Atmos. Chem. Phys. Discuss., 10, C12020–C12026, 2011
www.atmos-chem-phys-discuss.net/10/C12020/2011/

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 #1

1 General comments

Fang et al. present a new set of isotopic measurements of rainwater nitrate from an area subjected to significant anthropogenic influence. Concentration, δ15N and δ18O data are provided for two consecutive years (2008 and 2009), allowing the authors to i) attempt to derive seasonal patterns in the variations of δ15N and δ18O and ii) attempt to explore reasons for year-to-year variability. The paper is well written and the methods for chemical, isotopic analyses and their interpretation seem sound and wisely

used. My main concerns with this work, detailed below, pertains to the comparability of δ15N from various forms of "airborne reactive nitrogen", i.e., NOx, particulate or gas-phase nitrate, and nitrate found in precipitation, and the interpretation of δ18O variations through simplified mass-balance concepts.

Answer: We would like to extend our grateful thanks to you for your appreciation to our work and for your thorough, thought-provoking comments to our manuscript. All comments you raised, particularly the two main concerns, have been seriously taken into account when we revised the manuscript.

2 SpeciïňĄc comments

2.1 δ15N from NOx, particulate of gas-phase nitrate, and rainwater nitrate

Several publications have shown that δ15N of aerosol nitrate is very different from δ15N of rainwater nitrate at the same site. See e.g. a plot generated from the data presented in Freyer (1991), showing an offset on the order of 9‰ between rainwater and aerosol nitrate δ15N. In this case, aerosol δ15N is much higher than rainwater nitrate δ15N. Baker et al. (2007) reached opposite results from remote marine locations. This variable discrepancy was reviewed by Morin et al. (2009) (see in particular section 4.1.3). Caution is thus warranted when comparing δ15N data from different atmospheric matrices. In the ms, the authors often compare their δ15N values obtained from rainwater samples, to aerosol nitrate δ15N values. Before delving further into the interpretation of the data, the authors should make sure the reader is aware of this issue, which is not solved at the moment. This may have a signiïňĄcant impact on the interpretation of the results.

Answer: Thanks. This is a good concern. That was why we compared our results mainly with NO3- in wet deposition (precipitation) in the main text, although we also listed aerosol data in the table 4 (Appendix B in the revised version). In the revised manuscript, in order remind the readers of this issue, we have first added a line "Cautions may be needed when comparing δ15N data from different atmospheric matrices,

because the δ15N of aerosol NO3- is very different from that of rainwater NO3- in some studies (e.g., aerosol nitrate δ15N was 9‰ higher than rainwater nitrate δ15N in Julich, a moderately polluted city of German; Freyer, 1991, Appendix B) while is not in other studies (Baker et al., 2007; or see Morin et al., 2009)." Secondly, we have considered the table 4 as an appendix in the new version, and in the appendix we pointed out the atmospheric matrix clearly, such as precipitation, particulate, aerosol, or snowpack. Some results from other studies, including those from HNO3 vapor and snowpack have been listed in Table 4 (Appendix B in the revised version).

In addition, in response to the short comments from Prof. Savarino, in the revised manuscript we have presented the seasonal variations of concentration of O3, NO and NO2 during the study period and we conclude that "N isotopic exchange can not fully explain the observation in Guangzhou city". In details, please see the response to short comment or the revised manuscript).

2.2 Interpretation of δ18O of nitrate

δ18O is not an isotopic tracer that is conserved during chemical reactions, in contrast to Δ17O (the isotopic anomaly). Thus interpreting δ18O of nitrate for the contribution of various NOx oxidation pathways featuring different "δ18O signatures" is not entirely correct. The reason is that, unlike Δ17O, isotopic fractionation occurring at each step of any chemical mechanism can induce large variations between δ18O values of the reactants and the products (see e.g. Chakraborty and Chakraborty, 2003). The interpretation of seasonal variations of δ18O can therefore not be as detailed as could be the case with Δ17O. This must clearly be realized by the authors, and this point must be made clear to the reader. Along this line, references should be given to support the δ18O values provided for O3 and OH (e.g., page 21456, line 5). This may have a signiïňĄcant impact on the interpretation of the results.

Answer: Good. We agree. The references for δ18O of O3 and OH have been added in the revised manuscript. It is written now as "Using the minimum and maximum of δ18O

reported for O3 (+90 to +122‰ Krankowsky et al., 1995; Johnston and Thiemens, 1997) and OH (typically between -15‰ to 0‰ over the Asian continent, see maps from the Global Network of Isotopes in Precipitation, International Atomic Energy Agency, available at http://isohis.iaea.org), one can expect that the δ18O value of atmospheric NO3- will fall between +55‰ (assuming 2/3 oxygen atoms from O3 and 1/3 from OH) and +102‰ (assuming 5/6 oxygen atoms from O3 and 1/6 from OH) (see Hastings et al., 2003). As you will see, we have recalculated the expected minimum to be +55 in the revised manuscript, in response to the comment from reviewer #3. we have added a line "In this study, we observed that 18 samples (16% of the total samples) had δ18O values being lower than +55‰.The lowest was +33‰ (Fig. 1d), which, so far, is among the lowest ever reported in the world." (Discussion 4.4).

In order to make clear that the potential isotopic fractionation during each chemical pathway, we added a sentence there "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).". We have also modified other places of the discussion in the revised manuscript, for example, the calculation of expected minimum of δ18O of NO3- produced from the NO2 which is oxidized by peroxy radicals (Discussion 4.4).

3 Technical comments

page 21142, line 3 – 5 : to support statements relevant to the chemical oxidation pathways of NOx, one would expect references to standard atmospheric chemistry textbooks, such as Finlayson-Pitts and Pitts or Seinfeld and Pandis, rather than references to studies discussing isotopic measurements, as currently quoted.

Answer: Agree. Have done as suggested.

page 21442, line 6: "equilibrates" "equilibrates during the daytime"

Answer: Have done as suggested.

Page 21444, line 27: "lightning" should not be included in "biogenic emissions"

Answer: “lightning” has been deleted.

Page 21446, line 16: "mass-independent 17O anomaly" needs reformulation: mass independent fractionation (i.e., as a process) leads to a 17O anomaly, but the anomaly itself is not mass-independent, it is just an anomaly.

Answer: The sentences have been changed to be “Atmospheric NO3- is anomalously enriched in both the 18O/16O and 17O/16O isotopic ratios, due to the transfer from O3 to HNO3 during NOx oxidation reactions (Michalski et al., 2003). The use of the denitrifier method for δ15N measurements thus requires correction for the contribution of the mass-independent 14N-14N-17O (the m/z 45 signal) to the analyte N2O (see Hastings et al., 2003, 2004).”

Page 21446, line 20: "lowing" "lowering"

Answer: Done.

Page 21447, line 11: the stated lifetimes (1.2 and 0.27) should be supported by a reference. Also, such detailed numbers must refer to very speciïňĄc conditions. I recommend relaxing a little the accuracy of these numbers to make more general statements (or maybe rather give a range of accepted lifetime values).

Answer: Good. The lifetimes (1.2 and 0.27) have been removed in the revised manuscript. Page 21452, line 1: "(with 15N/14N ratio)" needs reformulation. It is not understood what is meant in this parenthesis.

Answer: Corrected to “with relatively high15N/14N ratio”.

Page 21454, line 15 : the denitriïňĄer method has currently been compared to other methods and showed no systematic bias, contrary to the tentative suspicion of such bias which was presented in Kendall et al. (2007). The relevant references are Chmura

et al. (2009) and Xue et al. (2010).

Answer: That statement has been removed now.

Page 21455, line 29: the large seasonal difference in δ18O was interpreted by Savarino et al. (2007) as a consequence of the role of stratospheric nitrate injection into the troposphere in late austral winter. Comparing this very different context to the seasonal variations found by the authors should thus be avoided.

Answer: One of the initial objectives of this study was to compare the seasonal variation found in a low latitude region with middle and high latitude regions. We agree that stratospheric nitrate injection into the troposphere in late austral winter in polar regions is very different from the setting in other seasons. Thus in the revised manuscript we modified our comparison: “. . .this difference is even greater than the seasonal difference of about 30‰ in coastal Antarctica when the austral later winter and early spring was excluded 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 (Savarino et al., 2007). . .”.

Page 21456, line 15 : "This pathway accounts for 4% of the annual inorganic NO3- on the global scale": this statement deserves more explanation (reference? origin of this assessment ? uncertainty ?)

Answer: It has been changed to “At night, NO3 can also react with dimethylsulfide (DMS) or hydrocarbons (HC), termed the NO3-+DMS/HC pathway here; this pathway accounts for 4% of the annual inorganic NO3- on the global scale based on a global model of Δ17O of atmospheric NO3- (Alexander et al., 2009)”. The work of Alexander et al. 2009 has been cited in the revised manuscript.

Page 21457, line 9: Hastings et al., 2003, is probably not an adequate reference to support the δ18O of atmosphere O2 (rather: Barkan and Luz, 2003).

Answer: We have changed it as suggested.

Page 21465, Table 1: Why are arithmetic means of $NO^{-}3$ presented? What is the value of such statistics ? The same applies to isotopic ratios. The authors should identify the most relevant kind of averaging method and use it consistently throughout the manuscript. For example, why are arithmetic averages presented in Table 2, rather than mass-weighted averages (which I understand the authors refer to "ïňĆux-weighted means", although I may be wrong here) ? To me mass-weighted averaged would make the most sense, especially when dealing with seasonal averages. This dampens the impact of isotopic outliers associated with low concentration levels.

Answer: Basically we agree. The reasons why arithmetic means of NO3- was presented 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 examined the season difference and source difference (Table 2 and Table 3); and 3) finally in many previous studied arithmetic means are presented rather than mass-weighted average. Thus the presentation on NO3- data remained unchanged in the revised version.

Page 21468, Table 4 : a few typos ("Aersol" "Aerosol", "Savario" "Savarino").

Answer: Done. Table 4 has been considered as an appendix in the revised version.

Please mention in the captions that isotopic ratios are expressed in ‰

Answer: Done.

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