General comments:

The Pearl River Delta (PRD) region is an important area for air quality research. This study provides a year-long observation of aerosol species using aerosol mass spectrometry. The paper's focus is given to secondary organic aerosols which account for about a quarter of submicron particle mass concentration. In general, the paper is well organized and clearly written. Presenting such an extensive observational dataset itself serves as a contribution to the atmospheric chemistry community. I only have a few minor comments on the current paper.

Responses: We thank the reviewer for acknowledging our efforts and for all the valuable comments.

Minor comments:

Comment: On the Q-ACSM data analysis: Previous studies used to have different categories for SOAs. For example, some studies have separated an aq-SOA (aqueous-processing SOA) component. Can the authors provide more information on the assumption and reasons for their choice of SOA categories?

Response: We learned from this comment. We did not find any literatures have resolved aqSOA factor on the basis of Q-ACSM measurements. However, we do find the aqSOA factor was resolved from Tof-ACSM measurements which differ with Q-ACSM mainly in resolution of spectrometer, and the aqSOA was characterized by high fraction of m/z 29 (CHO+) and high correlations with sulfate, for example the R^2 between sulfate and aq-SOA reached as high as 0.94 in Lei et al. (2021). The correlations between both LOOA and MOOA with sulfate in this study is below 0.5, thus do not support directly if they are related with aqueous phase reactions. To make readers aware of this, we added following discussions in Sect. 2.2:

"Note that a aqSOA factor (called aqOOA in these references) was previously resolved using the aerosol mass spectrometer measurements (Sun et al., 2016;Zhao et al., 2019) or time-of flight ACSM measurements (Lei et al., 2021), and the factor was resolved as aqSOA because of its high fraction of m/z 29 (CHO+) and high correlation with sulfate.

Comment: Fig.3 & Fig.5: Earlies studies reported fast formation of sulfate at haze episodes, which seems to be different from the measurements shown here. Can the authors show the reasons?
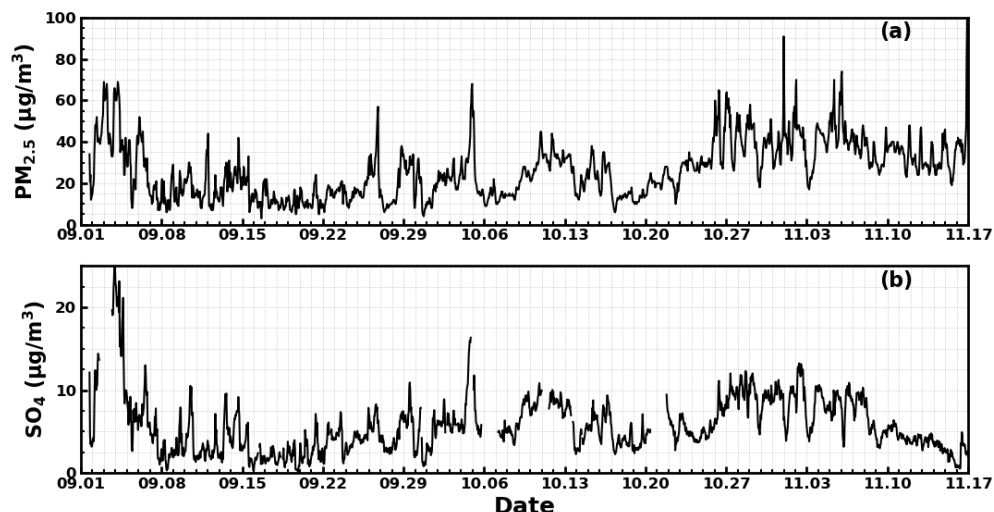

Figure 1. Time series of PM$_{2.5}$ (a) and sulfate (SO$_4$) (b) during autumn of 2020.

Response: Thanks for your comment. Sulfate is not the focus of this study, however, this is quite an interesting question and made us noticed that the sulfate evolution during the observations of our study differed much with results shown in previous studies. First, results shown in Fig.3 and Fig.5 do not reflect the formation rate of sulfate.   Sulfate contribute most to submicron aerosol mass during haze episodes of autumn, therefore the time series of sulfate and PM2.5 are shown in Fig.1 as an example. It can be seen that both PM$_{2.5}$ and sulfate rarely show accumulation characteristics that last several days, and shown strong diurnal variations, and fast sulfate formation can be observed in daily scale. This is quite different with results shown in Chen et al. (2021) as shown

in Fig.2, and the results shown in Chen et al. (2021) was observed also at Guangzhou urban area in autumn of 2018. During the observations of Chen et al. (2021), the continuous accumulation of sulfate in some haze episodes is remarkable and totally different with those in observations of this study. Results of these studies highlight the seasonal variations of aerosol chemical compositions might differ much among years. And the reasons behind this might be related with the changes of meteorological conditions and emission conditions. And for the difference between observations of Chen et al. (2021) with this study, the changes of meteorological conditions might play the dominant role, because relative small emissions changes might be expected from 2018 to 2020. To make this point clear to readers, the following discussions was added the Sect 3.2 of the revised manuscript:

"Note that seasonal variations of aerosol chemical compositions might differ much among years due to different meteorological conditions and emissions. For example, the evolution of sulfate during autumn in this study (Fig.S9) have remarkably different
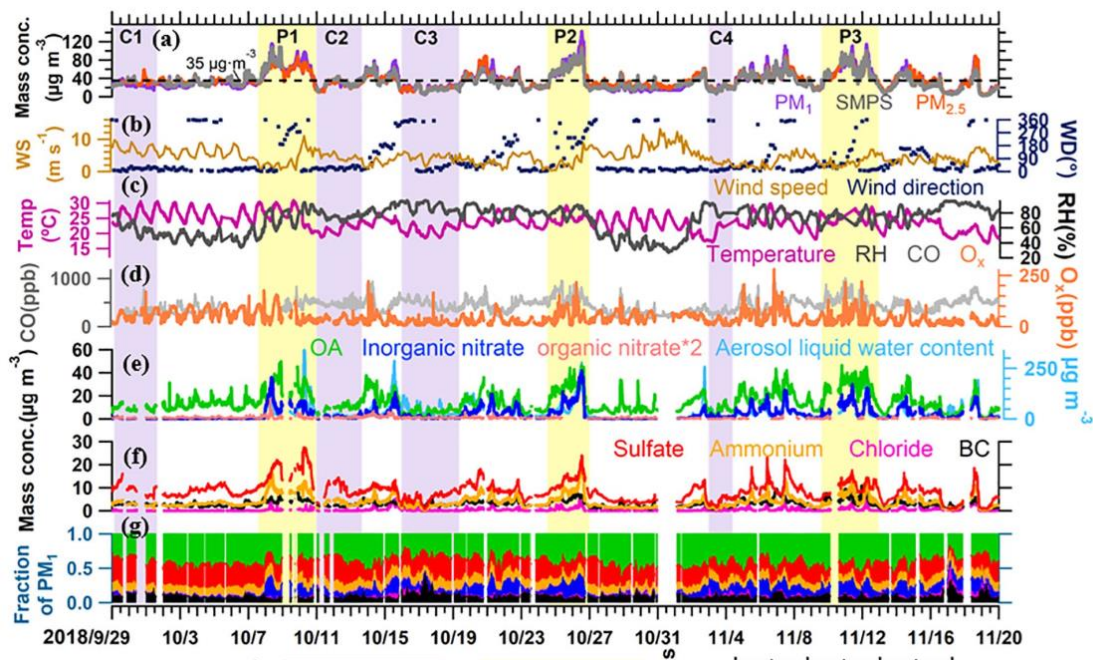

Figure 2. Time series of different parameters in Chen et al. (2021).

accumulation characteristics with those observed in autumn of 2018 as shown in Fig.1 of Chen et al. (2021a). Even so, SOA play significant roles in haze formations of Guangzhou urban area in all seasons hold based on results of existing literatures (Zhou

et al., 2020b)."

In addition, sulfate formation mechanism is a hot spot in recent years, however, most investigations on sulfate formations mechanism were done on the North China Plain. Synthesized research on the formation mechanisms of sulfate in the PRD region remain lacking, and might be one of our focuses in next years.

Comment: The variations of boundary layer height may affect the interpretation of the formation mechanisms of aerosol species. Can the authors provide more quantitative results on its influence?

Response: We agree with the reviewer that the variations of boundary layer height might affect significantly on the interpretation of the formation mechanisms, however, the observations of parameters that relate to planetary boundary layer (PBL) height evolutions is lacking. Reanalysis data of PBL might be available, however, my experiences told me that climatological analysis using reanalysis datasets might be ok, however not accurate enough for resolving hourly scale processes such as SOA formation within several hours. Therefore, in the data analysis of SOA formation, we only tried to qualitatively interpret the results and give clues on future studies. We thought about using CO to scale the observations as done in other studies, however, we found that only small decrease was observed in CO although other parameter such as POA is decreasing substantially, demonstrating that the CO variations reflect poorly PBL evolutions in strong CO source regions.

General comments:

This study reported a year-long AMS measurement data for NR-PM1 in Guangzhou urban area of the PRD, China, and then discussed the possible formation pathways of SOA and its significant role on haze occurrences in the region. Indeed, long-term AMS data was relatively scarce and thus valuable for better understanding the source contribution and formation pathways of aerosols in the atmosphere. This paper also presented some interesting scientific findings, e.g., haze formation mechanisms differed much among distinct seasons, significant roles of the coordination of gas-phase photochemistry and subsequent aqueous-phase reactions in quick daytime SOA formations, etc. However, in my opinion, several parts of the manuscript were not well organized and clearly described.

Response: We thank the reviewer for all the valuable comments and suggestions, which helped us to further improve the readability of our manuscript.

Detailed comments

Comment: L46-47, "reaching about 1.7 times that of primary organic aerosols …", grammar error.

Response: Revised as "reached about"

Comment: Introduction: should be entirely revised. Although long-term AMS data is valuable, it is not a scientific goal. The authors should more focus on the present understanding and deficiency of SOA formation, and how the long-term AMS data can help understanding it. The authors also need to summarize the main conclusions of previous long-term AMS studies, not just list these references, and clarify the advantage of this study.

Response: Many thanks for this valuable suggestion. We have revised the introduction as suggested by the reviewer:

"Ubiquitous submicron aerosols in the atmosphere not only deteriorate human health and visibility, but also impact climate through interactions with solar radiation

and clouds. Organic aerosols (OA) represent one of the most important and sometimes even dominant components (~10-90%) of PM1 (aerosol particles with aerodynamic diameter less than 1 μm) in urban, rural and remote areas (Zhang et al., 2007;Jimenez et al., 2009). OA can either be emitted directly from emission sources or be formed through atmospheric reactions of volatile organic compounds, the former is referred to as primary OA (POA) and the latter is referred to as secondary OA (SOA). An increasing number of researches show that SOA account for a large fraction of OA worldwide (Zhang et al., 2007;Zhang et al., 2011), and even dominate in some cases (Kuang et al., 2020). The implementation of strict emission reduction policies has significantly improved the air quality of Pearl River Delta (PRD) region, which is a highly industrialized area of China, and the annual mean concentration of PM2.5 (particulate matter with aerodynamic diameter less than 2.5 μm) has been brought down to less than 30 μg/m3 (Xu et al., 2020). However, the reduction of PM2.5 mass concentrations in PRD has slowed down substantially in recent years, which might be related to the significant increases in the proportion of secondary aerosols (Xu et al., 2020), especially for SOA. Insights into SOA formation mechanisms are important for air pollution improvement.

SOA formation mechanisms are a scientific hotspot of atmospheric chemistry in recent ten years since significant contributions of SOA to atmospheric aerosol mass were fully recognized (Zhang et al., 2007;Jimenez et al., 2009), however quite complex due to varying precursors, oxidants and formation pathways under different emission characteristics and meteorological conditions. As to SOA formation pathways, SOA can be formed through condensation of oxidized gas-phase organic vapors during the oxidation of volatile organic compounds (VOCs), this type of formed SOA was usually referred to as gasSOA (Kuang et al., 2020). SOA can also be formed in the aqueous phase through the further oxidation of dissolved VOCs which are usually products of gas-phase oxidation of VOCs, this type of SOA was usually referred as aqSOA (Ervens et al., 2011). Both field measurements and laboratory studies are needed in investigating detailed SOA formation mechanisms in different regions with field measurements provide insights into key oxidants and formation pathways, thus information from field

measurements are important for both designing laboratory experiments and targeting emission control strategies. Aerosol mass spectrometers are advanced on-line instruments that provide real time quantitative characterization of aerosol particle compositions (Jayne et al., 2000;Canagaratna et al., 2007;Jimenez et al., 2003). Positive matrix factorization (PMF) (Ulbrich et al., 2009) or a multilinear engine (ME-2) (Paatero, 1999;Canonaco et al., 2013) can be employed to further resolve different OA factors that are associated with different sources and formation mechanisms from the OA mass spectra. Using this technique, the SOA sources and formation mechanisms are extensively investigated in China (Zhou et al., 2020), and found that aqueous reactions in aerosol water contributed substantially even dominantly to SOA formations (Su et al., 2020) in haze episodes with daytime and nighttime SOA formations differ much due to different meteorological conditions and oxidants (Rollins et al., 2012;Huang et al., 2021).

In fact, in a specific region, the compositions, sources, and evolution processes differ much among seasons due to changes in emission sources and meteorological conditions (Li et al., 2015). Therefore, long-term observations that cover measurements of different seasons were usually needed for characterizing OA sources and SOA formation mechanisms, thereby helping to address the challenge of fine particulate matter pollution mitigation. Even though aerosol mass spectrometers have been widely used in China in recent years and the importance of long-term measurements, most studies have been conducted in specific periods due to its high cost and maintenance (He et al., 2011;Chen et al., 2021b;Qin et al., 2017), resulting in few long-term characterizations of the mass concentrations and chemical compositions of submicron particulate matter (PM1). The design of Aerosol Chemical Speciation Monitor (ACSM) has improved this problem to some extent (Ng et al., 2011;Sun et al., 2015;Canonaco et al., 2021). For example, based on 2-year ACSM measurements, Sun et al. (2018) investigate the distinct characteristics of PM1 compositions among different seasons in Beijing urban area and illustrated the dominant role of SOA in OA across different mass loading scenarios during all seasons.

Guangzhou is an expansive metropolis in the highly industrialized PRD region.

Using the aerosol mass spectrometer measurements and source apportionment technique, Qin et al. (2017) and Huang et al. (2011) reported that SOA contributed substantially to aerosol mass during autumn and winter in Guangzhou. Guo et al. (2020) found that OA played a dominant role in PM1 during winter in Guangzhou, with OA source apportionment emphasized the dominance of SOA. Guo et al. (2020) also suggested that gasSOA contributed predominantly to SOA formation during non-pollution periods, other mechanisms such as heterogeneous and multiphase reactions played more important roles in SOA formation during pollution episodes, however long-term aerosol spectrometer measurements hat help for characterizing OA source and SOA formation mechanisms in this region remain lacking. In this study, we performed a year-long continuous measurement of non-refractory submicron aerosols (NR-PM1) with an ACSM in urban Guangzhou from September 2020 to August 2021 to characterize POA sources and investigate SOA formation mechanisms in different seasons."

Comment: L123, "from which black carbon (BC) mass concentrations in winter and early spring", this sentence is confusing.

Response: Revised as "from which optically equivalent black carbon (BC) mass concentrations in winter and early spring were calculated."

Comment: Q-ACSM data analysis: this section was too redundant, I suggest to move some detailed analysis to supplement.

Response: Thanks for your suggestion, we discussed about this part and insist this part should be in the manuscript. Reasons are listed below: (1) PMF analysis of OA spectra is the key part because the identification of OA factors are fundamental for analysis in this study; (2) This is the first paper that resolved OA factors during entire year in the PRD region, direct presentations of detailed discussions about the usage of PMF tool and scientific considerations behind factor determination are important for readers, especially for those are fresh (The first author is fresh two years ago and suffered from learning how to discuss and determine PMF results).

Comment: 3.1: L229, L234, etc. In this section, the PBL and rainy conditions were repeatedly referred to explain the seasonal variations of PM1 and chemical componets. Could you provide detailed data about PBL and precipitation for it?

Response: Many thanks, we do not have the PBL data during the observations. The discussions are mainly associated with general seasonal variations of PBL in this region which is discussed in Yang et al. (2013), and this reference is added in the revised manuscript. The time series of precipitation is shown in the following Figure, and added as Fig.S9 in the revised supplement.
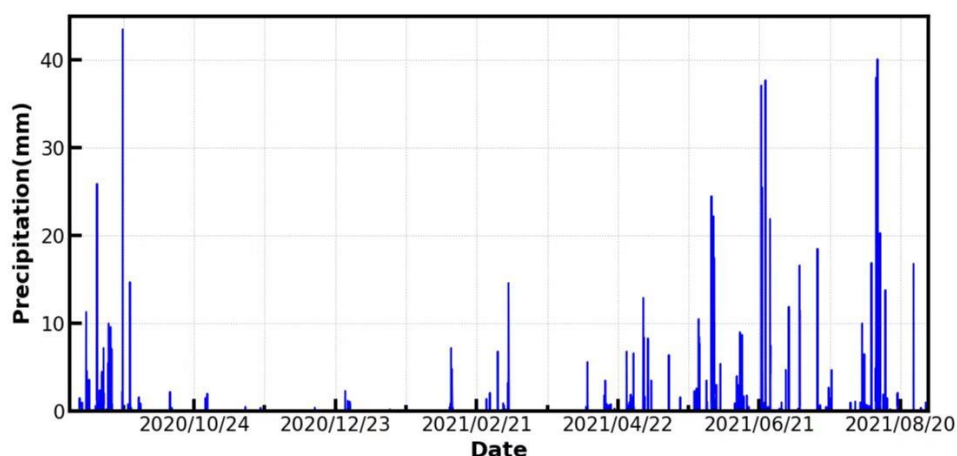
Time series of precipitation during the observations

Comment: L249-250: grammar error.

Response: revised as "Nitrate in summer and fall was relatively lower in summer and fall"

Comment: L259-261, why are there more traffic emissions in winter? Please provide more evidences.

Response: We re-checked the ratio between HOA/COA and didn't found higher HOA/COA ratio during winter, therefore our previous speculation is quite weak and we deleted this sentence.

Comment: L265-267, this sentence is confusing, please clarify it.

Response: This sentence was revised as:

"Overall, COA contributed about 19% of OA during the whole year which was close to that of HOA (18%). However, the contributions of COA and HOA to total OA differ much among seasons. The contributions of COA to OA were higher than that of HOA during warm months and lower than that of HOA in relatively cold months especially in winter."

Comment: 3.2 Significant contributions of secondary organic aerosols to haze formations in all seasons: it seems that the authors try to highlight the role of SOA in haze formations, however, I think it is overstated, at least in the section title. For example, in L286-299, the contribution of OA in generally decreased when PM1 concentration increased in fall. Similar trend of SOA could be found in other seasons (Figure 5).

Response: Yes, we want to highlight important roles of SOA in haze formations in all seasons. Haze formations mainly refer to absolute increase/accumulation of aerosol mass, the contribution of OA might decrease in some seasons however, contribution of SOA generally hold, demonstrating significant contribution of SOA increase to submicron aerosol mass increase as shown in left panels of Fig.5.

Comment: L431, 436, NO+ and NO2+ were not in right format.
Response: revised

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