Author's Response

Particulate-bound alkyl nitrate pollution and formation mechanisms in Beijing, China

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Editor Comment:

1.) Please comment on the fact that the alkyl nitrates range in the 1 ng/m3 range while the total aerosol accounts for >100 ug/m3. Please state clearly that these compounds do only account for 0.001% of the total PM. Please discuss the relevance of this minute contribution to PM as well as this very small contribution with respect to the statement in line 73 that ON typically make up 5 to 43% of the organic matter and the statement of a "key role of particulate-bound ONs" (line 79).

2.) Please reconsider item 11) of referee #3. Plotting the concentrations in log-scale would be very interesting if the DL is indeed 1 pg/m3.

Technical comments:
l. 48: change to "more oxidation potentially occurs"
l. 123: change to "in Beijing, which tend to be..."
l. 143 and other occasions: change "mass spectorgraphs" to "mass spectra"
l. 145 change "irons" to "ions"
l. 171 change "Method and spiked..." to "Measured and spiked ..."
l. 203 "single functional group"
l. 231 "the influencing factors and the mechanisms..."
l. 253 "high partitioning coefficient"
l. 297 "and may form..."
l. 298 "Research has shown...
l. 306 Please check numbering of Figures in the text: PM2.5 is shown in Fig 4 not Fig 6
l. 331 "we hypothesize"
l. 339 check numbering: NO2 is shown in Fig 6.
l. 348 "mean that particulate-phase..."
l. 356 "may form"

the formation
l. 357-358: "However, the formation mechanism needs further study."
l. 369 check numbering of Figure.
l. 376 check numbering of Figure.
l. 391 "we conclude ..."
l. 394 this is a Summary not Conclusions
Table 1: does it make sense to show the data with two significant digits?

Author's response:

Dear editor:
Thank you for your constructive comments and detailed revisions on our manuscript. We have carefully considered the suggestions and made some changes on the details of the manuscript accordingly. We have tried our best to improve this manuscript in order to it can be published successfully, please find our itemized responses and our revisions/corrections in below.

1.) Please comment on the fact that the alkyl nitrates range in the 1 ng/m3 range while the total aerosol accounts for >100 ug/m3. Please state clearly that these compounds do only account for 0.001% of the total PM. Please discuss the relevance of this minute contribution to PM as well as this very small contribution with respect to the statement in line 73 that ON typically make up 5 to 43% of the organic matter and the statement of a "key role of particulate-bound ONs" (line 79).

Reply: Thank you for your suggestions. We will revise the manuscript accordingly based on your comments. Although it was found in our study that the mass of C_9-C_{16} particulate-bound *n*-alkyl nitrates only account for 1‰ of $PM_{2.5}$, however C_9-C_{16} *n*-alkyl nitrates are only a little part of particulate-bound alkyl nitrates. Base on the pollution characteristics and trends of particulate-bound alkyl nitrates represented by C_9-C_{16} *n*-alkyl nitrates in this study, considering that there is a strong correlation between NOx, particulate-bound alkyl nitrates and $PM_{2.5}$, there are so many other particulate-bound alkyl nitrates that are unstudied and need further study. We think the effect of particulate-bound alkyl nitrates on $PM_{2.5}$ and haze formation should not be neglected and this research can provide a reference about the pollution characteristics of particulate-bound organic nitrates formed from anthropogenic emission sources and their contribution to particulate matter.

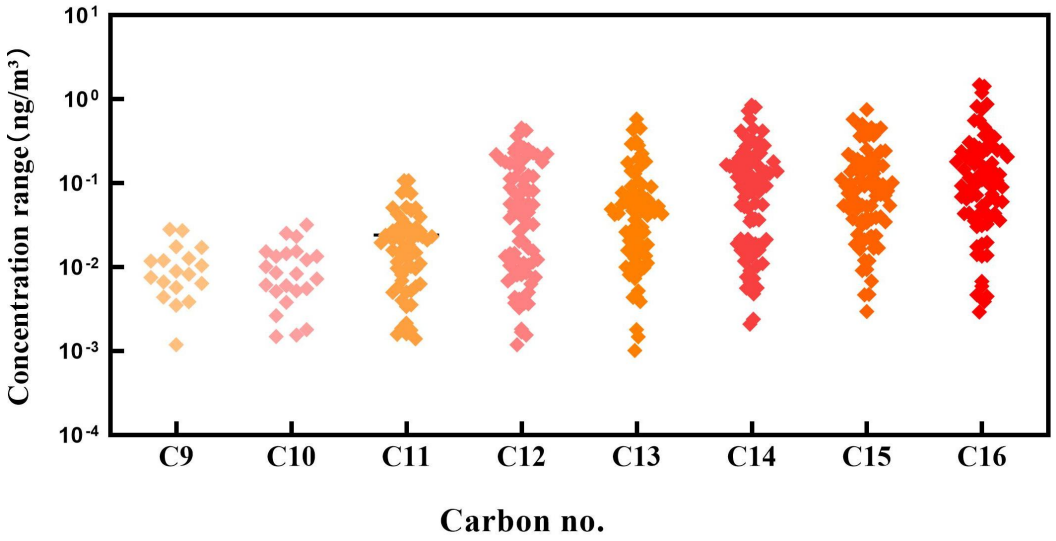
Modification: We have revised the manuscript accordingly based on your comments in Section 3.3 (**L388-402:** According to previous studies, organic nitrates make an important contribution to total aerosols (Xu et al., 2015) and particulate-bound ONs have a significant correlation with SOAs (Yu et al., 2019). Although it was found in our study that the mass of C_9-C_{16} particulate-bound *n*-alkyl nitrates accounts for only a small fraction of $PM_{2.5}$ (about 1‰), they are only a small part of particulate-bound alkyl nitrates. Considering the different carbon chain lengths, carbon frame structures and functional group substitution positions, etc., as well as isomers, and the pollution

characteristics and trends of C_9-C_{16} *n*-alkyl nitrates, we believe that the effect of particulate-bound alkyl nitrates on $PM_{2.5}$ and haze formation should not be neglected. In addition, studies have shown that NOx is the key factor in the formation of atmospheric aerosols (Rollins et al., 2012), the formation of alkyl nitrates is one of the major pathways for the conversion of NOx from radical forms into semi-permanent reservoirs (Shepson, 2007). At high NOx concentrations, the oxidation of hydrocarbon compounds in urban areas produces more than 100 different alkyl nitrates (Calvert and Madronich, 1987), Atherton and Penner calculated from model simulations that 5% of NOx can be converted to alkyl nitrates (Atherton and Penner, 1988). Therefore, we conclude that there is a strong correlation between NOx, particulate-bound alkyl nitrates and $PM_{2.5}$.).

2.) Please reconsider item 11) of referee #3. Plotting the concentrations in log-scale would be very interesting if the DL is indeed 1 pg/m3.

Reply: Thank you for your suggestions. In order to reflect the magnitude differences between the concentrations of the samples, we will plot the concentrations in log-scale in Figure 4 according to your comment.

Modification: We have modified the Figure 4 (**L678**).



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Reply: Thank you for your comments, we will modify our manuscript according to your suggestions in the appropriate places of the article and revise the data in Table 1 from retain two digits after the decimal point to three significant digits.

Modification: We have modified the manuscript base on technical comments (**L48:** more oxidation potentially occurs; **L124:** in Beijing, which tend to be; **L144&L147:** mass spectra; **L146:** ions; **L172:** Measured and spiked; **L204:** single functional group; **L232:** the influencing factors and the mechanisms; **L254:** high partitioning coefficient; **L298:** and may form; **L299:** Research has shown; **L307:** Figure 4; **L331-332:** we hypothesize; **L340:** Figure 6; **L349:** mean that particulate-phase nitrate; **L357:** may form; **L358-359:** However, the formation mechanism needs further study; **L370:** Figure 4; **L377:** Figure 7; **L401:** we conclude; **L406:** Summary) and revised the Table 1 (**L711**).

We would like to thank you again for taking the time to review our manuscript.

Reference:

Atherton, C. S. and Penner, J. E.: The transformation of nitrogen oxides in the polluted troposphere, Tellus B, 40, 380, doi: 10.3402/tellusb.v40i5.16003, 1988.

Calvert, J. G., and Madronich, S.: Theoretical study of the initial products of the atmospheric oxidation of hydrocarbons, J. Geophys. Res. Atmos., 92, 2211-2220, doi: 10.1029/JD092iD02p02211, 1987.

Shepson, P. B.: Organic nitrates, Volatile Org. Compd. Atmos., 269-291, doi: 10.1002/9780470988657.ch7, 2007.