Responses to Reviewer #2

We appreciate this reviewer for the useful comments and suggestions, which greatly improve the quality of the manuscript. We revised the MS accordingly. The point-to-point responses to all the comments are given below in blue.

The manuscript studied the vertical distribution of particle-phase dicarboxylic acids, oxoacids, and α-dicarbonyls in urban Beijing during the 2015 Victory Parade period based on the 325-meter tower by using GC/MS, Ion Chromatography, and OC/EC analyzer. This study showed that concentrations of oxalic acid at 120 m and 260 m were more abundant than that at 8 m during the sampling period because of higher oxidation at high altitude. Vehicular exhausts were demonstrated as the main contributor for phthalic acid. Although this study did many correlation analyses in section 3, simple correlation analyses didn't effectively evidence the sources and formation of species such as oxalic acid. In addition, many results and conclusions in section 3 were concluded with indefinite words such as may, causing that the conclusions were too speculative. Therefore, the authors should provide some stronger evidences in this section. This study further indicated the sources of organic acids based on meteorological parameters and FLEXPART-WRF model analyses. However, the source analysis at each sampling altitude was not showed. Is there any difference in the source of organic acids at each altitude? Because the study conducted on the vertical measurement, the data is valuable compared to the ground base. I might ask the author to make significant improvement on this paper before they can be accepted in the ACP.

Response: The real atmospheric environment is complex, where diverse formation mechanisms of organic aerosols exist. Field campaign estimates the dominant mechanism of aerosol components based on the atmospheric variables, which can not reveal the detailed mechanisms of organic compounds like smog chamber study. Owing to the insufficient data, the PMF analysis run at each altitude existed high uncertainties, thus the PMF source apportionment analysis is to the overall results in our study.

The sample numbers will be considered to increase at each altitude. Simultaneously, more

analyses will be employed to the aerosol samples to better estimate the relative contribution of sources and secondary process at different height.

This paper firstly investigates the vertical distribution of diacids, oxoacids and α-dicarbonyls in Beijing, analyzes the primary sources and secondary processes in clean and polluted days, and demonstrates the feedback of organic acids under the control of anthropogenic emissions. Such measurements in the troposphere are also critical for estimating the regional transport to air quality in Beijing, which are favorable for chemical transport models to better evaluate the vertical contributions of local emissions, regional transport, aqueous and photochemical oxidation processes. Furthermore, the synchronous measurements, like Chemical Ionization Mass Spectrometer, is considered to use in combination with the sampling of diacids, oxoacids and α-dicarbonyls in gas and particle phase to better understand the gas-particle transformation of these acids at different heights.

P13 L21: How to exclude the contribution of accumulation of local emissions? Other evidences of aqueous-phase oxidation also should be provided.

Response: The local emissions also contributed to diacids and related compounds in polluted days. Owing to the increase of relative humidity in the low troposphere, the aqueous formation of oxalic acid enhanced in the polluted days, which was more important than local primary emissions.

Hydrated glyoxal (Gly) and methyglyoxal (MeGly) can ultimately produce oxalic acid (C_2) via the formation of glyoxylic (ωC_2) and pyruvic (Pyr) acids as intermediates (Carlton et al., 2007;Carlton et al., 2009;Tan et al., 2010). The concentration ratio of relative abundance of C_2 in total diacids (C_2/total diacids) is known as a useful marker to assess the aerosol oxidation level, because C_2 is the end product mostly formed via the oxidation of longer carbon-chain diacids and other precursors in the atmosphere (Kawamura and Bikkina, 2016). Therefore, the relationships for $C_2/\omega C_2$, C_2/Pyr, C_2/Gly and C_2/MeGly with C_2/total diacids were applied to better understand the aqueous formation of C_2. Compared to clean days, good coefficients were obtained for $C_2/\omega C_2$, C_2/Pyr, C_2/Gly and C_2/MeGly with C_2/total diacids in polluted days, which generally decreased with the sampling height. This phenomenon suggested that the vertical transformations of ωC_2, Pyr, Gly and MeGly

to form C_2 were more clearly observed at the ground surface due to the higher relative humidity. It's worth noting that the value order of relative humidity was 8 m > 120 m > 260 m (Fig. S1).

Furthermore, the relative content of C_2 in water-soluble organic carbon (C_2-C/WSOC) showed different vertical distributions and variations in clean and polluted days. Aged organic aerosols are usually characterized by the larger contribution of oxalic acid to WSOC (C_2-C/WSOC). For example, C_2-C/WSOC ratio was higher in the photochemically aged aerosols collected at Hong Kong (6.8%) (Ho et al., 2011) and Mount Hua (6.3%) (Meng et al., 2014) compared with the ratio (0.17%) in Ulaanbaatar aerosols that are significantly affected by substantial anthropogenic emissions (Jung et al., 2010). Due to the high temperature and relative humidity, the photochemical reaction is active in Hong Kong (Ho et al., 2011). Mount Hua is the highest mountain in central China and is a typically isolated site to investigate the atmospheric long-range transport of organic compounds (Meng et al., 2014). In contrast, diacids and related compounds in winter were mainly associated with uncontrolled wastes plastic burning, coal power plants and vehicular emissions in Ulaanbaatar (Jung et al., 2010). Generally, in clean days, the C2-C/WSOC ratio showed relatively large values at upper heights in this study (Fig. 9a). Moreover, in the transition from clean to polluted days, the C2-C/WSOC ratio values at the ground level, 120 m and 260 m slightly increased. However, in the more polluted days, C_2-C/WSOC ratios at the ground level were obviously higher than those at 120 m and 260 m owing to the accumulation of pollutants and moisture in ground surface atmosphere, which also supported the conclusion that the increased aqueous-phase oxidation may be a major source of oxalic acid in polluted days.

P4 L21: why were the blank samples only collected for half a minute? I saw that $PM_{2.5}$ samples were collected for 23 h.

Response: The field blank is sampled to see whether the aerosol samples have been polluted during the operation process, including the placing and collecting processes of the filter, which takes a few seconds. This sampling procedure doesn't aim to see the environmental impact during sampling time. Please see the definition of field blank at

website (https://www.lcslaboratory.com/field-blank/).

P5 L6: Grammatically something wrong.

Response: Corrected.

P8 L4: How to exclude other sources (e.g., long-range transport, aqueous or heterogeneous reactions) for SOC?

Response: We have modified the sentence to avoid contradiction. "The SOC/POC ratios at 120 m (1.8 ± 0.79) and 260 m (1.9 ± 0.92) were higher than those at the ground level (0.51 ± 0.3) (Table. S1), demonstrating that more aged aerosols accumulated at upper layers (Fig. 2f)."

P8 L10: other sources should be discussed. Please see the above comment.

Response: We have modified the sentence in the revised manuscript. "These vertical phenomena were also observed for total oxoacids and α-dicarbonyls, suggesting that the aging level of diacids and related compounds slightly increased at 260 m of the atmosphere."

P12 L16: C_3/C_4 should be C_2/C_3?

Response: Corrected.

P13 L9: What is the definition criteria of polluted episodes?

Response: The pollution level is defined by air quality index (AQI), and is classified as light (101 − 150), moderate (151 − 200), heavy (201 − 300) and extremely heavy (301 − 500) pollution by Chinese Environmental Protection Ministry. Zhao et al. (2017) has also investigated chemical composition and diurnal variations of submicron aerosol species at ground level and 260 m during same polluted episodes in overlapped sampling time.

P14 L15-16: Definition of pollution level should be provided.

Response: The pollution level is defined by air quality index (AQI) according to local report from environmental monitor station. AQI is calculated from the following equation:

$$AQI = \frac{AQI_h - AQI_l}{C_h - C_l}(C - C_l) + AQI_l$$

C is the pollutant concentration. AQI_l and AQI_h are AQI values corresponding to C_l and C_h, respectively. C_l and C_h are lower and upper limits near the pollutant concentration. AQI_l, AQI_h, C_l and C_h are constants, which can be obtained from the document of Technical Regulation on Ambient Air Quality Index (HJ 633 − 2012) issued by Chinese Environmental Protection Ministry. AQI is classified as light (101 − 150), moderate (151 − 200), heavy (201 − 300) and extremely heavy (301 − 500) pollution by Chinese Environmental Protection Ministry. We have added the definition of pollution level in the manuscript. Please see lines 9 – 10 in page 13.

P17 L8: Was the coal combustion included in the anthropogenic emissions? Maybe need related literature?

Response: Zhang et al. (2008) found that the saturated *n*-diacids (C_3 − C_{10}), unsaturated diacids (fumaric, maleic, phthalic, isophthalic and terephthalic acids) and related organic precursors, such as n-alkanes, PAHs and unsaturated fatty acids, can be directly emitted by industrial and residential coal combustion in China. Guo et al. (2013) reported that the contribution of coal combustion was associated with cooking in urban outskirts and rural areas during Beijing 2008 Olympics. Coal combustion accounted for 5.8 ± 5.5% and 7.8 ± 4.6% of the measured OC under the control on anthropogenic emissions (Guo et al., 2013), which was similar to the result in our study. The uncontrolled coal combustion in the rural areas was an important source to hopanes and PAHs in Beijing (Yu et al., 2018; Ren et al., 2018; Guo et al., 2013).

Coal combustion is an important anthropogenic source (Zhu et al., 2018), which largely influence the mass concentrations of organic compounds in China, especially in winter (Wang et al., 2012; Wang et al., 2006; Yu et al., 2018; Ren et al., 2018; Sun et al., 2016; Sun et al., 2013; Wang et al., 2019). We have added the reference and corrected the mistake in the revised manuscript. Please see lines 7 − 9 in page 17.

P17 L22: Same question as above.

Response: We have added the reference and corrected the mistake in the revised manuscript. "In this paper, PMF analysis showed that the contributed fraction of anthropogenic emissions (49 − 55%), including biomass burning, motor vehicles and coal combustion (Zhu et al., 2018), to diacids and related compounds were larger than that of secondary formation pathways (37 − 44%)." Please see lines 21 − 23 in page 17.

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