

Review of Zhang et al. entitled "Particulate organic nitrates in eastern china: variation characteristics and effects of anthropogenic activities"

This study presents the measurements of six different organic nitrates in the particle phase in places in China that are representative of both urban and rural environments. The levels and diurnal patterns of these nitrates are reported and their correlations with other factors such as meteorological conditions and anthropogenic tracers are discussed. Overall, the paper is clearly written and reports the measurements of a very important SOA constituent in China. However, one is left with an impression that the manuscript is simply reporting values and numbers other than a thorough analysis of the sources and transformations of these organic nitrates in the atmosphere. Prior to publication the authors should endeavor to provide a more mechanistic and quantitative discussion about various physical and chemical conditions/factors associated with the observed patterns of organic nitrates at different sampling sites.

General:

The manuscript has been largely improved in terms of the identification of organic nitrates using tandem mass spectrometry techniques. The observations of neutral losses of NO₂ and HNO₃ upon fragmentation of the parent ions certainly provide strong evidence for the presence of the -ONO₂ functional group in the analytes of interest. The quantification of organic nitrates, however, is a big limiting factor in the accuracy and reliability of the data presented here. While I understand that the authentic standards for most nitrates studied here are not available (not all of them though, some monoterpene derived nitrates can be synthesized), using surrogates as an alternative could certainly bring large uncertainties to the measurements, which need to be assessed carefully. Specifically, one important question to answer is that is the electrospray ionization efficiency of the surrogates (depends on which functional group is ionized) on the same order of magnitude as the compound of interest?

The authors have spent almost the entire text describing the measurements of individual organic nitrates at different sampling sites: their concentrations during the day and nighttime, mass fractions in the total organic matters, and their correlations with other trace species like SO₂. However, a mechanistic and quantitative exploration of the temporal variations and spatial distributions of different nitrates is lacking. A couple of examples:

1. The entire section of 3.2 'Diurnal difference of PONs' centers on discussing the different concentrations and patterns of organic nitrates in the day vs. night at different sampling sites. However, the mechanisms leading to such a pattern are barely explored. Figure 3 shows that the nighttime concentrations of MHN215 and PKN229 are only half of their daytime concentrations,

in contrast to almost all the other cases where the daytime and nighttime nitrate concentrations are quite comparable. It is well known that organic nitrates can be produced from NO₃-initiated dark chemistry. A simple correlation analysis performed here does not provide any quantitative insights into the role of nighttime chemistry in the observed diurnal pattern of nitrates. The authors are suggested to do some calculations based on the NO_x and O₃ measurements to assess the intensities of nighttime chemistry (including both ozonolysis and NO₃ oxidation) at different observational sites. Such a calculation is the first step to evaluate the contribution of nighttime chemistry to the production of organic nitrates.

2. The authors observed a positive correlation between organic nitrates and SO₂ and attributed such a correlation to that reactions of SO₂ with stabilized Criegee intermediates produced from ozonolysis of monoterpenes could potentially promote the formation of organic nitrates. Such a conclusion is rather hasty and needs further observational evidence as support. The authors need to first consider: Are there any positive correlations between organic nitrates and other anthropogenic tracers such as NO_x and CO? Are the temporal variations of organic nitrates simply a result of a sequence of pollution episodes caused by for example, high emissions or stagnant meteorological conditions? Furthermore, it is very important to keep in mind that the products from SCI+SO₂ reactions are not necessarily low in vapor pressure and thus constituting potential precursors of SOA, not to mention that the stable products from SCI+SO₂ reactions do not contain any -ONO₂ functional groups and further oxidation steps are required to produce organic nitrates. Such a hypothetical reaction scheme is inconsistent with the chemical structures proposed for each nitrate listed in Table 1, which suggest that most organic nitrates identified, at least those monoterpene derived nitrates, are first generation products from OH/NO₃ initiated oxidation of monoterpenes.

Specific:

Page 1, Line 25-30: Please carefully evaluate whether or not the SCI+SO₂ reactions are associated with the observed nitrate production in the particle phase.

Page 2, Line 42: Clarify here oleic acid is mostly of anthropogenic origin.

Page 2, Line 49: Compounds with low vapor pressure are more likely condensing to particle phase and thus recognized as potential SOA precursor.

Page 2, Line 51: The references cited here are for the organic sulfate formation under acidic conditions, not nitrates.

Page 4, Line 139: Methanol is considered a very polar solvent, similar to water. Have the authors found any evidence of nitrate hydrolysis in pure methanol solvent? Have the authors tried to use

some nonpolar solvents such as acetonitrile? Any difference in terms of the quantification of organic nitrates?

Page 5, Line 160-165: Please explain why some nitrates have neutral losses of NO₂ while others have HNO₃ losses upon fragmentation?

Page 7, Line 280-285: Unless the measured nitrates are representative of unique tracers of coal burning aerosols, or other identified tracers of coal burning exhibited strong correlations with the nitrates, it is otherwise an invalid conclusion that the increase of PONs is due to coal burning activities.

Page 9, Line 330: The association of organic nitrate with the inorganic components in the particle phase does not necessarily establish any causal relationships. If it is the salting in effect as proposed by the authors, please provide some quantitative evidence.

Page 9, Line 360-365: Again, a positive correlation of RHs with organic nitrates in the particle phase does not necessarily establish any causal relationship. High RHs may just simply promote the photochemistry by generating more OH radicals, or high RHs is likely associated with a pollution episode. Keep in mind that the deliquescence RHs for various inorganic components in the particle phase are essential in determining the aerosol water content and its role in dissolving more water-soluble compounds (caution that some organic nitrates investigated in this study are not considered highly water soluble).

Page 18, Figure 2: In addition to the proportion of each organic nitrate species, please also show the total OM mass at different sampling sites.

Page 21, Figure 7: Please change the color code for PKN229 and LDKN247. It is hard to differentiate these two species based on the current blue hues.