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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 #2

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Review of "Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China" by Fang et al. Atmospheric Chemistry and Physics Discussions

General comments:

Fang et al present an impressive dataset of two years of wet deposition (e.g. rain) NO_3^- N and O isotopic composition in a region of China characterized by heavy air pollution. The authors use concentration along with δ^{15}N and δ^{18}O in order to provide some constraint on seasonality of N sources to this landscape as well as

atmospheric cycling of NO_x. 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 justified, 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 influence of a poorly characterized isotopic influence by a peroxyl radical pathway for explaining 'anomalous' $\delta^{18}O$ composition as well as only minimal attention given to the potential influence of other mechanisms that might be controlling variability of $\delta^{15}N$ in NO_3^- found in rain.

Specific Comments:

1. The role of a peroxyl radical associated pathway of NO_x oxidation on NO_3- 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 NO_x pool? Is there any other evidence that supports this as a potentially important player in the NO_x cycle for this environment or any others? Again I feel that this may be an important finding/discussion point for the paper and the manuscript would benefit (and readers too!) from a more thorough discussion of the potential influence of this pathway.

2. What about other factors that might control $\delta^{15}N$ of NO_3-/HNO_3 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 $\delta^{15}N$ of NO_3-. For example,

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a. Higher ozone in polluted areas promotes higher NO_2 concentrations and lower $\delta^{15}N$ of NO_3^- (Freyer et al., 1993). Thus, could seasonal variation in the $\delta^{15}N$ of NO_3- be related to changes in the relative sizes of the NO and NO_2 pools as it relates to O_3?
b. Changes in temperature and/or humidity can influence interactions between HNO_3 vapor and aerosol NO_3^-. Could seasonal changes in temperature be influencing the partitioning of N between these two forms and hence influence the isotopic composition of the component in rain?
c. How high is the particulate load? Is the NO_3^- particle associated? Particles can be important reactive surfaces – any insight into variability of the particulate composition and/or seasonality or concentrations?
d. The precipitation samples contained substantial NH_4^+. Therefore, I wonder about the dynamic equilibrium between NH_4NO_3 and HNO_3 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 NO_3^- would be in the form of particulate NO_3^- (vs HNO_3 vapor). The isotopic discrepancy between these two pools could have important implication for measured NO_3^- in rain as several studies have shown (Baker et al., 2007; Elliott et al., 2009; Freyer 1991).

3. There seems to be a lot of attention and comparison with other studies of atmospheric NO_3^- 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 artic NO_x 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.

Technical Corrections:

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

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P21440, L17: Should this be “altitude” or “latitude?”
P21441, L6: You define NO_x as a ‘sum of NO and NO_2’ as is traditionally done. However, a sum is a singular object and should be used grammatically so throughout the paper. “NO_x contributes”, “NO_x is”, “NO_x dominates” – and so on.
P21441, L7: “. . .and are thus important factors. . .”
P21441, L17: Awkward sentence. Rephrase “The dominant source of NO_x emissions is expected to have shifted. . .”
P21441, L19: “. . .due to increased vehicle usage and power plant emissions.”
P21441, L23: Not sure the Figure 1 is needed.
P21441, L24: Not clear how you can expect to control anthropogenic production of NO_x from natural processes such as lightning?
P21442, L2: “NO_x is. . .”
P21442, L5: “NO_x is. . .”
P21442, L22: “Nitrogen stable isotopic composition of atmospheric deposition. . .”
P21443, L2: “vehicular NO_x emissions measured from tailpipe. . .”
P21443, L29: “This explains the higher δ^{18}O . . .”
P21444, L1: “in winter than in summer in previous studies”
P21444, L7: “and proximity of stationary source. . .”
P21444, L9: Elliott et al did not use ‘dual’ isotopes – only δ^{15}N.
P21447, L20: “Annual N load from precipitation is the sum. . .”
P21448, L16: falling
P21448, L18: falling
P21450, L7: Is this mean a flux weighted value? P21450, L26: “. . .was also found to significantly influence. . .”
P21452, L22: “Partitioning of NO_x sources using. . .”
P21453, L14: “using a simple two end-member mixing model.”
P21543, L14: Were flux-weighted average used for this mixing analysis?
P21453, L28: “may be higher than our assumed value. . .”
P21455, L9: “donates fewer O atoms”

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P21455, L22: “When the air temperature. . .” P21456, L12: provide reference for this statement.
P21456, L15: provide reference for statement.
P21456, L17: provide reference for this statement. Please explain why the DMS/HC pathway would necessarily lead to higher $\delta^{18}O$ than the N_2O_5 pathway.
P21457, L4-11: Invoking a peroxyl radical pathway is a potentially important explanation/finding/conclusion – but there needs to be more discussion about the supporting work done on the influence of this pathway on the isotopic composition of NO_3^-.
Table 1, 2, and 3: No need to report arithmetic mean. Should be using flux-weighted means for all calculations involving $\delta^{15}N$ – in particular the mixing model calculations. There also appears to be some slight disagreement among Tables 1, 2, and 3 regarding weighted $\delta^{15}N$ values.
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.
Fig 1: Not sure if this is needed.
Fig 2: Recommend using shading for warm vs cool seasons.
Fig 3: Maybe also provide a map of the region?
Fig 6: When looking at this figure, 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 $\Delta^{17}O$ of atmospheric NO_3^- in general), if this were to be plotted against inverse concentration (e.g. a Keeling plot) could this be used to help bracket the endmember composition for a mixing model? I also recognize that the concentration of NO_3^- in precipitation results from more complex processes than simple mixing of two endmembers, but perhaps this could be a point off of which to build some discussion (just a thought).

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