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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.

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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, δ^{15}N and δ^{18}O data are provided for two consecutive years (2008 and 2009), allowing the authors to i) attempt to derive seasonal patterns in the variations of δ^{15}N and δ^{18}O 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 δ^{15}N from various forms of "airborne reactive nitrogen", i.e., NO_x, particulate or gas-phase nitrate, and nitrate found in precipitation, and the interpretation of δ^{18}O variations through simplified mass-balance concepts.

2 Specific comments

2.1 δ^{15}N from NO_x, particulate of gas-phase nitrate, and rainwater nitrate

Several publications have shown that δ^{15}N of aerosol nitrate is very different from δ^{15}N 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 δ^{15}N. In this case, aerosol δ^{15}N is much higher than rainwater nitrate δ^{15}N. 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 δ^{15}N data from different atmospheric matrices. In the ms, the authors often compare their δ^{15}N values obtained from rainwater samples, to aerosol nitrate δ^{15}N 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 significant impact on the interpretation of the results.

2.2 Interpretation of δ^{18}O of nitrate

δ^{18}O is not an isotopic tracer that is conserved during chemical reactions, in contrast to Δ^{17}O (the isotopic anomaly). Thus interpreting δ^{18}O of nitrate fro the contribution of various NO_x oxidation pathways featuring different "δ^{18}O signatures" is not entirely correct. The reason is that, unlike Δ^{17}O, isotopic fractionation occurring at each step

of any chemical mechanism can induce large variations between δ^{18}O values of the reactants and the products (see e.g. Chakraborty and Chakraborty, 2003). The interpretation of seasonal variations of δ^{18}O can therefore not be as detailed as could be the case with Δ^{17}O. 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 δ^{18}O values provided for O_3 and OH (e.g., page 21456, line 5). This may have a significant impact on the interpretation of the results.

3 Technical comments

page 21142, line 3 – 5 : to support statements relevant to the chemical oxidation pathways of NO_x, 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.

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

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

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

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

Page 21447, line 11 : the stated liftimes (1.2 and 0.27) should be supported by a reference. Also, such detailed numbers must refer to very specific 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).

Page 21452, line 1 : "(with ^{15}N/^{14}N ratio)" needs reformulation. It is not understood

what is meant in this parenthesis.

Page 21454, line 15 : the denitrifier 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).

Page 21455, line 29 : the large seasonal difference in δ^{18}O 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.

Page 21456, line 15 : "This pathway accounts for 4% of the annual inorganic NO_3^- on the global scale" : this statement deserves more explanation (reference ? origin of this assessment ? uncertainty ?)

Page 21457, line 9 : Hastings et al., 2003, is probably not an adequate refence to support the δ^{18}O of atmosphere O_2 (rather : Barkan and Luz, 2003).

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 "flux-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.

Page 21468, Table 4 : a few typos ("Aersol" → "Aerosol", "Savario" → "Savarino"). Please mention in the captions that isotopic ratios are expressed in ‰.

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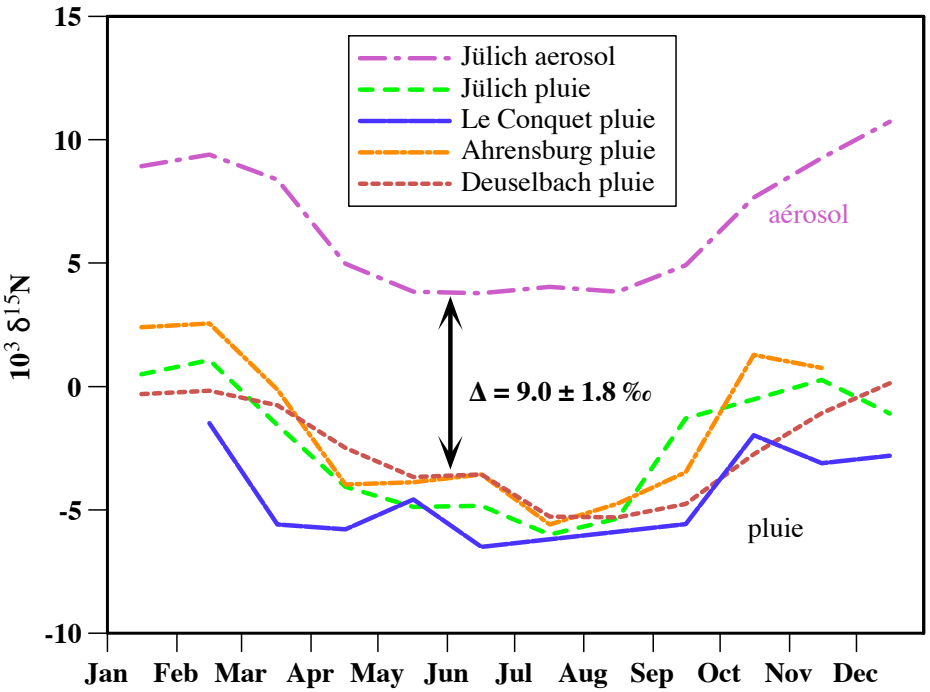

Fig. 1. Rain ("pluie") and aerosol d15N values from locations in Europe, from Freyer (1991), showing the large difference between d15N of aerosol and rainwater nitrate.