” Line 21-22 – I

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disagree that “temperature well controls  $\delta 18\text{O}$ .” Only as much as 22% of the variance is explained by the correlation shown in the figure; therefore not even in close to a majority of the variance is explained by temperature. Further the authors should explain why this relationship should exist if they believe this is an important interpretation of their data.

Answer: Good. In the revised version, a definition of  $\Delta 17\text{O}$  has been given. “Higher” has been corrected to “lower”. “As expected, temperature well controls  $\Delta 18\text{O}$ ” has been reworded as “As expected, temperature controlled  $\Delta 18\text{O}$  in this study”. The reason for such a relationship is that  $\text{N}_2\text{O}_5$  is thermally decomposed (meaning that  $\text{N}_2\text{O}_5$  is relatively more dominant in cool season than in warm season), which was mentioned at the beginning of the paragraph.

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

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