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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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We would like to thank Prof. Savarino for his rapid comments on our work. Our answers to his comments are given below.

I'm wondering if the authors have to opportunity to compare their 15N ratio with the NO2/NOx ratio in their urban site. Freyer et al., (jgr, 98, 14791, 1993) proposed an analytical approach focusing on the nitrogen isotopic exchange between NOx, limited by the photochemistry. Even if this paper treated the NOx species, a comparison with nitrate might be useful.

Answer: Freyer (1978, 1991) found higher 15N/14N ratios in atmospheric nitrate in

winter than in summer in Julich, a small city in Germany. Similar seasonal pattern was observed elsewhere (e.g., Pretoria in South Africa, Heaton, 1987). Higher 15N/14N ratios in winter was attributed to nitrogen isotope exchange between NO and NO2, which enriches 15N in the more oxidized form. This nitrogen isotope exchange occurs more likely in the seasons when the NO2/NOx ratio and O3 concentration is low, as demonstrated in the winter time at Julich (Freyer et al., 1993). In the case of our study site in Guangzhou city, we found that monthly mean NO2/NOx ranged from 0.6 to 0.76 in 2009, with a valley in summer (Fig. 1). We don't have NO data for 2008. But NO2 concentration was positively correlated to NO concentration in 2009 ($P < 0.001$, data not shown). Thus we can infer that NOx/O3 ratio may have a similar seasonal pattern as NO2/O3 during the study period. Low NO2/NOx and NOx/O3 ratios (favoring nitrogen isotopic exchange) in the summer of 2009 may partly explain relatively higher δ15N in precipitation NO3- during the same time period (Fig. 2c of our manuscript under review for ACP).

In 2008, we found higher δ15N values in precipitation NO3- in the winter at our study site, as observed at Julich. However, the seasonal patterns of NOx/O3 ratios, and NOx and O3 concentration (Fig. 1) are opposite to those at Julich where showed high NO2 fraction and high O3 but low NOx in summer. So nitrogen isotopic exchange can not explain the observation in Guangzhou city. We conclude that the seasonal pattern of δ15N values in precipitation NO3- may be mainly influenced by NOx sources, as seen in Bermuda (Hasting et al., 2003). We will add this this discussion to the revised version. Thanks.

Regarding their analytical method, I wonder if the difference in 18O of their rain water and the laboratory water used with their USGS standards can be the reason for their lower nitrate 18O. As writen, it appears to me than the oxygen exchange during incubation is not properly treated by their calibration method if sample and standard water matrix are different.

Answer: A good concern. We can rule out the influence induced by the difference

in 18O of their rain water and the laboratory water used with their USGS standards. The δ18O of H2O was measured to be -3 to -10‰ at a site, about 90 km west of Guangzhou city and average to around -6‰ in southern China (Liu et al., 2010), where our rain water samples were collected. In our laboratory (Tokyo, Japan) where isotope analysis was performed, δ18O of the laboratory water was about -8‰Ṡo we expect that the difference is two small to drop the δ18O of rain NO3-. This concern will be taken in the revision, however.

Also a small technical error, page 21455, line 20: "systematically lower" and not "systemically higher".

Answer: Thanks. It will be corrected.

References

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Additional information for Figure 1: Data is from http://www-app.gdepb.gov.cn/EQPublish/raqi.aspx).

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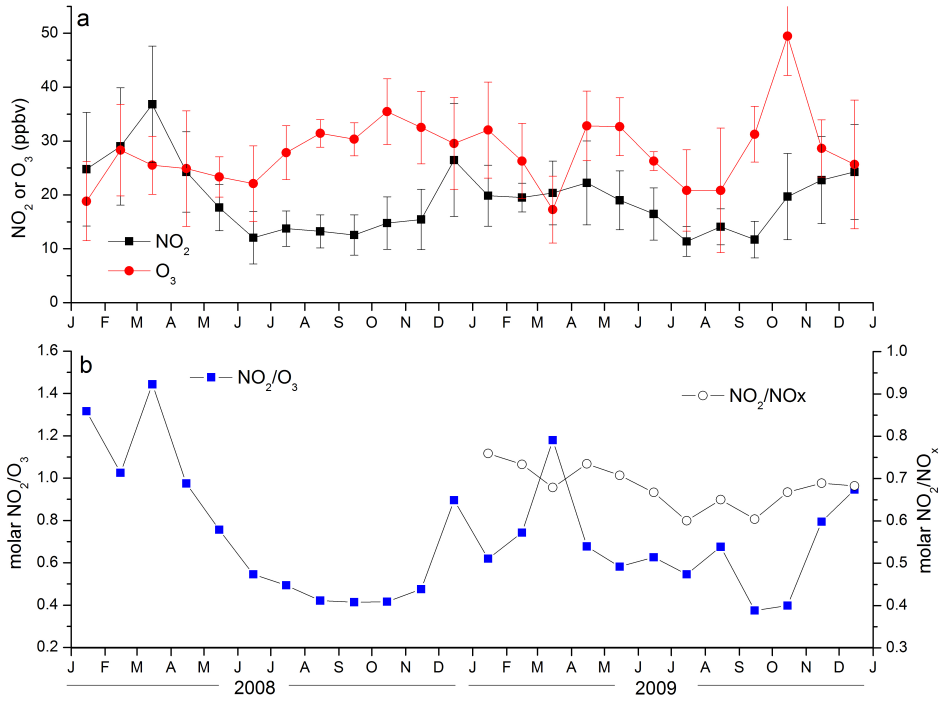

Fig. 1. Seasonal changes in NO2 and O3 concentrations (a, monthly mean of three monitoring site in Guangzhou), molar ratios of NO2/O3 and NO2/NOx during the study course in Guangzhou city.