Responses to review comments-2 (RC2, by the Anonymous Referee #1)

General comments

This work conducted comprehensive analyses for organic nitrates in ambient PM2.5 samples. The authors take advantage of the availability of PM2.5 samples collected in four different sites in China and aim to identify major influential factors on organic nitrates formation in the different atmospheric environments through examining correlation relationship with organic nitrates and some co-emitted species.

However, this manuscript is just simply reporting the semi-quantified data of organic nitrates without any convincing and direct evidence to show the influence of anthropogenic pollutants to organic nitrates. This paper just provided non-robust discussion to support the previous reported results without any creative design and idea. Although the authors have the data from four different sites, the limited sample numbers cannot provide typical seasonal or diurnal information. They need a large dataset to prove their conclusions. Therefore, based on the significant weaknesses described above, publication is not recommended.

Response: organic nitrates, produced via complex and ambiguous mechanisms, are important components of secondary organic aerosol. Since most authentic standards are not commercially available at present, it becomes a common quantitative method to capture the specific organic nitrate concentrations by using surrogate standards for research purposes. Currently, only a few articles presented the characteristics of organic nitrates in the real atmosphere at the molecular level, especially in polluted atmospheric environment in eastern China. In this work, we determined six kinds of monoterpene and oleic acid-derived organic nitrates and revealed their variation characteristics in the environment with high biogenic and anthropogenic emissions in eastern China. Further analyses with the assistant of backward trajectories and tracers for biomass burning and coal combustion confirm the effects of anthropogenic activities on organic nitrates. Coal combustion for industrial production and residential heating, via CIs+SO_2 and acid catalytic-reactions, possibly plays a greater role in the formation of organic nitrates than the previously assumed. In addition, 34 more samples have been supplemented in the revised manuscript to provide more reliable variation trends.

Specific comments

1. Line 114: Please provide sample numbers for each sampling site.

Response: the sample numbers have been added in Table 1.

2. Line 176: The author mentioned that they employed surrogates to semi-quantify organic nitrates. The employment of surrogates that even don't contain the nitrooxy group would introduce large uncertainty for accurate quantification of organic nitrates because the different functional groups can

introduce large differences for MS response. The authors even used different surrogates for different kind of organic nitrates but compared with the data together. The authors should find some methods to decrease the discrepancy or try to evaluate the uncertainty.

Response: the responses of n-pentane, amyl nitrate, isosorbide, and isosorbide 5-nitrate in the mass spectrometer have been measured. The results show that the difference in the response caused by the nitrate functional groups is smaller than one order of magnitude. Specifically, the difference in the response between n-pentane and amyl nitrate is 60.9% ±7.2% and the difference between isosorbide and isosorbide 5-nitrate is 66.6% ±2.7%. Indeed, there is an inherent difference in the responses of surrogate standards and analytes. However, the nitrate group does not cause a difference more than one order of magnitude. In this study, the structures and the retention time of the surrogate standards we selected are very close to those of analytes. Therefore, in our view the concentrations of organic nitrates can be estimated reasonably and further used for exploring the variation characteristics.

The contents of comparisons among PON concentrations quantified with different surrogates have been modified in the revised manuscript. The revised descriptions are as follows.

Line 202–205, "*Among these monoterpene-derived organic nitrates, MHN215 was the dominant species, with an average concentration of 51.9–212 ng m*$^{-3}$*, followed by PKN229 (10.0–113 ng m*$^{-3}$*), HDCN247 (9.5–21.6 ng m*$^{-3}$*) and PSON295 (3.1–9.6 ng m*$^{-3}$*). Among the oleic acid-derived organic nitrates, the average concentration of OAKN359 (34.1–146 ng m*$^{-3}$*) was much higher thanOAHN361 (0.7–4.1 ng m*$^{-3}$*).*"

Line 244–245, "*The large proportion of monoterpene-derived organic nitrates in PONs was also observed in southeastern United States (23–44% in mole) and in East Asia (Ayres et al., 2015; Lin et al., 2012)*"

The following description has been removed from the manuscript.

Line 225–226 in the original manuscript: "*MHN215 constituted the largest fraction of the identified PONs at all four sampling sites, accounting for 35–58%, followed by OAKN359 and PKN229.*"

In addition, we calculate the uncertainty of recovery and repeatability to measure the uncertainty in the detection. The results are as follows and have been added to the revised version.

Line 183–185, "*Based on the uncertainty in the recovery (±12.7%) and the repeatability (±4.1%), the overall uncertainty for the measurements was estimated to be 13.3%.*"

3. Line 184, the authors provided the recoveries for surrogate standards with only 60%. Based on my knowledge, the recoveries should in +- 20% to prove the effectiveness of an extraction method.

Response: the recoveries obtained in this study to some extent depend on the molecular type of the target compounds. In the previous study, the recoveries of some similar organic acid, such as pinic acid, pinonic acid, and camphor sulphonic acid, were about 74% (Kristensen and Glasius, 2011). In this study, we have updated the recoveries for surrogate standards and evaluated the uncertainty based on a large number of recovery experiments. The following information has been updated and added in the revised manuscript.

Line 182–183, "*Recoveries of (1R, 2R, 5R)–(+)-2-hydroxy-3-pinanone, ricinoleic acid, and (-)-10-camphor sulfonic acid in six spiked samples were 71 ±9%, 64 ±4%, and 78 ±4%, respectively*."

4. Line 188, please provide the comparison chromatogram between LC/orbitrap MS and LC/Iontrap MS.

Response: the extracts of the collected PM$_{2.5}$ samples were analyzed partly by the LC/TSQ MS and partly by the LC/Orbitrap MS. The chromatograms have been added in Fig. S1 in the supporting information.

Line 191–195, "*In addition, the extracts of PM$_{2.5}$ samples were analyzed partly by the triple quadrupole tandem mass spectrometer and partly by the Orbitrap mass spectrometer (chromatograms can be seen in Fig. S1). The determination results from both mass spectrometers for the same samples showed good consistency, indicating the reliability of the quantifications of organic nitrates from the low-resolution triple quadrupole tandem mass spectrometer.*"

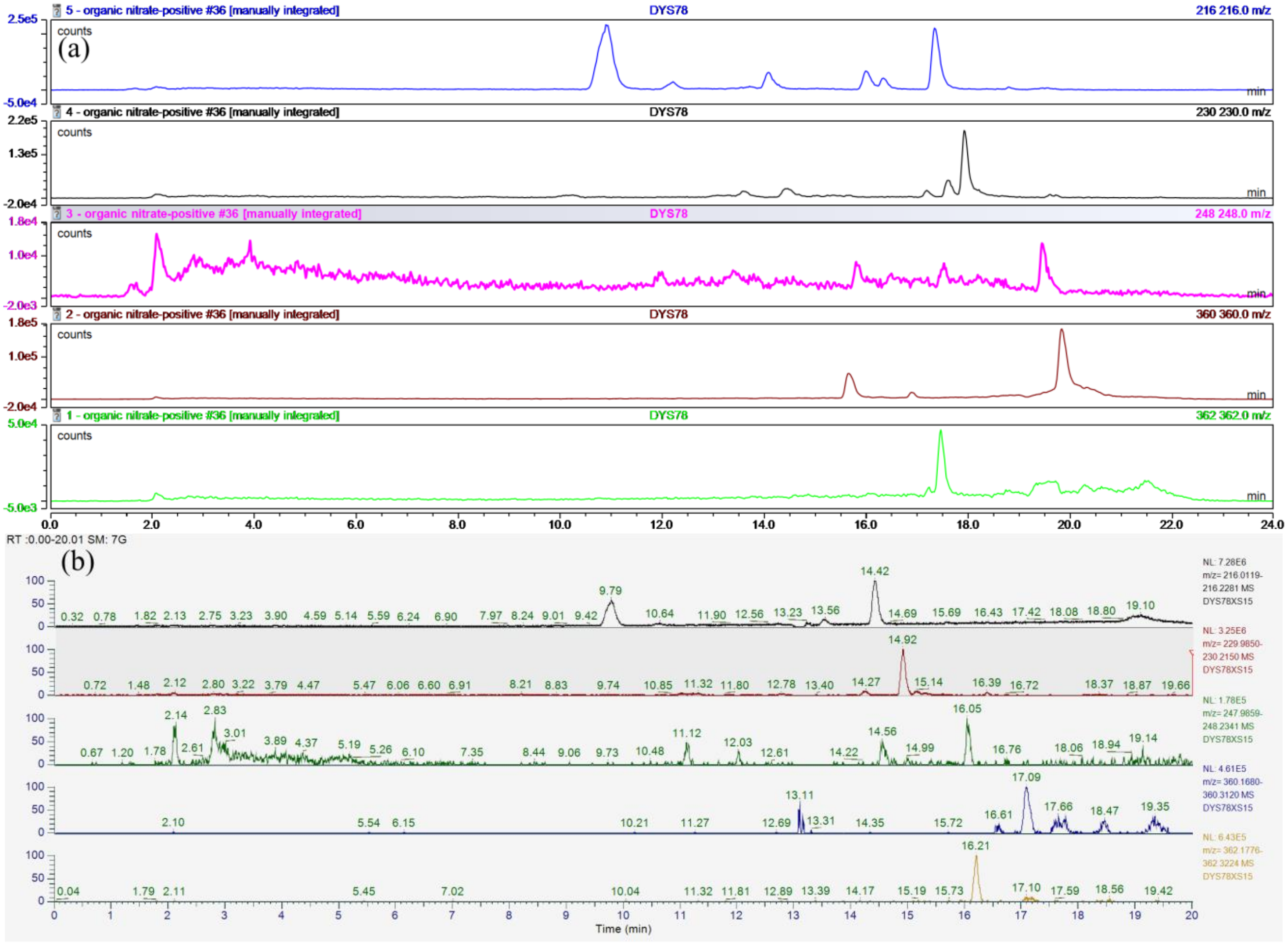


Figure S1. Chromatograms of ambient $PM_{2.5}$ samples for (a) ultra-performance liquid chromatography coupled with electrospray ionization and triple quadrupole tandem mass spectrometry and (b) ultra-high performance liquid chromatography equipped with electrospray ionization and orbitrap mass spectrometry.

5. Line 215, it mentioned: "increased emission of BVOCs in summer facilitated the secondary formation of PONSs." It's better to show some VOCs data, including such as isoprene, monoterpene and etc. If the authors didn't have detected data for their sites, maybe they can find some reported data near their sites. Still, the very limited number of samples in DY summer and winter may difficult to provide typical seasonal contrast (N~15). Because based on some work on monoterpene derived organosulfates, the formation of them may be more related to anthropogenic pollutions with a higher level in winter than in summer.

Response: At the DY site in winter and summer, we collected VOCs samples and subsequently detected the concentrations of isoprene. The data of isoprene has been shown in Fig. S2. Although the sampling periods of VOCs and $PM_{2.5}$ did not entirely overlap, it can still indicate the seasonal difference in BVOCs emission and the ambient concentration at the DY site, i.e., the concentration of isoprene in summer is 19 times higher than that in winter.

After additional data of $PM_{2.5}$ samples were supplemented, there were 26 and 21 samples at the DY site in summer and winter, respectively. Here we wanted to demonstrate that two factors likely affected the formation and concentrations of organic nitrates. One factor is "*the intense photochemical activities (e.g. 71.2 ppb of ozone)*" which was linked to biomass burning and was discussed in detail in section 3.3.2. The other factor is "*the increased emission of BVOCs*" which was partially caused by biomass burning and partially due to the abundant biological resources and high temperature in summer.

Line 225–226, "*the intense photochemical activities (e.g. 71.2 ppb of ozone) and increased emission of BVOCs in summer (see Fig. S2) facilitated the secondary formation of PONs.*"

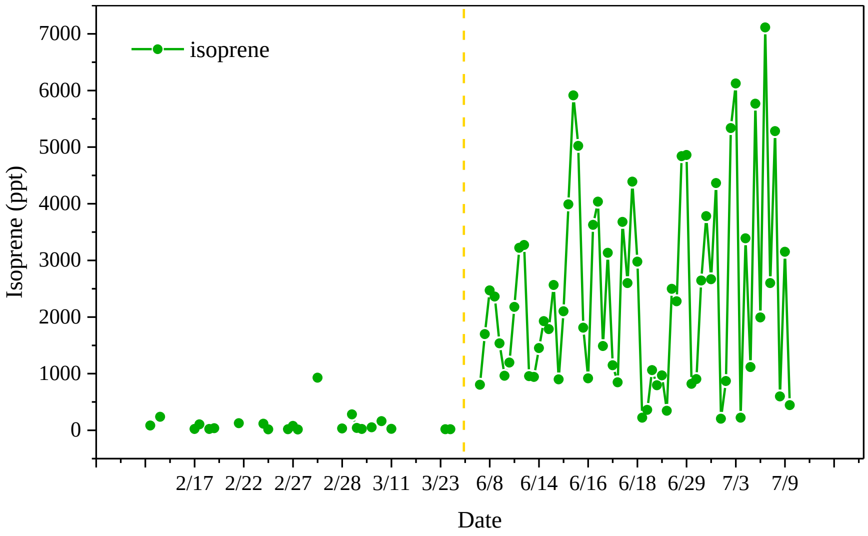


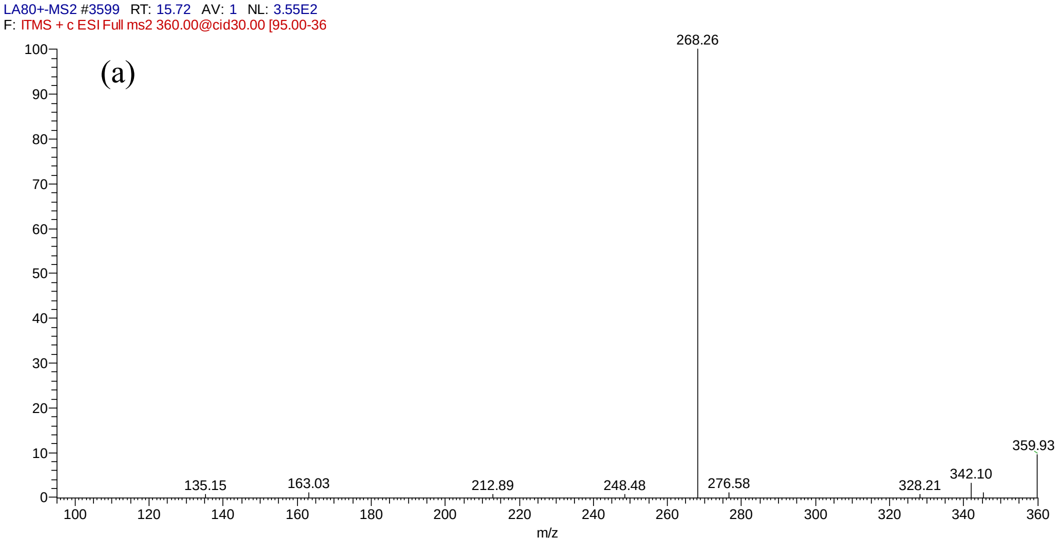
Figure S2. Comparison of isoprene concentrations in winter and summer at the DY site.

6. Line 243, the author detected the higher concentration of OAKN 359 (~100 ng/m^3), OAHN 361 based on surrogate standard and got the conclusion that significant influence of cooking and oil processing on the SOA in urban and rural areas in eastern China. First, the authors don’t know the difference of MS response; therefore, it is possible that these compounds can have the large MS response but deficient concentration. Second, it’s better to provide the MS/MS spectrum to prove MW 359 and MW 361 compounds share the same carbon skeleton with oleic acid.

Response: the related sentence has been modified as follows.

Line 223–225, “*The identification and quantification of oleic acid-derived organic nitrates in this study confirm that the impact of cooking and oil processing on SOA in urban areas is more significant than that in rural areas in eastern China.*”

As shown in Figure R2, the MS/MS spectrum of MW 359 exhibits signal peaks at m/z 342 and m/z 268 and 264 from the molecular ion and the fragments which are formed by loss of H_2O and HNO_3+C_2H_5, respectively. The MS/MS spectrum of MW 361 exhibits signal peaks at m/z 344, m/z 300, and m/z 256 which are formed by loss of H_2O, NO_3, and NO_3+CO_2, respectively. Similarly, as reported by the Human Metabolome Database (HMDB) (Wishart et al. 2017) (see Fig. R2), the MS/MS spectrum of ricinoleic acid exhibits peaks at m/z 279 and m/z 235 which are formed by loss of H_2O and CO_2, respectively. In spite of the above MS/MS spectrum information, it is rare to use the MS/MS spectrum to confirm the carbon skeleton, because the MS/MS spectrum mainly provides the information of characteristic functional groups. In addition, it is not suitable to determine the carbon skeleton by nuclear magnetic resonance (NMR), because the sample solutions are mixed with many kinds of organic compounds. In this study, the structure of MW 359 and MW 361 are identified by the molecular weights and the characteristic fragments reported by Docherty and Ziemann (2006).



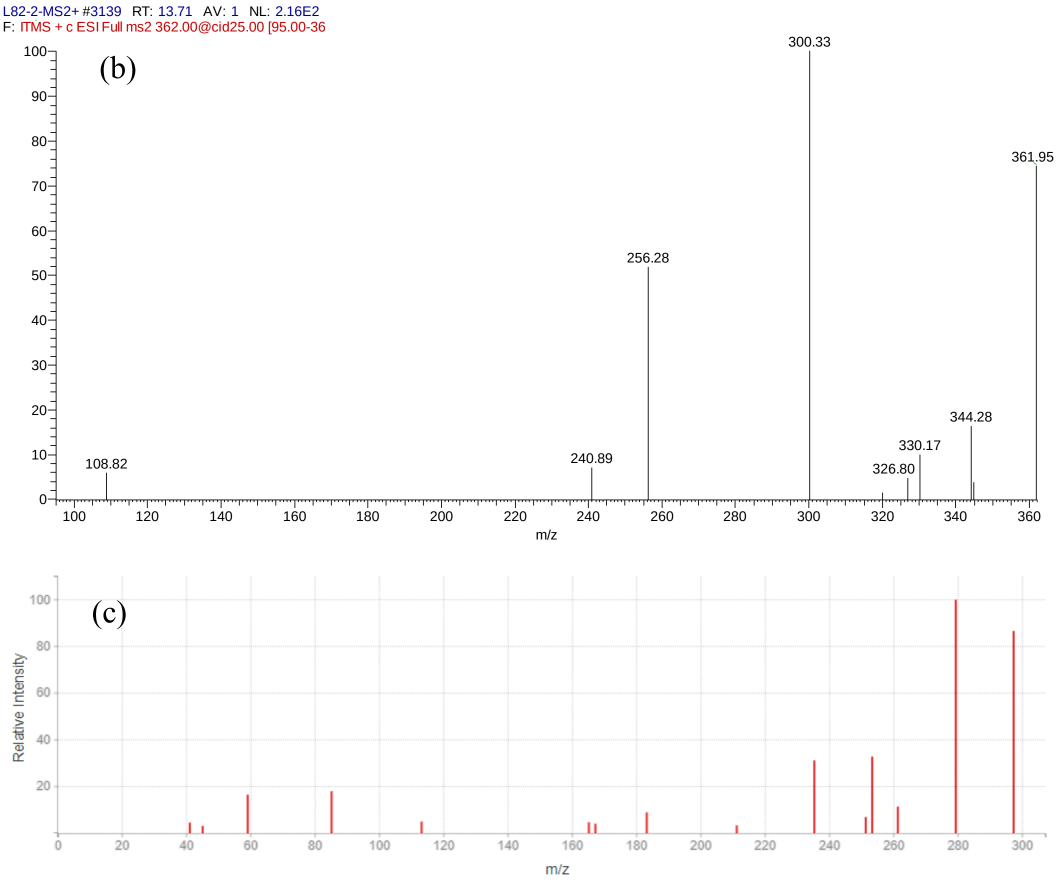


Figure R2. The MS/MS spectrum of (a) MW 359, (b) MW 361, and (c) ricinoleic acid (Wishart et al., 2017).

7. In section 3.3.1, the author showed a strong correlation with SO_2 and LDKN 247 and got the conclusion that SO_2 promotes the formation of LDKN 247 through limonene CIs. First, please exclude the possibility of transportation that can lead to the strong correlation as well. Second, MW 247 organic nitrates can form from β-pinene (Clafin and Ziemann, JPCA, 2018) with two carbonyl groups, one hydroxyl group and one nitrooxy group. However, there's no research reported the β-pinene could react with SO_2 or O_3 to generate CIs. And the emission of β-pinene is larger than limonene.

Response: we estimated the concentration of PONs after removal of transportation impact, the moderately strong correlation between the estimated locally formed PONs and SO_2 confirm the large impact of coal combustion on the formation of PONs. The estimation method and the added discussion are as follows.

Line 334–342, "*At the DY site in winter, PONs was moderately correlated with CO ($r = 0.61$, $p < 0.01$, see Fig. 6 (c)), which indicates that the transport possibly had an effect on the concentration of PONs. However, the relationship between PONs and NO_2 or CO was negligible or weak ($r = 0.17$, $p < 0.41$ and $r = 0.43$, $p < 0.05$, respectively) at the JN site. It means that transport was not the controlling factor* *for the strong correlation between PONs and SO_2. With an assumption that the PONs were partly affected by transport and this portion was linked to the CO concentration, the PONs associated with air mass transport was roughly estimated by $[PONs]_{trans}=69.27\times[CO]+55.38$. The locally produced PONs was then approximated by subtracting this part from transport. As shown in Fig. 6 (d), the moderately strong correlation between locally formed PONs and SO_2 confirms the large effect of coal combustion on the formation of PONs during the measurement periods.*"

8. We thank the reviewer for the helpful information about another possible generation pathway of LDKN 247. As stated in Clafin and Ziemann (2018), they identified the formation of LDKN 247 from β-pinene which was initiated by NO_3 in an environmental chamber, with a mole fraction of 7.7%. Noticeably, the proportion of LDKN 247 is not high and it may be even lower in the real complex atmosphere. Another limitation for the formation of LDKN 247 from β-pinene is that only nocturnal process was studied and there is no evidence for the daytime generation. Therefore, it still needs further investigations to confirm the contribution to LDKN 247 in the ambient air. The hypothesis that we propose here for the reaction of SO_2 and pinene-derived CIs is based on the similar ring structure and carbon-carbon double bonds of pinene and limonene. Furthermore, many organic nitrates detected in our study are derived from both α- and β-pinene, and the emission of α-pinene is much higher than β-pinene (Cheng et al., 2018). In the revised manuscript, the reference of Clafin and Ziemann (2018) has been added in Table 2 and the name of LDKN 247 has been changed to hydroxydicarbonyl nitrate (HDCN 247) in order to avoid misleading.Line 354, please provide the previous research to support that BB can lead to more VOCs emission.

Response: as shown in Figure R3, higher concentrations of ambient isoprene were observed during the periods of biomass burning than usual, indicating the intensive emissions of BVOCs from biomass burning. Two related references have been added in the revised manuscript.

Line 397–398, "*biomass burning also led to increased emissions of BVOCs (Andreae and Merlet, 2001; Xu et al., 2018)*"

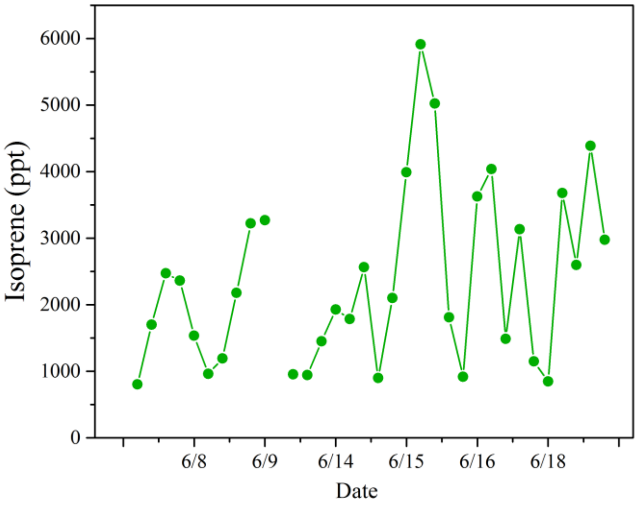


Figure R3. The concentration of isoprene at DY site in summer

9. Figure 5, “LDKN248” should be “LDKN247”

Response: thanks for the correction. LDKN 247 has been changed into the new name of “HDCN 247” in the revised manuscript.

10. Figure 9(a), the number of blue points is 9. (b) the number of blue dots is 10.

Response: Figure 9(a) shows the data points during daytime, while 9(b) shows data points at nighttime. The reason why the numbers of data points are different in the two figures is that the numbers of the daytime and nighttime samples are not equal.

11. Table 2, “(MW = 295, PSON 295” should be “(MW = 295, PSON 295)”

Response: the omission of the bracket has been added.

References:

Cheng, X., Li, H., Zhang, Y., Li, Y., Zhang, W., Wang, X., Bi, F., Zhang, H., Gao, J., Chai, F., Lun, X., Chen, Y., Gao, J., and Lv, J.: Atmospheric isoprene and monoterpenes in a typical urban area of Beijing: Pollution characterization, chemical reactivity and source identification, Journal of Environmental Sciences, 71, 150-167, https://doi.org/10.1016/j.jes.2017.12.017, 2018.

Docherty, K. S., and Ziemann, P. J.: Reaction of oleic acid particles with NO3 radicals: Products, mechanism, and implications for radical-initiated organic aerosol oxidation, Journal of Physical Chemistry A, 110, 3567-3577, 10.1021/jp0582383, 2006.

Kristensen, K., and Glasius, M.: Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring, Atmospheric Environment, 45, 4546-4556, https://doi.org/10.1016/j.atmosenv.2011.05.063, 2011.

Wishart, D. S., Feunang, Y. D., Marcu, A., Guo, A. C., Liang, K., Vázquez-Fresno, R., Sajed, T., Johnson, D., Li, C., Karu, N., Sayeeda, Z., Lo, E., Assempour, N., Berjanskii, M., Singhal, S., Arndt, D., Liang, Y., Badran, H., Grant, J., Serra-Cayuela, A., Liu, Y., Mandal, R., Neveu, V., Pon, A., Knox, C., Wilson, M., Manach, C., and Scalbert, A.: HMDB 4.0: the human metabolome database for 2018, Nucleic Acids Research, 46, D608-D617, 10.1093/nar/gkx1089, 2017.