

Estimation of particulate organic nitrates from thermodenuder-aerosol mass spectrometer measurements in North China Plain

General comments:

This work introduces a combination of thermodenuder technique and high-resolution aerosol mass spectrometry measurements (TD-AMS method) for quantifying particle-phase organic nitrates (pON) in North China Plain. The observations are compared with another two approaches, “NO_x method” and “PMF method”, that have been used for ambient pON quantification in previous studies. The TD-AMS method does not require any assumption of NO⁺/NO₂⁺ ratios of pON, which can be significantly different between secondary pON generated from different types of precursors and reaction conditions. The major uncertainties of the TD-AMS method is the assumption of pON volatility. This work fits into the scope of Atmospheric Measurement Techniques although more detail/quantitative discussion on the limitations and uncertainties of the TD-AMS method is required. It will be very beneficial to the scientific community if this work can provide some recommendation/pointers on the selection of appropriate method (among the three methods used in this work) for quantifying pON based on their ambient observations. The current form of discussion is a bit biased toward interpretation of pON formation chemistry and comparison with previous studies. Overall, I recommend this work to be considered for AMT publication after addressing the specific comments below.

Major comments:

- Introduction: The potential advantages of TD-AMS method (e.g., temporal variation of R_{ON} for better understanding of pON formation chemistry, etc.) that over NO_x and PMF methods should be clearly highlighted in the introduction.
- NO_x method: Page 4, Lines 2-6: The major reasons for the differences of R_{AN} between pure ammonium nitrate and ambient nitrate should be provided. Does this observation imply that ammonium nitrate was not the major contributor of NO_x⁺ signals during the “high NO₃” periods? What were the average organic aerosol mass loadings during the “high NO₃” periods and how organic aerosol signals at m/z 30 and 46 may affect the accuracy of NO_x⁺ peak fitting? Please define R_{AN} and R_{ON} in this paragraph.
- PMF method: Page 4, second paragraph: (1) although the detailed PMF analysis is not the focus of this work, it is recommended to provide a brief description on how the inclusion of NO⁺ and NO₂⁺ signals may affect the PMF results interpretation. (2) Lines 13-16: It is unclear whether the reported values of RIE and CE were applied to PMF method only or all the three methods.
- TD-AMS method: (1) The two major assumptions of the TD-AMS method are a) complete evaporation of inorganic nitrates at 90°C and b) the mass fraction remaining of CHN and CHNO fragments equal to that of total pON. To be considered for AMT publication, it is particularly important to provide more quantitative description on the uncertainties of TD-AMS method due to these major assumptions and/or conduct sensitivity tests for the related calculation parameters in order to evaluate the performance of TD-AMS method. (2) Page 4, Lines 25-26: Ambient NO_x⁺ signals can be from both inorganic and organic nitrate so that the argument of pON dominated the total particulate organic nitrogen compounds in NCP is not well supported. (3) Page 5, Lines 3-4: Please elaborate how mixing state of aerosol particles can affect vaporization temperature of inorganic nitrate. (4) Page 5, Line 16-17: The values of R_{AN} were determined by ambient NO⁺/NO₂⁺ ratios instead of ammonium nitrate as

discussed in the NO_x method. It is unclear whether the values of R_{AN} were determined in the same way for both NO_x and TD-AMS methods. If so, it is misleading to subscript “AN” along the discussion in this section.

- Page 7, Line 1: It seems that the PMF method only include NO⁺ and NO₂⁺ signals from SOA factors for pON quantification. However, chemical composition of “POA” factors can be affected by atmospheric aging. Please clarify. This also highlight the importance of including some detail of PMF method in the experimental section.
- Page 7, Line 19-10: Please specify the type of anthropogenic emissions at rural site that are much higher than those observed at urban site.
- Page 8, Lines 18-20: Were the averaged $R_{ON,Cal}$ values between day and night time significantly different in statistical point of view? Please provide standard deviations for the $R_{ON,Cal}$ as well. It is recommended to add diurnal patterns of $R_{ON,cal}$ in Figure 3.
- Section 3.3 and Figure 4: Substantial increase of pON was observed at high mass loadings in Beijing winter (Figure 4b). Please elaborate more on this observation.

Minor comments:

- Figure S2-S3: The resolution of these figures are too low.
- Page 4, line 25: Please specify the panels of Figure 1 that are referring.