We are very grateful for the anonymous reviewer's positive assessments of the manuscript and insightful comments for further improvement. We have revised the manuscript by fully taking the reviewers' suggestions into account. Please find our point-to-point replies below in blue, and the specific changes in the revised manuscript and SI are highlighted here in red.

Reviewer 2

The manuscript analyzed the water-soluble and water insoluble organic carbon in a coastal megacity of China. The sources and contributions of WSOC and WIOC to $PM_{2.5}$ were explored with Bayesian stable isotope mixing model, and the water solubility of fresh and aged SOC in the coastal megacity of China were revealed. The study is important and meaningful, while there are still some questions need to be clarified to improve the manuscript.

Specific comments:

1. I am confused about how the BSIM and PMF model used in the source apportionment of the TC and WSOC. The author should re-organize section 2.3 to make it clear.

As described in section 2.3, The four sources, including traffic, biomass burning, the fresh SOC and aged SOC were resolved by PMF model. The author also obtained the stable carbon isotope fingerprints by traffic emission samples collected in tunnels, fresh SOC simulated through petrol vehicle bench tests, aged SOC samples collected at a background monitoring station and biomass burning samples simulated through laboratory experiment.

Did the fingerprint above were used as prior information in the BSIM model? What about the $\delta^{13}C/‰$ values of the four sources? How could the author verify the representation of the four source fingerprints and that they can be properly used in Shenzhen?

Response:

We sincerely appreciate your suggestion. The PMF model referred to in section 2.3 of the manuscript serves to determine the potential source of TC and WSOC for further refined source apportionment using the BSIM model. We have already re-organized section 2.3 to make it much clear. At lines 142-147 in the revised manuscript, we have provided a more detailed description of the role of the PMF model in this study:

'In this study, we firstly employed the PMF model to identify the potential sources of TC and WSOC (Text S1), with the aim of reducing the uncertainty of the subsequent BSIM model and verifying the reliability of the BSIM results. The PMF results showed that traffic emissions, SOA, and biomass burning are the major contributors to carbonaceous aerosols in Shenzhen, which were similar to the previous results in Guangzhou (Huang et al., 2014).'

In this study, stable carbon isotope fingerprints of traffic emissions, fresh and aged SOC, and biomass burning sources were obtained, along with mass spectral signatures of biomass burning source (f_{60}), and all these fingerprints were used as prior information for the BSIM model. Additional clarification on this point has been incorporated at lines 159-160 in the revised manuscript:

'The measured profiles of the four sources were used as prior information in the BSIM model

for the follow-up analyses.'

The specific $\delta^{13}C$/‰ values for the four sources were detailed in Table 1. The four source fingerprints used in this study were all compared with the results from relevant literatures in Table S3 in the Supplementary Information (SI). The comparison demonstrated that the stable carbon isotope values of each source measured in this study closely aligned with literature findings and fell within the range of source spectra reported in other studies, which confirms the reliability of the four source fingerprints employed in this study. Regarding this point, we have also included further elucidation at lines 175-177 in the revised manuscript:

'The stable carbon isotope measurements from the four sources align with the range observed in global datasets, thus affirming the reliability of the four source fingerprints utilized in this study.'

2. This study firstly employed BSIM model to quantify the contributions of fresh and aged SOC to WSOC and WIOC. The author claimed the consistence of the results from BSIM and PMF model. My question about the method used in this study is what is the advantages of the BSIM model compared with PMF model? Why was the result of BSIM model used for the final analysis?

Response:

Thank you for your comment. The most significant advantage of the BSIM model over the PMF model in this study is its capability to simultaneously quantify fresh and aged SOC in TC and WSOC. In the source apportionment of offline $PM_{2.5}$ samples based on the PMF model, the absence of mass spectrometry information makes it impossible to differentiate between fresh and aged SOC in TC. Consequently, only the overall SOC source can be apportioned. Therefore, PMF model could not provide further quantification of the water solubility characteristics of SOC. Hence, the BSIM model results were employed in this study as the final analysis. This point has been clarified in section 2.3 of the revised manuscript (lines 151-156):

'Since the PMF model lacks the mass spectral information of offline $PM_{2.5}$ samples, it fails to distinguish between fresh SOC and aged SOC in TC, making it challenging to investigate the water solubility characteristics of the SOC based on PMF results. BSIM model simultaneously quantified of fresh and aged SOC separately in both TC and WSOC, thereby enabling an estimation of SOC water solubility. This capability is used for the final analysis in this study.'

3. Line137-138, the SOC was divided into fresh SOC and aged SOC based on the oxidation state, what is the exact values of the average oxidation state of carbon (OSc) or O/C of the two SOC sources?

Response:

Thank you for your comment. The O/C ratios ranged from 0.51 - 0.62 for fresh SOC and the mean O/C ratio for aged SOC was 0.98 in this study, both of which were close to the O/C ratios calculated by the PMF model for fresh SOC (0.43) and aged SOC (1.01). We have improved the accuracy and clarity of the descriptions in lines 164-166 and lines 169-170 of the revised manuscript:

lines 164-166: 'The oxygen-carbon ratios (O/C) of fresh SOC samples in this study ranged from 0.51 to 0.62, indicating a low oxidation state (Ding et al., 2012).'

lines 169-170: 'These aged SOC samples exhibited a high O/C value of 0.98, suggesting their highly oxidized state (Zhu et al., 2016).'

4. Line 162, table 1 showed the $\delta^{13}C$/‰ values of the four sources in TC and WSOC, I noticed that the value of $\delta^{13}C$/‰ for different OC showed obvious overlap, for example, the values of fresh SOC in WSOC and TC were lower and higher than that of traffic source, respectively? How did the sources were determined being clearly separated by the values of $\delta^{13}C$ with the existence of the obvious overlap of the $\delta^{13}C$/‰?

Response:

Thank you for your comment. Stable carbon isotope values of atmospheric particulate matter from different sources may overlap for a number of reasons. For instance, the values of fresh SOC and traffic emissions are likely to overlap primarily because some fresh SOC could be further generated by traffic emissions, and different components of the same source may possess similar stable carbon isotope values. Besides, particulate matter fractions from different sources may undergo distinct physical and chemical processes in the atmosphere, along with carbon isotope fractionation, all of which could contribute to changes in stable carbon isotope values.

Although the overlap degree of stable carbon isotope values from different sources may affect the accuracy of the Bayesian approach, it's essential to note that the Bayesian approach is a probabilistic model that utilizes both a priori information and a likelihood function to estimate the contribution of sources. This approach enables probabilistic estimation of contributions from different sources. In addition, it can also integrate information from multiple markers and sources, thereby mitigating the effects of overlap and enhancing the robustness of source apportionment analyses.

In this study, the following methods were employed to mitigate the impact of $\delta^{13}C$ values' overlapping between different sources on the BSIM model. First, the number and type of potential sources of TC and WSOC were identified in advance based on the PMF model, avoiding the uncertainty of interference from unrelated sources. Secondly, in addition to stable carbon isotopes, the chemical tracer marker of biomass burning source (f_{60}) provided additional information to the BSIM model, which helped to improve not only the apportionment accuracy of biomass burning source, but also the overall accuracy of the BSIM model.

The following content has been added to section 2.3 in the revised manuscript (lines 179-184): 'Although there is some overlap among the $\delta^{13}C$ fingerprints of different sources, the Bayesian approach allows for probabilistic estimation of the contribution of different sources and can also integrate information from multiple markers and sources to mitigate the effects of overlap. In this study, the PMF model was used to reduce the uncertainty of interference from unrelated sources, and the chemical tracer marker of biomass burning source (f_{60}) was also integrated to minimize the effect of this overlap.'

5. Line332, the meaning of the dots and lines in Figure 5a should be added.

Response:

Thanks for the suggestion. The meaning of the dots and lines has been added in the caption of Figure 5a (Now Figure 6a in revised manuscript). The specific additions are as follows:

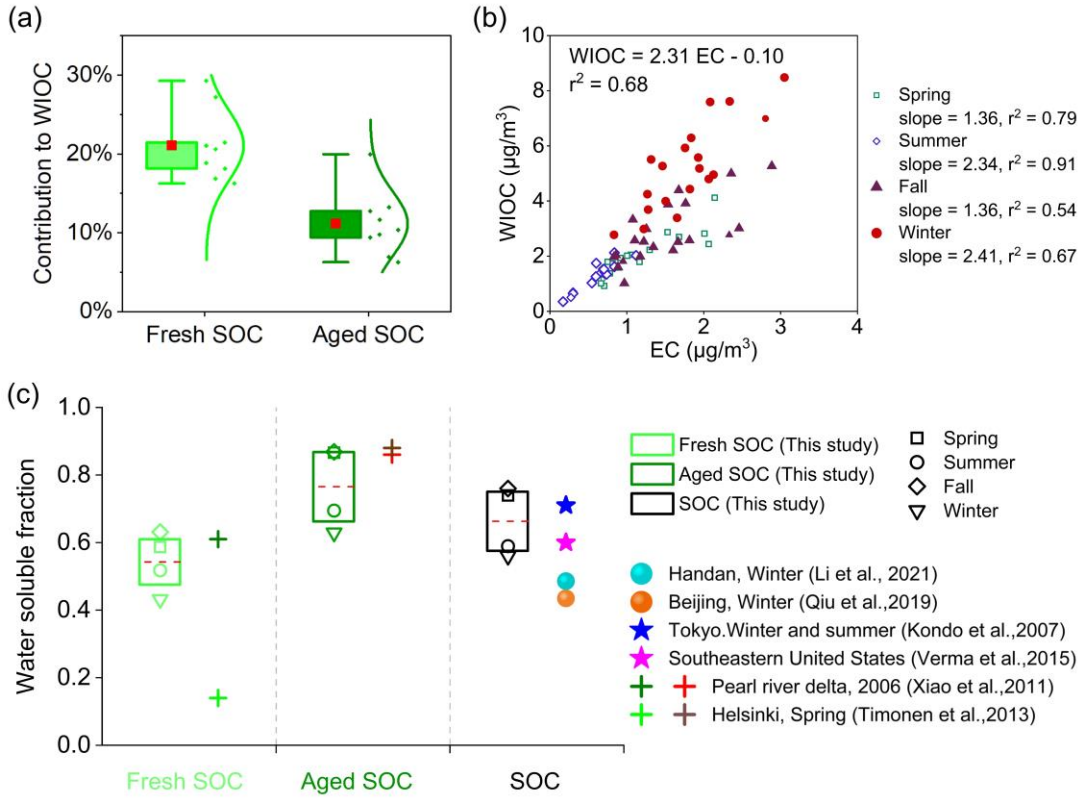

Figure 6. (a) Left is the box and whisker plots of fresh and aged SOC contributions to WIOC, the upper and lower of the box representing the 75th and 25th percentiles, and the red squares featuring mean values. The dots on the right show the contribution of fresh and aged SOC to WIOC across seasons and sites, the curve demonstrates its normal distribution. (b) Scatterplot of WIOC versus EC by season, (c) Comparison of the water-soluble fraction of SOC (fresh SOC, aged SOC, SOC) in this study (box and whisker plots) with those in other related literature (colored markings on the right). The upper and lower of the box represent the 75th and 25th percentiles and the dashed red lines indicate mean values.

6. Line 338-339, the reference has been listed in the legend of figure 5, so it doesn't need to be listed in the caption here.

Response:

Thanks for the suggestion. The references have been removed from the caption of Figure 5 (Figure 6 in revised manuscript).

7. The subdivided OOAs were name as fresh SOC and aged SOC in the manuscript, while they were named MO-OOA and LO-OOA in Figure S4. Please make the names of these items consistency through the manuscript or add some statement of the difference.

Response:

Thank you very much for raising this point. Since fresh SOC and aged SOC, as well as LO-OOA and MO-OOA, were differentiated by the degree of oxidation of SOC in our study, and the O/C ratios of fresh SOC and LO-OOA, as well as aged SOC and MO-OOA, were close to each other, we have adjusted the names of the two to be consistent as you suggested. Specifically, we have renamed LO-OOA and MO-OOA in Figure S5 and SI as fresh SOC and aged SOC, respectively.

‘According to Fig. S5, factor 1 displayed the highest percentage of EV values for *m/z 44* (CO_2^+) and WSOO (73 % and 63 %, respectively), with an oxygen-carbon ratio (O/C) of 1.01, which is highly oxidized and identified as aged SOC source. Factor 2 exhibited EV values of 64% for *m/z 57* ($C_4H_9^+$), 29% for WSOC, 27% for *m/z 44*, and 23% for WSOO. In addition, factor 2 had a lower level of oxidation with an O/C ratio of 0.43, and was therefore identified as fresh SOC source.’

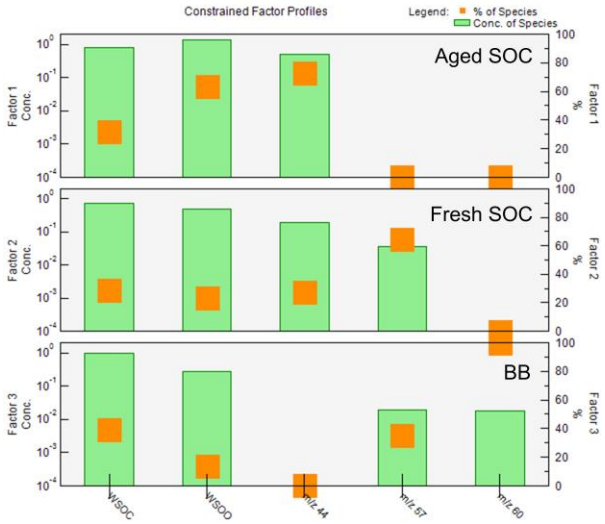

Figure S5. The source profiles resolved by PMF for WSOC.