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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.

Anonymous Referee #3

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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 (NOx), the precursor of atmospheric nitrate. As such, they conclude that the nitrogen isotopic composition of nitrate shows an impact of anthropogenic emissions of NOx, 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.

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 21442 (lines 23-27), the authors specify that the isotopic composition of HNO3 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 N2O5 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 HNO3, since, for example, Jarvis et al. 2008 were able to explain their entire range of observation of d18O 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 d18O for comparison with their

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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 HNO3 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/figures.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 HNO3 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 HNO3 in the region?

P 21446-21447 – The authors should make the calculation of how much they expect the presence of NO2- to impact their results. While the amount of NO2- relative to NO30 may be small, the impact is partially based on the exchange of NO2- 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 NO2- could be very different.

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.

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.

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 NOx 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).

P 21442 line 20 – this is an equilibrium reaction.

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 d15N of nitrate.

P 21446 line 21 – "lowing" should be "lowering"

P 21447 – The authors should mention what meteorological dataset is used with HYPLIT 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 precip 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.

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.

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P 21455 line 12 – Define D17O. Line 20 – “higher” should be “lower” Line 21-22 – I disagree that “temperature well controls d18O.” 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 a important interpretation of their data.

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