Responses to reviewer comments

We thank the reviewers for their detailed, helpful, and overall supportive comments. We have revised the manuscript to account for each comment. Responses to the individual comments are provided below. Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. Line numbers in the response correspond to those in the revised manuscript text file.

Reviewer #1

This manuscript presents chemical analysis results of submicron organic aerosols in Beijing during summer. It mainly uses two types of aerosol mass spectrometers and compares the measurement results with each other. Due to different detection schemes, the authors found that the OA determined by SP-AMS are quite different from that of HR-AMS OA. In particular, vehicle-related OA might be detected more by SP-AMS; cooking OA, was not associated with BC; a unique biomass burning OA, on the other hand, was only significantly observed on BC cores. The work provides valuable contribution into understanding the chemical behaviors and therefore the impacts on air quality and climate of OA. It can be accepted for publication in ACP, this reviewer has however a few minor comments as listed below:

(1) There are a few typos, grammar or format errors in the manuscript that should be corrected, for example, in Line 38, Line 67, Line 79, Line 235-236, Line299, etc.

Thanks for the comment. The typos, grammar, and format errors in the manuscript mentioned above were corrected, and a thorough check is also conducted to correct other errors

(2) Line 114: it is not clear what is the "BC-free species" referring to.

Now we changed it to non-BC containing particles.

(3) Line 114-116: Explain a bit more why HR-AMS can measure Type I and II, and SP-AMS for Type II and III.

We added a sentence in Lines 117-121: "*NR-PM_1 can be quickly vaporized by the 600 ^oC tungsten vaporizer of HR-AMS and be detected. The SP-AMS used here was equipped only with the Nd-YAG intra-cavity infrared laser (1064 nm) (tungsten vaporizer was physically removed), it can selectively detect BC-containing particles only, which include Type II and Type III species.*

(4) Line 150-155: Did you perform corrections, for example, on elemental ratios, between the two AMS as you state there could be some mass spectral differences due to measurement schemes?

Yes, scaling factors of 1.10 for H:C and 0.86 for O:C by Canagaratna et al. 2015 were applied.

(5) Line 248: I suggest to delete this sentence.

As suggested, this sentence is removed.

(6) Line 280-282: As you state that HOA quantification might be influenced by the changes of collection efficiency. Can you explain a bit more about the possible influences of the collection efficiency on other OA factors?

The possible influences on CE has been described in Lines 151-155:"*It should be noted that the BC quantification will not be affected by particle bouncing without the tungsten vaporizer, which could affect the CE in the standard HR-AMS measurements (Canagaratna et al., 2007). However, the CE will be governed by the overlap of the particle beam and laser beam (Lee et al., 2017;Massoli et al., 2015;Willis et al., 2014).*"

(7) Line 320: Is it possible that the A-BBOA fraction (for example, <5%) in total NR-PM_1 is too low to be resolved by the PMF?

Yes, this is possible. The A-BBOA might be included in the NR-PM_1 MO-OOA as described in Lines 321-323.

(8) Figure 6: It is better to put the legends adjacent to the HR-AMS and SP-AMS plots directly in d, to make it clear.

Done

Reviewer #2

Wang et al. compare the OA properties by parallel measurements using SP-AMS and HR-AMS respectively, in summer Beijing. The AMS technique is suitable for online quantification of OA and in particular SP-AMS can provide a unique piece of OA that coated on rBC cores. The findings are therefore unique and valuable to understand the OA composition and chemistry in megacities like Beijing. The overall interpretation of the data is reasonable and the paper is well written, I suggest its acceptance in ACP after the following minor issues are well addressed.

(1) During the APHH campaign, another type of mass spectrometer (single particle mass spectrometry) was used to elucidate the OA properties too. Some studies should be included here to facilitate the interpretation.

Thanks for the suggestion, we have added two references by using single particle MS techniques in the revised manuscript.

Chen, Y.; Cai, J.; Wang, Z.; Peng, C.; Yao, X.; Tian, M.; Han, Y.; Shi, G.; Shi, Z.; Liu, Y.; Yang, X.; Zheng, M.; Zhu, T.; He, K.; Zhang, Q.; Yang, F. Simultaneous measurements of urban and rural particles in Beijing – Part 1: Chemical composition and mixing state. Atmos. Chem. Phys., 20, 9231-9247, 10.5194/acp-20-9231-2020, 2020a.
Chen, Y.; Shi, G.; Cai, J.; Shi, Z.; Wang, Z.; Yao, X.; Tian, M.; Peng, C.; Han, Y.; Zhu, T.; Liu, Y.; Yang, X.; Zheng, M.; Yang, F.; Zhang, Q.; He, K. Simultaneous measurements of urban and rural particles in Beijing – Part 2: Case studies of haze events and regional transport. Atmos. Chem. Phys., 20, 9249-9263, 10.5194/acp-20-9249-2020, 2020b.

(2) Some typos or citation formats do not follow the ACP style, please check and revise.

We have carefully checked the manuscript.

(3) In the instrumentation section, some necessary technical details are missing. For example, what is the m/z range of the OA mass spectra for HR-AMS and SP-AMS? Time resolution? Operation modes (V or W?) Is the tungsten vaporizer physically removed or turned off in SP-AMS?

Thanks for the comment. The m/z range of the OA mass spectra for HR-AMS and SP-AMS reported in this study is across m/z 12-120 as described in Lines 161. The operation mode is described in Lines 153-154 as well. However, we added a statement for technical details in Lines 123-125: "*Briefly, the two AMS were operated under the mass quantify favorable mode (V-mode) with a time resolution of five minutes.*" And a statement in 117-121: "*NR-PM1 can be flash vaporization via the 600 ºC tungsten*

vaporizer of HR-AMS and thus to be detected. For BC-containing particles, due to the SP-AMS equipped a Nd-YAG intra-cavity infrared laser (1064 nm) module, it can selectively detect BC-containing particles (Type II and Type III) with the tungsten vaporizer be moved."

(4) Xie et al (Atmos Environ 2019; 213:499-504) shows different PMF results from this study, is it because the datasets used for PMF analysis are different?

There are two reasons for the difference of PMF results between this study and the one reported by Xie et al. One reason is caused by the different PMF inputs. For example, in Xie's report, only carbon clusters and OA mass spectra were used in the PMF analysis, while ion fragments from inorganic species (e.g., SO+, SO+, NO+, NO2+, Cl+, HCl+, NH+, and NH2+) were also included in the PMF analysis. Another reason is because of the amount of dataset, in Xie's study, there are only 9 days (from June 4 to 13), while there are 26 day (from June 4 to 30).

(5) Line 316-319: The ABBOA is not separated in the HR-AMS dataset, is it likely because that the ABBOA contains more refractory components?

Although this can be investigated further but we think it is unlikely. Most organics are non-refractory and there is no specific reason that BBOA contains more refracrtory components than other types of OA. In addition, according to previous studies of SP-AMS, the evaporation of non-BC species associated with BC core are under lower temperature. The reason why the A-BBOA was not separated in HR-AMS measure OA might be caused by its low mass fraction in the total OA (but not that low in BC-PM_1 OA), for example, less than 5% of total OA.

(6) References: Line 504-516, the references are the same, but repeated twice.

Corrected.

(7) Figure 5: There are only four ion families here. How about the nitrogen-containing organic ions, although they may have little influences?

The nitrogen-containing organic ion fragments were also involved in the PMF analysis as shown in the Figure 2, however, those signals are relatively very low, and for better comparison, nitrogen-containing organic ion fragments were not shown here.

Characterization of ~~Submicron Organic Particles~~submicron organic particles in Beijing ~~During Summertime~~during summertime: Comparison ~~Between~~between SP-AMS and HR-AMS

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ABSTRACT

Black carbon (BC) particles in Beijing summer haze play an important role in regional radiation balance and related environmental processes. Understanding the factors that lead to variability ~~in~~of the impacts of BC remains limited. Here, we present observations by a soot-particle aerosol mass spectrometer of BC-containing submicron particulate matter (BC-PM_1) in ~~the summer of 2017 in~~ Beijing, China during 2017 summer. These observations were compared to concurrently measured total non-refractory submicron particulate matter (NR-PM_1) by a high-resolution aerosol mass spectrometer (HR-AMS). Distinct properties were observed between NR-PM_1 and BC-PM_1 ~~related~~relevant to organic aerosol (OA) composition~~ with hydrocarbon~~. Hydrocarbon-like OA in BC-PM_1 was found to be up to two-fold higher than that in NR-PM_1 in fresh vehicle emissions, suggesting that a part of HOA in BC-PM_1 may be overestimated, likely due to the change of ~~the~~ collection efficiency of SP-AMS. Cooking-related OA was only identified in NR-PM_1, whereas aged biomass burning OA (A-BBOA) was a unique factor only identified in BC-PM_1. The A-BBOA was linked to those heavily coated BC, which may lead to enhancement of light absorption ability of BC by a factor of two via the "lensing effect". More-oxidized oxygenated OA identified in BC-containing particles was found to be slightly different from that observed by HR-AMS, mainly due to the influence of A-BBOA. Overall, these findings highlight that BC in urban Beijing is ~~partly~~partially of agricultural fire origin and, a unique biomass burning-related OA associated with BC may be ubiquitous in aged BC-PM_1, and this OA may play a role in affecting air quality and climate that has not previously been fully considered.

1. Introduction

Black carbon (BC) is an important component of atmospheric aerosol that exerts negative effects on regional radiation balance ~~(Bond et al., 2013) and human health (Janssen, 2012). It absorbs solar radiation, leading to direct atmospheric heating (Ramanathan and Carmichael, 2008). Indirectly, BC-containing particles (BCc) can also serve as cloud condensation nuclei upon mixing with hydrophilic species (e.g., sulfate), resulting in changes in cloud properties (Wu et al., 2019). Inhalation of BC is associated with adverse health impacts such as respiratory diseases and birth defects (Janssen, 2012).~~(Bond et al., 2013) and human health (Janssen, 2012). It absorbs solar radiation, leading to direct atmospheric heating (Ramanathan and Carmichael, 2008). Indirectly, BC-containing particles (BCc) can also serve as cloud condensation nuclei upon mixing with hydrophilic species (e.g., sulfate), resulting in changes in cloud properties (Wu et al., 2019). Inhalation of BC is associated with adverse health impacts such as respiratory diseases and birth defects (Janssen, 2012).

BC particles are released to the atmosphere directly and usually mixed with non-BC materials (e.g., inorganic and organic) from incomplete fuel combustion and open fires ~~(Ramanathan and Carmichael, 2008;Bond et al., 2013;Chen et al., 2013).~~(Ramanathan and Carmichael, 2008;Bond et al., 2013;Chen et al., 2013). Non-BC species also can coat onto primary BCc in the atmosphere through condensation and/or coagulation processes ~~(Lee et al., 2017).~~(Lee et al., 2017). These atmospheric processes gradually alter the mixing state and the morphology (e.g., from an externally-mixed fractal structure ~~(Buseck et al., 2014) into an internally-mixed "core-shell" structure (China et al., 2015)) of BCc.~~(Buseck et al., 2014) into an internally-mixed "core-shell" structure (China et al., 2015)) of BCc. These alterations can enhance the light absorption capacity of the BC core via the "lensing effect" due to the increased light absorption cross-section as a result of the enhanced coating thickness ~~(Saleh et al., 2015;Cappa et al., 2012).~~(Saleh et al., 2015;Cappa et al., 2012). Additionally, the chemical constituents of BCc may dynamically change during the aging processes, which also lead to changes in the light absorption capacity of the particles ~~(Wang et al., 2019;Wang et al., 2017).~~(Wang et al., 2019;Wang et al., 2017). Because these physical

and chemical processes of both organic and inorganic species inside BCc continuously alter particle properties throughout the lifetime of the particles, great uncertainty remains in quantifying the light absorption ability of BC ~~(Liu et al., 2018;Liu et al., 2019).~~(Liu et al., 2018;Liu et al., 2019). Understanding the relationship of mixing state and chemical composition to the light absorption properties of BCc, as well as its spatiotemporal distribution, is of importance to accurately evaluate the impacts of BC in regional air quality.

Aerodyne high-resolution aerosol mass spectrometry (HR-AMS) ~~(Canagaratna et al., 2007)~~(Canagaratna et al., 2007) has been widely applied in field studies to investigate the chemically-resolved composition of non-refractory submicron particulate matter (NR-PM_1, species that vaporize at temperature < 600 °C)~~(Li et al., 2015;Lee et al., 2013;Sun et al., 2012;Ge et al., 2012b;Ge et al., 2012a;Xu et al., 2019c;Sun et al., 2014).~~(Li et al., 2015;Lee et al., 2013;Sun et al., 2012;Ge et al., 2012b;Ge et al., 2012a;Xu et al., 2019b;Sun et al., 2014). However, the working temperature of the standard HR-AMS tungsten vaporizer (600 ºC) is not sufficient to vaporize refractory species such as BC. To overcome this limitation, soot-particle aerosol mass spectrometry (SP-AMS) is developed ~~(Onasch et al., 2012).~~(Onasch et al., 2012). In addition to the standard tungsten vaporizer, SP-AMS is equipped with a laser vaporizer (with a wavelength of 1064 nm) which selectively heats BC (core), together with the non-BC species mixed with it ~~(Wang et al., 2016).~~(Wang et al., 2016). This novel technique makes it possible to compare the compositions of submicron BCc (BC-PM_1) and NR-PM_1, allowing a more accurate assessment of the impacts of BC. However, a question is whether the ion fragments of organic species ionized by the 70eV electron impact of SP-AMS and HR-AMS are the same in terms of different thermal schemes. It has been reported that the mass spectra of NR-PM_1 organic have high m/z 44 (mainly CO_2^+) signal, while the mass spectra of BC-related organics have high m/z 43 ($C_3H_7^+$ and $C_2H_3O^+$) signal. The reason for this is the SP-AMS provides vaporization of the BC-PM_1 at lower temperatures compared to the standard tungsten vaporizer of the HR-AMS, resulting in less overall fragmentation and therefore less CO_2^+ production in the laser, in addition, the lower fragmentation also causes the

presence of more ion fragments at m/z > 100 amu in the SP-AMS mass spectra compared to that of HR-AMS ~~(Canagaratna et al., 2015b;Massoli et al., 2015).~~(Canagaratna et al., 2015b;Massoli et al., 2015). Nevertheless, quantification of BC-PM_1 organic aerosol (OA) factors identified from positive matrix factorization (PMF) has been reported that were not significantly affected by the differences of mass spectra between HR-AMS and SP-AMS ~~(Lee et al., 2017;Massoli et al., 2015).~~(Lee et al., 2017;Massoli et al., 2015).

To date, there have only been a few studies that have compared the differences of species in BC-PM_1 and NR-PM_1 ~~(Lee et al., 2017;Collier et al., 2015;Massoli et al., 2015). Lee et al.~~(Lee et al., 2017;Collier et al., 2015;Massoli et al., 2015). Lee et al. found that cooking-related organic aerosol (COA) may externally mix with BC in summertime California ~~(Lee et al., 2017).~~(Lee et al., 2017). The COA factor was identified in NR-PM_1 organic aerosol (OA), but not in the BC-related OA. Wang et al found that transported biomass burning organic aerosol could be thickly coated on BC in central Tibetan Plateau and significantly enhance the light absorption capacity of BC cores ~~(Wang et al., 2017).~~(Wang et al., 2017). Interestingly, the transported biomass burning organic aerosol was not resolved in NR-PM_1 OA particles from concurrent HR-AMS measurements ~~(Xu et al., 2018).~~(Xu et al., 2018). These studies suggest that BC-related OA may undergo different atmospheric processes compared to those do not contain BC.

Beijing is a megacity known for high particulate matter (PM) concentrations. BC-PM_1 during haze events of summertime Beijing may have distinct sources and properties than other locations in the world. As a part of the UK-China Air Pollution and Human Health (APHH) project summer campaign ~~(Shi et al., 2019).~~(Shi et al., 2019; Chen et al., 2020a; Chen et al., 2020b). in this study, we focus on the differences of individual species between BC-PM_1 and NR-PM_1 regarding their chemical composition, mass loadings, sources, and formation pathways in summertime in urban Beijing. Results from this study provide a better understanding of the formation mechanism of OA particles in Beijing haze and valuable insights in assessing their impacts on air quality.

2. Experiments

2.1. Sampling site and period

The observations were conducted at a rooftop laboratory (8 m above ground level) in the Tower Division of the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (CAS) in urban Beijing (39°58′N, 116°22′E), China, from 4 to 29 June, 2017. This site has been reported multiple times to be a typical urban observation location ~~(Xie et al., 2019b;Liu et al., 2019;Wang et al., 2019;Qiu et al., 2019;Xu et al., 2019a;Xie et al., 2019a).~~(Xie et al., 2019b;Liu et al., 2019;Wang et al., 2019;Qiu et al., 2019;Xu et al., 2019a;Xie et al., 2019a). The site is located around the North 3rd Ring Road of Beijing. A highway is approximately 360 m to the east and a lot of restaurants (e.g., Sichuan style and BBQ) are within 100 m on the north side.

2.2. Instrumentation

Two Aerodyne Aerosol Mass Spectrometers (AMS), including a laser-only Soot-Particle AMS (SP-AMS) and a High-Resolution Time of Flight AMS (HR-AMS) were deployed to measure chemical compositions and size distributions of BC-PM_1 and NR-PM_1, respectively. Three types of species were measured during the campaign: NR-PM_1, including ~~BC-free~~non-refractory species that don't mix with BC (Type I) and non-refractory species that mixed with BC (Type II), and BC-PM_1 (BC core and both refractory and non-refractory species coated on the core)(Type III). NR-PM_1 can be quickly vaporized by the 600 ºC tungsten vaporizer of HR-AMS ~~is capable of measuring Type I and Type II, while laser only~~ and be detected. The SP-AMS ~~can measure~~used here was equipped only with the Nd-YAG intra-cavity infrared laser (1064 nm) (tungsten vaporizer was physically removed), it can selectively detect BC-containing particles only, which include Type II and Type III species. A shared $PM_{2.5}$ cyclone inlet (Model URG-2000-30ED) with 3 Lpm flowrate and a diffusion dryer were used prior to the sampling. The detailed information on the operation of HR-AMS and SP-AMS during the sampling campaign can be found in previous literature ~~(Xie et al., 2019a;Xu et al., 2019d).~~(Xie et al., 2019a;Xu et al., 2019b). Details of tuning,

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calibration, and configurations of the two AMS instruments can be seen in our previous papers ~~(Wang et al., 2019;Xu et al., 2019a;Xu et al., 2019d).~~(Wang et al., 2019;Xu et al., 2019a;Xu et al., 2019b). The two AMS were operated under the V-mode which is favorable for mass quantification with a time resolution of five minutes. Mixing ratios of O_3, and NO_2 (Thermo Fisher Scientific, model 49*i* and model 42C) were measured in parallel simultaneously. Vertical meteorological parameters, including temperature (*T*) and relative humidity (*RH*), were measured from the IAP 325m meteorological tower.

2.3. Data Analysis

AMS data analysis was performed by using Squirrel 1.57 and Pika 1.16I based on Igor Pro 6.37 (WaveMetrics Corp.). The measurement of filtered air was performed for 24 hours before the start of the campaign to determine the detection limits of various aerosol species and to adjust the fragmentation table. The relative ionization efficiency (RIE) of BC was calibrated with Regal Black (RB, REGAL 400R pigment black, Cabot Corp.). The average ratio of C_1^+ to C_3^+ ionized from pure BC (RB) was determined to be 0.53, which minimizes the influence of C_1^+ from non-refractory organics. The RIE of BC was determined to be 0.17 based on calibrations performed before, in the middle, and at the end of the campaign. RIEs of NO_3^-, SO_4^{2-}, NH_4^+ were determined to be 1.1, 0.82, and 3.82, respectively, and default values of 1.3 and 1.4 for RIEs of Chl and Org were applied, respectively ~~(Canagaratna et al., 2007).~~(Canagaratna et al., 2007). Consistent with BC-PM_1 measurements in previous studies, the RIEs calibration of NO_3^-, SO_4^{2-}, NH_4^+ were performed before the tungsten vaporizer was removed, by assuming those RIEs remain unchanged throughout the campaign ~~(Wang et al., 2017).~~(Wang et al., 2017). Polystyrene latex (PSL) spheres (100-700 nm) (Duke Scientific Corp., Palo Alto, CA) were used to calibrate the particle size distribution before the campaign. The collection efficiency (CE) of 0.5 were applied for both HR-AMS and SP-AMS in this study. It should be noted that, the BC quantification will not be affected by particle bouncing without the tungsten vaporizer, which could affect the CE in the standard HR-AMS measurements ~~(Canagaratna et al., 2007).~~(Canagaratna et

al., 2007). However, the CE will be governed by the overlap of particle beam and laser beam ~~(Lee et al., 2017;Massoli et al., 2015;Willis et al., 2014).~~(Lee et al., 2017;Massoli et al., 2015;Willis et al., 2014). Both HR-AMS and SP-AMS resolved mass concentrations of NR-PM_1 and BC were calculated based on V-mode high-resolution fitting. Due to different vaporization schemes between the HR-AMS and SP-AMS, mass spectra from these two instruments even for the same population of aerosols are not entirely the same. Because laser-only SP-AMS generally results in less overall fragmentation, its mass profile may contain more large *m/z* fragments and less small *m/z* fragments compared to that from HR-AMS~~(Massoli et al., 2015).~~(Massoli et al., 2015). In addition, the elemental ratios of organics reported here, i.e., oxygen-to-carbon and hydrogen-to-carbon ratios (O/C and H/C) were calculated based ~~the "Improved-Ambient (I-A)" method(Canagaratna et al., 2015a).~~on the "Improved-Ambient (I-A)" method(Canagaratna et al., 2015a) (scaling factors of 1.10 for H:C and 0.86 for O:C were applied for elemental ratios calculated from SP-AMS data)

~~Positive matrix factorization (PMF)(Paatero and Tapper, 1994)~~Positive matrix factorization (PMF)(Paatero and Tapper, 1994) was performed on the high-resolution organic mass spectra matrix of both NR-PM_1 and BC-PM_1 (e.g., BC (C_x^+), and species associated with BC) across m/z 12–120 using PMF Evaluation Tool written in Igor ~~(Ulbrich et al., 2009), following the standard procedure (Zhang et al., 2011). Four types of organic aerosol (OA) from total NR-PM_1 (see our previous paper)(Xu et al., 2019c) and five OA factors from BC-PM_1 were identified.~~(Ulbrich et al., 2009), following the standard procedure (Zhang et al., 2011). Four types of organic aerosol (OA) from total NR-PM_1 (see our previous paper)(Xu et al., 2019b) and five OA factors from BC-PM_1 were identified. C_x^+ was involved in the calculation of elemental ratios (e.g, O/C and H/C) of PMF OA factors. All data presented in this paper were averaged hourly and are presented at local time (Beijing Time, UTC+8).

3. Results and discussion

3.1. Overview of observations

Figure 1 shows the temporal variations of selected chemical species during the

campaign. Information for other variables is provided in the supplementary materials (SM). The two cases labeled in Figure 1 are of interest. Case I (June 8-13) was characterized with high NO_2 concentrations (average 26.7 ± 13.5 ppb, Table S1) and relatively low O_3 concentrations (41.7 ± 30.0 ppb) with NO_2-to-O_3 ratio of 0.64. Case II (June 17-22) was featured by low NO_2 (14.9 ± 5.9 ppb) and high O_3 (84.6 ± 30.6 ppb) concentrations with an NO_2-to-O_3 ratio of 0.18. Unlike winter Beijing haze pollution, *RH* remained at a relatively low level (36.5 ± 15.3%), which is not expected to play a significant role in OA formation during the campaign (Figure 1b and Figure S1). In contrast, a strong correlation has been observed between temperature and O_3 (r^2 = 0.53). The temperature was higher on average in Case II (29.8 ± 3.8 ºC) than in Case I (26.1 ± 4.1 ºC).

The mass concentrations and mass concentration ratios of organic (Org), sulfate (SO_4^{2-}) and nitrate (NO_3^-) in NR-PM_1 (in solid line) and BC-PM_1 (in dotted line) are shown in Figures 1c-e. High correlations were observed between BC-PM_1 and NR-PM_1 measurements for SO_4^{2-} (r^2 = 0.70) and NO_3^- (r^2 = 0.86), but not for Org (r^2 = 0.49). This result suggests that, BC-PM_1 Org has distinct sources or formation pathways from NR-PM_1 Org. Comparing two cases, the average mass ratios of BC-PM_1 to NR-PM_1 for SO_4^{2-} and NO_3^- in Case I (0.24 ± 0.11 and 0.37 ± 0.12) were close to those in Case II (0.19 ± 0.06 and 0.31 ± 0.07). However, ratios of BC-PM_1 to NR-PM_1 for Org were a factor of greater for Case I (0.74 ± 0.32) compare to Case II (0.46 ± 0.13). During the nighttime, this ratio increases to almost unity in Case I. Additionally, BC concentration in Case I (average 2.6 ± 1.6 μg m^{-3}) was 1.5 folds higher than in Case II (average 1.7 ± 0.8μg m^{-3}). The implication is that the organic is mostly associated with BC and likely comprised of freshly emitted compounds in Case I. This is also evident by the moderate correlation between NO_2 and BC-PM_1 Org (r^2 = 0.42) in Case I. On the other hand, the lower Org ratio in Case II with higher O_3 concentrations indicates greater oxidation and secondary processes in non-BC particles.

3.2. Source apportionment of BC-PM_1 OA

To further investigate the differences between organics in NR-PM_1 and BC-PM_1,

the comparison of PMF OA factors between NR-PM_1 and BC-PM_1 Org is necessary. Four factors were identified from PMF analysis of the NR-PM_1 Org matrix, including hydrocarbon-related OA (HOA), cooking OA (COA), less-oxidized oxygenated OA (LO-OOA), and more-oxidized oxygenated OA (MO-OOA). ~~Details of the NR-PM_1 PMF analysis can be found in our previous study (Xu et al., 2019d).~~Details of the NR-PM_1 PMF analysis can be found in our previous study (Xu et al., 2019b). Here we only present the PMF results of the SP-AMS measured BC-PM_1 Org. As shown in Figure 2, five factors were resolved by PMF with factors including a HOA, a less oxidized OOA (OOA1), three more-oxidized OOA factors were recombined into one OOA factor (MO-OOA= Aged- biomass burning organic aerosol (A-BBOA) + OOA2 + OOA3). Diagnostic plots of this PMF solution is presented in Figure S2.

HOA consists of a series of hydrocarbon fragments ($C_xH_y^+$) in its mass spectrum (Figure 2f), thus having a low O/C ratio (0.13) but a high H/C ratio (1.62). It has a r^2 of 0.92 with $C_4H_9^+$ (m/z = 57) and a r^2 of 0.57 with NO_x (Figure 2a), indicative of its sources from vehicle emissions~~(Xu et al., 2019b).~~ (Xu et al., 2019a). It also correlated tightly with BC (r^2 of 0.70) and a series of polycyclic aromatic hydrocarbons (PAHs) ions, e.g., $C_9H_7^+$ (m/z 115, r^2 of 0.63).

The second factor has a remarkably high fraction of the biomass burning organic aerosol (BBOA) marker ions of $C_2H_4O_2^+$ (m/z = 60) (1.31%) and $C_3H_5O_2^+$ (m/z = 73) (1.34%) in its mass spectrum (Figure 2g), much higher than that observed in non-BBOA (e.g., 0.3% at m/z = 60) in previous studies ~~(Sun et al., 2016;Xu et al., 2019b;Wang et al., 2017).~~(Sun et al., 2016;Xu et al., 2019a;Wang et al., 2017). As expected, the temporal variation of this factor correlated tightly with those of $C_2H_4O_2^+$ and $C_3H_5O_2^+$ (r^2 of 0.71 and 0.72, respectively). In addition, the mass spectrum of this factor is strikingly similar to that of the transported BBOA which was observed at a remote site in the central Tibetan Plateau ~~(Wang et al., 2017),~~(Wang et al., 2017), with a r^2 of 0.97. Here we categorized the transported BBOA as aged-BBOA (A-BBOA) identified in this study. Similar to the A-BBOA observed in Tibetan Plateau, which has an O/C ratio of 0.51, this factor also has a relatively high O/C ratio of 0.48, greater than that of primary BBOA (O/C of 0.18−0.26~~)(Wang et al., 2017).~~)(Wang et al., 2017). These

findings support that the second factor may be associated with the oxidation of biomass burning emissions. The temporal variation of ABBOA in the Tibetan Plateau was reported to be highly correlated with the potassium ion fraction (K^+, r^2 of 0.78), and $K_3SO_4^+$ (r^2 of 0.92). However, the temporal variation of the second factor in this study is only correlated well with that of $K_3SO_4^+$ (r^2 of 0.64) but not K^+ (r^2 of 0.01). The reason for this phenomenon is that the major source of K^+ in remote sites like the Tibetan Plateau was long-distance transport of K_2SO_4 particles, which probably from biomass burning-related K-containing salts interacts with H_2SO_4 ~~(V. Buxton et al., 1999).~~(Buxton et al., 1999). In contrast, there are multiple primary sources of K^+ in PM_1 (e.g., diesel-vehicle emissions, and mainly KCl particles) in urban areas (Figure S3). Based on these observations, $K_3SO_4^+$ could be defined as an external A-BBOA indicator. Moreover, a previous transmission electron microscopy study also ~~shown~~showed that significant agricultural BBOA was mixed with soot and transport from the North China Plain to urban Beijing, meanwhile, K_2SO_4 was also identified within those ~~impact single BBOA soot particles (Li et al., 2010).~~single BBOA-soot particles (Li et al., 2010). Hence, this second factor is identified as A-BBOA that was subjected to oxidation during transport to the measurement area as presented in the fire-point map and three-day back trajectories (Figure S4). June should be the month ~~of maximum agricultural related biomass burning in the North China Plain, although we thought that this burning had been banned in recent years because of air quality concerns (Shen et al., 2019). The implication is that the effectiveness of banning straw burning may be overestimated.~~with maximum agricultural-related biomass burning in the North China Plain, although we thought that such burning activities had been banned in recent years (Shen et al., 2019).

~~The OOA1 factor has an O/C of 0.28 (Figure 2h). Similar to the NR-PM_1 LO-OOA(Xu et al., 2019c),~~The OOA1 factor has an O/C of 0.28 (Figure 2h). Similar to the NR-PM_1 LO-OOA (Xu et al., 2019b), it is highly correlated with $C_2H_3O^+$ (r^2 of 0.72). The $C_2H_3O^+$ ion (m/z = 43) is an important component of secondary organic aerosol (SOA~~)(Collier et al., 2015;Ng et al., 2011)~~)(Collier et al., 2015;Ng et al., 2011) and the diurnal patterns of the OOA1 and $C_2H_3O^+$ both show a great enhancement around

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noontime (Figure S5), indicating the importance of secondary formation of less oxidized organic aerosol through daytime photochemical activity.

The OOA2 factor has an O/C of 0.42 (Figure 2i) and the OOA3 factor has a smaller O/C of 0.32 (Figure 2j). OOA2 correlated strongly with sulfate (r^2 of 0.92; Figure 2d) and OOA3 correlated highly with nitrate (r^2 of 0.97; Figure 2e). These features agree well with the ~~previously~~previous observation for low-volatility OOA (sulfate-related OOA) and semi-volatile OOA (nitrate-related OOA) in Tibetan Plateau ~~(Wang et al., 2017).~~(Wang et al., 2017).

3.3. Comparison of NR-PM_1 and BC-PM_1 OA factors

The sum of the above-mentioned BC-PM_1 A-BBOA, OOA2, and OOA3 fractions is comparable to the NR-PM_1 MO-OOA factor, based on their high O/C ratios. Figures 3a-c are comparisons of the mass loadings of HOA, LO-OOA, and MO-OOA in both NR-PM_1 and BC-PM_1. NR-PM_1 HOA, LO-OOA, and MO-OOA are strongly correlated with their counterpart fractions of BC-PM_1, with r^2 values of 0.68, 0.60, and 0.61, respectively. In Case I, most of the time, the mass loadings of BC-PM_1 HOA and MO-OOA are higher than those in NR-PM_1, while LO-OOA shows the opposite trend. In Case II, the mass loadings of BC-PM_1 HOA are also generally higher than those of NR-PM_1 HOA, however, NR-PM_1 MO-OOA and LO-OOA are almost two folds higher than those of BC-PM_1. Figures 3d-f are comparisons of the fractions of HOA, LO-OOA, and MO-OOA in NR-PM_1 and non-BC material in BC-PM_1 (coatings), respectively. In Case I, the fractions of HOA and MO-OOA internally-mixed with BC are almost two times and four times higher, respectively, than those in NR-PM_1, whereas the two LO-OOA fractions closely track each other. In Case II, two LO-OOA fractions are still overlapped, but compared to Case I, the fraction of HOA in BC-PM_1 coatings is over four times that of NR-PM_1 HOA, and the difference between the two MO-OOA fractions is smaller.

As shown in Figure 4, the average of BC-PM_1 HOA fractions (0.27 ± 0.17 and 0.11 ± 0.07, respectively) are higher than those in NR-PM_1 (0.12 ± 0.08 and 0.02 ± 0.02, respectively) in both Case I and Case II, indicating that HOA particles is more internally mixed with BC compared to other OA materials. However, the possibility that RIE of OA coating may be lower than the default RIE value should also be considered.

The average mass loadings of NR-PM_1 LO-OOA in both Case I and Case II were higher than those of BC-PM_1. However, the fraction of LO-OOA in both NR-PM_1 and BC-PM_1 coatings were very close to each other during the two cases, with an average value of 0.23 ± 0.10 and 0.25 ± 0.12, respectively, indicating that the probability of LO-OOA condensation onto the two different types of particles is similar.

A greater difference between the MO-OOA fractions in NR-PM_1 and BC-PM_1 was observed in Case I than in Case II, and there is more MO-OOA in BC-PM_1 than in NR-PM_1 in Case I. A similar comparison between NR-PM_1 MO-OOA with BC-PM_1 MO-

OOA without A-BBOA can be found in SI (Figure S6), which shows closer fractions in both Case I and Case II. Therefore, one possibility ~~which~~that may cause higher MO-OOA fraction in BC-PM_1 than that in NR-PM_1 in Case I is the presence of the BC-PM_1 A-BBOA, which is only identified from the BC-PM_1 OA. More details of the BC-PM_1 A-BBOA are discussed in Section 3.4.

3.4. Characteristics of A-BBOA in BC-containing PM_1

Figure 5 shows the high-resolution mass spectra of A-BBOA observed in Nam Co (June 2015) and Beijing (June 2017) by laser-only SP-AMS. A mass spectra very similar to that observed in Beijing was also observed in Nanjing (February 2017~~)(Wu et al., 2019),~~)(Wu et al., 2019), with a r^2 of 0.95. The A-BBOA observed in Nam Co (the Tibetan Plateau) was found in the thickest coated and internally-mixed BC-PM_1 (the mass ratio of coatings to BC core (R_{BC}) can reach 14), which enhances the light absorption ability (E_{abs}) of the BC core by a factor of 1.5 to 2.0 via the "lensing effect".

As shown in Figure 6, A-BBOA was associated with those large particles (D_{va} > 300nm) which were also heavily-coated (R_{BC} > 9, Figure 6a and 6c). Because A-BBOA is a moderately aged OA, the OSc was very steady when R_{BC} > 9 (Figure 6c). Figure 6b presents the fractions of the OA factors (left) and the degree of light absorption enhancement (E_{abs}, estimated by the mass ratios of BC measured by Aethalometer model 33 and SP-AMS), as a function of R_{BC}. Figure 6d shows the temporal variations of the fractions of NR-PM_1 OA and BC-PM_1 OA from 15:00 to 24:00 on June 17, 2017 when the highest A-BBOA concentrations were observed. There is a significant enhancement of A-BBOA which may account for up to 60% of the total OA coatings, which could enhance the BC-PM_1 MO-OOA fraction (within the purple frame in the bottom panel of Figure 6d).

In this study, A-BBOA was only observed by SP-AMS and was indeed only associated with BC. It is likely that A-BBOA was emitted together with BC when burning biomass fuel, and was oxidized subsequently during the transport. However, we cannot exclude the possibility that A-BBOA can be detected by HR-AMS. For example, it might be included in NR-PM_1 MO-OOA factor. Without separating A-

BBOA from other organic species, the source apportionment for HR-AMS may obscure air-quality- and climate-related implications of A-BBOA in the atmosphere, such as the enhancement of aerosol light absorption ability (Figure 6b).

4. Conclusions and implications

Online chemical characteristics of BC and its associated species was for the first time elucidated in urban Beijing in summer, and compared with those of NR-PM_1 species. The biggest difference between the two measurements was in the composition of the organic species. In particular, we found BC in urban Beijing in June is partially of agricultural fire origin and, an unique biomass burning-related OA factor (A-BBOA) which was moderately aged, only existed in thickly coated BC-PM_1 (R_{BC} > 9), but not NR-PM_1. The unique A-BBOA could make up a significant portion of BC coating material. ~~In addition to Beijing, similar A-BBOA was also identified in other locations, such as central Tibet Plateau (Wang et al., 2017) and Nanjing (Wu et al., 2019).~~In addition to Beijing, similar A-BBOA was also identified in other locations, such as central Tibet Plateau (Wang et al., 2017) and Nanjing (Wu et al., 2019), suggesting that it may be ubiquitously present in BC-PM_1 in ambient atmosphere.

BBOA species are known to constitute a large portion of light-absorbing organics (brown carbon, BrC). The delay of BBOA oxidation and its longer duration time on BC cores can extend the impacts of BC. Moreover, together with our previous study of BC-associated A-BBOA in Tibet, results presented herein demonstrate that A-BBOA could lead to thick coating on BC cores, meaning a significant "lensing effect" to the enhancement of BC light absorption ~~(Liu et al., 2017).~~(Liu et al., 2017). As a key component of BC coating, presence of this factor may also alter the bulk hygroscopicity of BC-PM_1. It could therefore affect its ability as cloud condensation nuclei (CCN~~)(Wu et al., 2019).~~)(Wu et al., 2019). Overall, the emission, evolution and transport of such A-BBOA, may influence the atmospheric behaviors and influence the role of BC in the air quality and climate (e.g., radiative forcing and precipitation). We propose that future laboratory, field, and modeling studies are needed to verify the presence of A-BBOA, and to evaluate the regional environmental impacts of it.

Data availability. The data in this study are available from the authors upon request (caxinra@163.com).

Supplement. The supplement related to this article is available online at: xxx.

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Author contributions. JF, DL, YW, JZ, WX, CX, FS and XG conducted the measurements and analyzed the data. JF, JY and PO wrote the first draft, JZ, PO, YQ, XZ, AL, SM, PF, DJ, QZ, YS, MC and XG contributed to the analyses and improvement of the paper. JF and XG contributed to the revision of the paper.

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ABBREVIATIONS

BC Black carbon

PM_1 Particulate matter with an aerodynamic diameter smaller than 1 μm

NR-PM_1 non-refractory PM_1

BC-PM_1 BC-containing particles in PM_1

BrC Brown carbon

HR-AMS High-resolution aerosol mass spectrometer (Aerodyne Research Inc.)

SP-AMS Soot-particle aerosol mass spectrometer (Aerodyne Research Inc.)

IE Ionization efficiency

RIE Relative ionization efficiency

HRMS High-resolution mass spectra

PMF Positive matrix factorization

OA Organic aerosol

SOA Secondary organic aerosolO/C Oxygen-to-carbon ratio

H/C Hydrogen-to-carbon ratio

A-BBOA Aged biomass burning organic aerosol

SV-OOA Semi-volatile oxygenated organic aerosol

LV-OOA low-volatility oxygenated organic aerosol

MO-OOA more-oxidized oxygenated organic aerosol

LO-OOA less-oxidized oxygenated organic aerosol

R_{BC} mass ratio of BC coatings to BC

D_{va} Vacuum aerodynamic diameter

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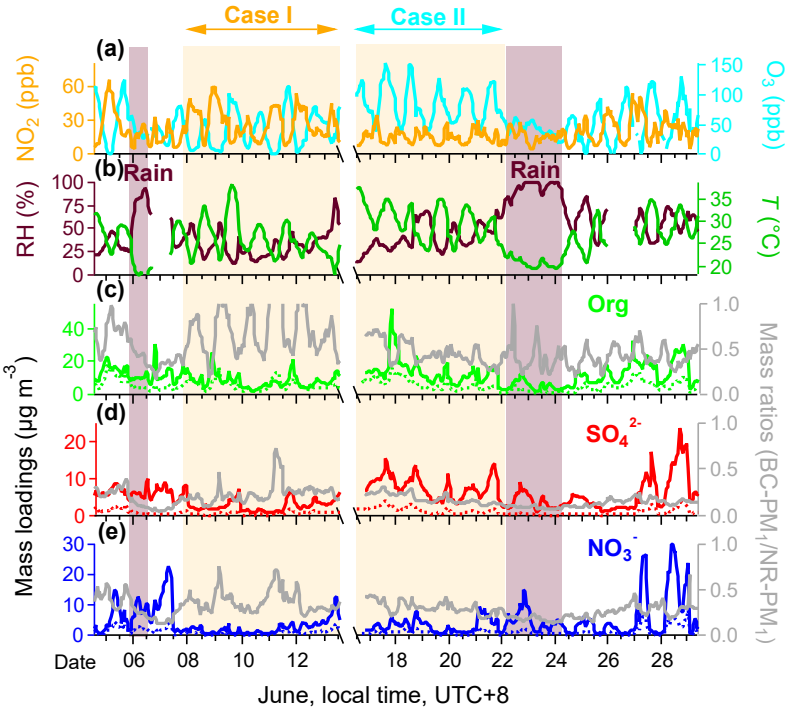
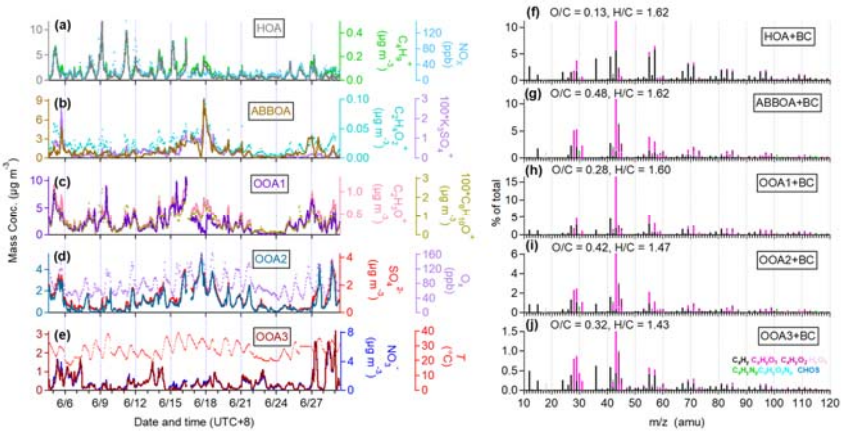


Figure 1. Temporal variations of selected chemical species measured in Beijing on June 4 -29, 2017. (a) mixing ratios of nitrogen dioxide (NO_2) and ozone (O_3); (b) 15-m relative humidity (*RH*) and temperature (*T*); (c-e) on the left are the mass loadings of organic (Org), sulfate (SO_4^{2-}) and nitrate (NO_3^-) measured by HR-AMS and SP-AMS, and on the right are mass ratios of individual BC-PM_1 species to NR-PM_1 species (e.g., BC-PM_1 Org to NR-PM_1 Org). The NR-PM_1 species measured by HR-AMS is in solid line, and the BC-PM_1 species measured by SP-AMS is in the dotted line. The shaded areas are raining periods. The observation period is divided into two cases according to the mixing ratio of nitrogen NO_2, Case I and Case II, which represent high NO_2 and low NO_2 mixing ratios, respectively.



747

748 **Figure 2.** Temporal variations (left panels), high-resolution mass spectra (right panels) of five OA

749 factors in summer 2017: (a) and (f) HOA, (b) and (g) A-BBOA, (c) and (h) OOA1 (LO-OOA), (d)

750 and (i) OOA2, and (e) and (j) OOA3. Also shown in the left panels are the time series of other

751 tracers, including $C_4H_9^+$, NOx, $C_2H_4O_2^+$, $K_3SO_4^+$, $C_6H_{10}O^+$, $C_2H_3O^+$, SO_4^{2-} and NO_3^-.

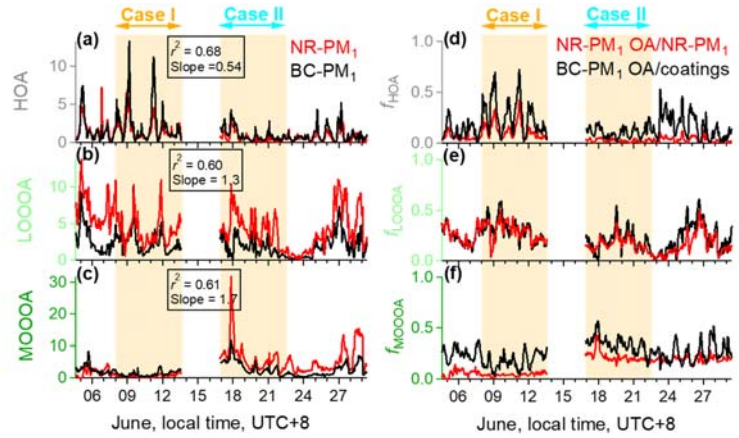


Figure 3. Temporal variations of NR-PM$_1$ and BC-PM$_1$ (a-c) HOA, LO-OOA, and MO-OOA (left panels) and (d-e) their fractions. NR-PM$_1$ OA factors are in red, and the BC-PM$_1$ OA factors are in black. Here BC-PM$_1$ MO-OOA is the sum of A-BBOA, OOA2 (sulfate-related OOA), and OOA3 (nitrate-related OOA).

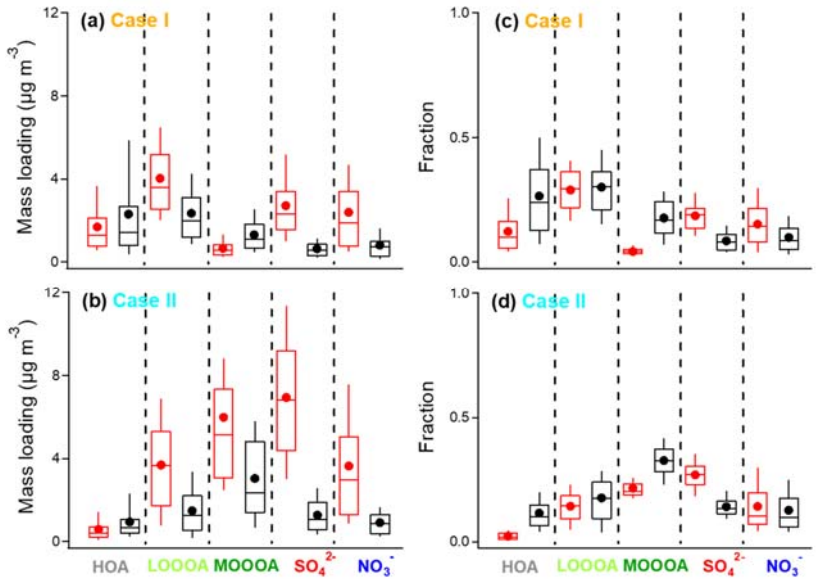
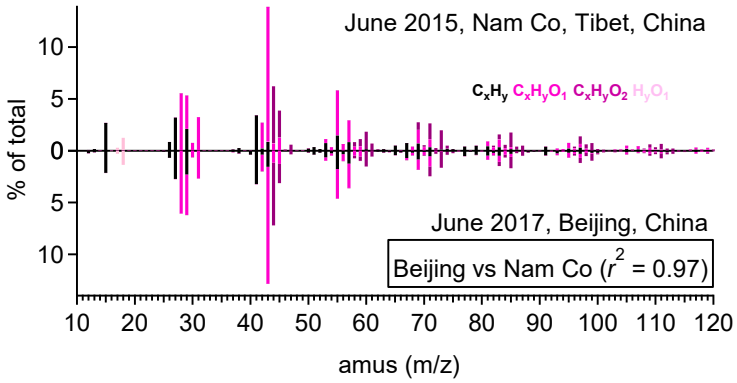


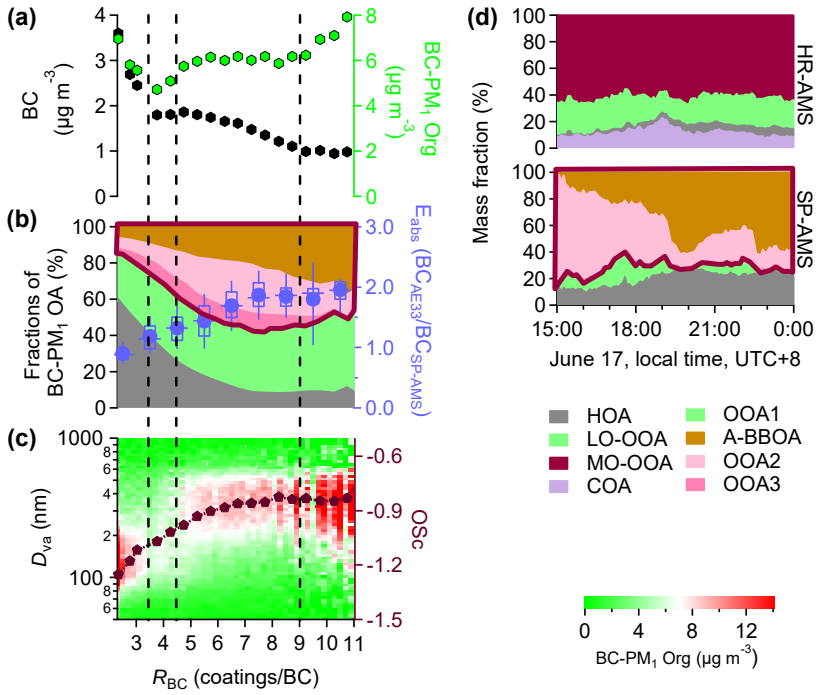
Figure 4. Box plots of mass loadings and fractions of five selected species (HOA, LO-OOA, MO-OOA, SO_4^{2-}, and NO_3^-) in Case I and Case II. The bounds of boxes represent quartiles, the whiskers indicate the 90th and 10th percentiles, and the lines and dots inside the boxes are median and mean values. NR-PM_1 OA factors are in red, and the BC-PM_1 OA factors are in black.



762

763 **Figure 5** Comparison between the high-resolution mass spectra of A-BBOA obtained in Nam Co

764 (June 2015) and Beijing (June 2017) (nitrogen-containing ions are not shown here).


(a)
BC (μg m-3)
BC-PM1 Org (μg m-3)
(b)
Fractions of BC-PM1 OA (%)
Eabs (BCAE33/BCSP-AMS)
(c)
Dva (nm)
OSc
RBC (coatings/BC)
(d)
Mass fraction (%)
HR-AMS
SP-AMS
15:00
18:00
21:00
0:00
June 17, local time, UTC+8
HOA
LO-OOA
MO-OOA
COA
OOA1
A-BBOA
OOA2
OOA3
BC-PM1 Org (μg m-3)

765

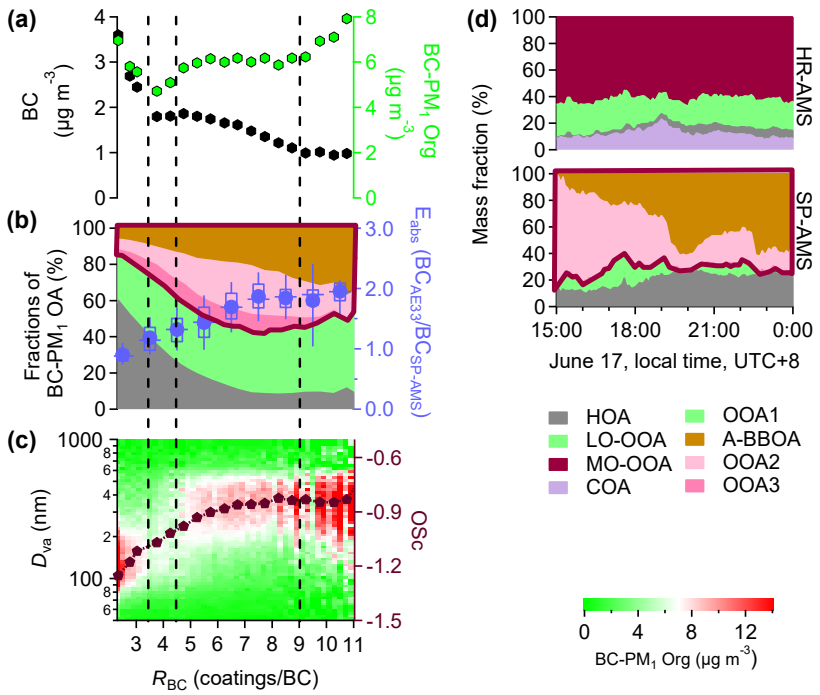


Figure 6. (a-c) the mass loadings of BC, BC-PM_1 Org, fractions of BC-PM_1 OA factors, E_{abs}, the oxidation state (OSc = 2*(O/C) – (H/C)) of BC-PM_1 Org, and the size distribution of BC-PM_1 Org as a function of coating thickness (R_{BC}). (d) temporal variations of OA fractions of NR-PM_1 and BC-PM_1 from 15:00 to 24:00 on June 17, 2017.

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