Response to Reviewer's Comments

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Response to Reviewer #1

This manuscript belongs to the results of APHH 2016 winter campaign, it reports measurement results on the chemical properties of black carbon and the coating materials on the black carbon cores. It used a specific Aerodyne soot-particle aerosol mass spectrometry, which allows to analyze exclusively black-carbon containing particles. This technique avoids interferences from other non-BC containing particles, therefore can elucidate more accurately and directly the properties and evolution of BC in ambient air. Such type of measurement was for the first time conducted in wintertime Beijing, the data and results are thus very valuable. I agree its publication in ACP after some minor revisions suggested below:

Authors' reply: We thank the reviewer for his very positive feedback, and our point-to-point replies to the reviewer's comments are listed below.

(1) Is there any review paper to introduce this APHH campaign, and how does this paper contribute to the overall goal of this campaign? It should be mentioned.

Authors' reply: Yes, by the time of submission, the overview paper is not yet posted. It is now mentioned in the manuscript: Shi, et al.: Introduction to Special Issue – In-depth study of air pollution sources and processes within Beijing and its surrounding region (APHH-Beijing), Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-922, 2018.

(2) The details of PMF analysis results were not mentioned, a diagnostic plot can be provided, at least in the attachment, to justify the choice of PMF solution.

Authors' reply: As requested by the reviewer, we have added a diagnostic plot of the PMF results as Fig. S2 in the supplement to justify the PMF results.

(3) Did the authors observe fullerene-related carbon cluster ions in the mass spectra of Beijing BC aerosols?

Authors' reply: Yes, we have observed fullerene-related carbon clusters during this campaign. In fact, we will publish the observation results regarding fullerenes from Beijing and also other sites in another paper, therefore we did not include them here

(4) Some modifications on the figures are necessary. For example, Font sizes in Fig 4 appear to be small; mass spectra in Fig.7 are less clear.

Authors' reply: As suggested, we have modified the figures (especially Figs. 4 and 7) to have a better quality.

(5) In Fig.6, the RBC ranges for clean and pollution periods are different, it is better to compare the variations on the same scale?
Authors' reply: In Figs.6c and 6d, the R_{BC} ranges are set on the same scale.

(6) One general suggestion is that this dataset is unique as it measures only BC-particles in a highly polluted environment, the reviewer feels the discussion needs more comparisons with results in other locations or environments. As mentioned by the authors, such measurements were conducted in other sites in US, and Europe, even it is very scarce in China. This can help to show what is special or different or important of the findings observed in Beijing, and what are the implications of such findings to the atmospheric chemistry.
Authors' reply: Thanks for the suggestion. We in fact have included some comparisons with previous results including in Los Angeles, London, etc. during our discussion. Per the request, we have made some necessary minor changes in revising the manuscript. Please see the modified version for details.

Response to Reviewer #2

BC also called as soot is an important aerosol from incomplete combustion of fossil fuels and biomass burning. Understanding the soot mixing state in polluted air of Beijing, it is quite important issue to evaluate their potential optical, hygroscopic, and human health. The authors used one SP-AMS to determine mixing state of soot particles collected in Beijing during the wintertime. They found coating/BC ratio was at 5.0, much smaller than highly aged soot in other places. Also, they studied coating chemical species and their possible formation mechanism. The scope of this study is suitable for ACP. However, the paper need to one substantial revision before it can be published. I list several concerns about the conclusions.
Authors' reply: We thank the reviewer for his valuable comments, and our point-to-point replies to the reviewer's comments are listed below.

(1) L28-29 deleted very (2) L30 only
Authors' reply: Done

(3) L33-34 how do the result indicate dominant contributions from primary emissions? You can say that these particles might source from local emissions instead of long-range transport particles. Am I right?
Authors' reply: We agree that this may not be appropriate, and we deleted this sentence.

(4) L35- 36, 38-40, seemly for me, the conclusion is contrast. One you mentioned primary emission. Other one you want to mention the secondary species.
Authors' reply: We agree with that the description is not very specific. In line with comment (3), we have modified the description. "Positive matrix factorization shows presence of significant primary fossil fuel and biomass burning organics."

(5) L41 at-during

Authors' reply: done

(6) L44-45, I don't think the conclusion is from your solid result. Most you speculate these results. (7) L44-47 the conclusion cover all the possible. I would ask the author revise it carefully. What is your conclusions during the sampling period. If these solid conclusions are not from this study, you need to remove it. Seemly, I like to see what you find on BC particles not for haze formation.
Authors' reply: The conclusions are based on our results, but are indeed only for BC-particles and two specific cases during the sampling period. We agree that over-interpretation should be avoided. Therefore, we have carefully revised this sentence. "However, for individual pollution events, sometimes primary species could also play a dominant role, as revealed by the compositions of BC-particles in two polluted episodes during the sampling period."

(8) L56 Morphology of BC might be altered greatly. These citations don't supply any morphology of BC particles. You need find others from electron microscopies.
Authors' reply: We have cited a couple of electron microscopic studies, including:
Wang, Y., Liu, F., He, C., Bi, L., Cheng, T., Wang, Z., Zhang, H., Zhang, X., Shi, Z., and Li, W.: Fractal Dimensions and Mixing Structures of Soot Particles during Atmospheric Processing, Environmental Science & Technology Letters, 4, 487-493, 10.1021/acs.estlett.7b00418, 2017.
Li, W., Sun, J., Xu, L., Shi, Z., Riemer, N., Sun, Y., Fu, P., Zhang, J., Lin, Y., Wang, X., Shao, L., Chen, J., Zhang, X., Wang, Z., and Wang, W.: A conceptual framework for mixing structures in individual aerosol particles, J. Geophys. Res. - Atmos., 121, 13,784-713,798, 10.1002/2016JD025252, 2016.

(9) L77, I don't agree with the claim. For example, Wu et al., 2017. Size distribution and source of black carbon aerosol in urban Beijing during winter haze episodes. Atmos. Chem. Phys. 17 (12), 7965-7975. The study seemly, give the online BC-containing particles in Beijing.
Authors' reply: Sorry, our claim is not clear, we meant to say that no chemical characterization of BC-containing particles only. It is now changed. And in fact, the work mentioned here was already cited as a previous work on BC-particles in Beijing.

(10) L161 Discussion, deleted s
Authors' reply: done

(11) L260-261, L284-285, L331-332 L347-348, all the parts discussed the aqueous reactions for nitrate and SOA formation during the nighttime. I take a look at the data from the study. It is too simply to get such conclusion. I might ask the authors cite more related references here. For example, Wu et al., 2018. Environmental Science & Technology Letters 5 (3), 160-166;Sun et al., 2018. Journal of Geophysical Research: Atmospheres 123 (2), 1234-1243.Kuang et al., 2016. Geophysical Research Letters 43 (16), 8744-8750.

Authors' reply: Thanks for the references provided. The aqueous-phase production of secondary species was a possible pathway in a qualitative manner. The references provided, which are also conducted in NCP, in fact strongly support our postulated aqueous-phase pathway therefore are very useful. They have now been cited along with our discussion in the main text. "Similarly, nitrate and sulfate formations driven by high RH in North China Plain have been proved previously (Kuang et al., 2016; Sun et al., 2018;Wu et al., 2018)."

(12) L278-279 I don't understand the sentence. Why was the large decrease of organics coating concentration?
Authors' reply: Since R_{BC} is the ratio of concentrations of total coating material to BC cores. There was a drop of R_{BC} at 4:00pm, however, since nitrate/BC, sulfate/BC and chloride/BC did not decrease around 4pm (there was even an increase of nitrate/BC), the decrease of R_{BC} must be caused by the decrease of organic/BC. And Fig.4f further shows that it is in fact the portions of BBOA and FFOA decreased since the OOA1/BC and OOA2/BC in fact increased. We have revised the sentence in the text. "In fact, the 4:00pm R_{BC} drop was mainly caused by the large decrease of Org/BC (as SO_4^{2-}/BC, NO_3^-/BC and Cl^-/BC did not decrease at 4:00pm, Fig. 5d) - mainly the portions of fossil fuel and biomass burning OA (Fig. 4f). "

(13) L292 at-during
Authors' reply: done

(14) L307 This can be expected for urban aerosols. I don't understand it. Why?
Authors' reply: We have expanded this sentence. "As BC-containing particle in urban Beijing were likely influenced by multiple local/regional primary sources, relative amount of secondarily formed coating species would be less than those of highly aged BC, therefore a lower R_{BC} is expected."

(15) L328 of-at (16) L269 miss comma after ws (17) L317 at two polluted episodes
Authors' reply: done

(16) For section 3.5.2 Seemly, the authors found different coating species on soot particles. FE, the author found large SOA; SE the author proposed large POA instead of SOA. Do the authors answer how POA associated with BC? If these particles were emitted from sources, these mixing should occur in all the time, not just SE. Were there different sources in SE and FE? Seemly, the author didn't supply any wind and backtrajectories here. I would ask the authors carefully check the data. Make sure the differences in FE and SE are large. Here the authors only compared the organics. What about the sulfate and nitrate are in the coating of BC there. I am certainly struggling on the part.
Authors' reply: As requested, we have added the back trajectories, wind rose plots, as well as the vertical distributions of wind speeds/directions during these two episodes. It shows clearly that these episodes are very different, and therefore they would have

different sources. Yes, it is likely that a portion of the POA associated with BC might come from the sources (they mixed together with BC from the source), and such a portion might be present all the time. Nevertheless, what we try to demonstrate here is that: during FE, significant production of secondary species (likely from aqueous-phase reactions) of sulfate, nitrate and OOA1 led to the significant increase of BC-particles, while during SE, it was mainly the POA led to the extremely high loading of BC-particles. This can be seen clearly from the composition pie charts (Figs. 7a and 7b). Also, please note the major inorganic components including sulfate, nitrate, chloride and ammonium were also shown. Increases of inorganic species were also observed during FE not only organics, while during SE, inorganic species were significantly lower than those of the average case. We have modified the writing to make our arguments clear and straightforward.

Characterization of black carbon-containing fine particles in Beijing during wintertime

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For *Atmospheric Chemistry & Physics*

Abstract

Refractory black carbon (BC) is a product from incomplete combustion of fossil fuel, biomass and biofuel, etc. By mixing with other species, BC can play significant roles in climate change, visibility impairment and human health. Such BC-containing particles in ~~very~~ densely-populated megacities, like Beijing, may have specific sources and properties, that are ~~very~~ important to ~~the~~ haze formation and air quality. In this work, we characterized exclusively the BC-containing particles ~~only~~ in urban Beijing, by using a laser-only Aerodyne soot particle aerosol mass spectrometer (SP-AMS), as a part of the Air Pollution and Human Health (APHH) 2016 winter campaign. The average mass ratio of coating-to-BC (R_{BC}) was found to be ~5.0~~, much smaller than those of highly aged BC, indicating dominant contributions from primary emissions.~~. Positive matrix factorization ~~indeed~~ shows ~~the dominance~~presence of significant primary fossil fuel and biomass burning organics~~.~~ (64% of total organics). Yet secondary species, including ~~both~~ sulfate, nitrate and oxygenated organic aerosol (OA) species, could have significant impacts on the properties of BC-containing particles, especially for ones with larger BC core sizes and thicker coatings. Analyses of ~~the~~ sources and diurnal cycles of organic coating reveal significant afternoon photochemical production of secondary OA (SOA), as well as ~~the~~ nighttime aqueous production of a portion of highly oxygenated OA. Besides SOA, photochemical production of nitrate, not sulfate, ~~was very~~appeared to be important. Further investigations on BC-containing particles ~~at~~during different periods show that, on average, more polluted periods would have more contributions from secondary species, and more thickly coated BC tended to associate with more secondary species, indicating the important role of chemical aging to the ~~air~~ pollution of BC-containing particles in urban Beijing during wintertime. However, for individual pollution events, ~~aqueous-phase production of sulfate, nitrate and SOA might aggravate the pollution obviously under high relative humidity conditions, while sometimes local~~ primary ~~emissions~~ (~~species (fossil fuel,~~ coal and biomass burning emissions) could ~~lead to serious and extremely~~also play a dominant role, as revealed by the compositions of BC-particles in two polluted ~~event too.~~ episodes during the sampling period.

1. Introduction

Black carbon (BC) is generated from incomplete combustion of carbon-based fuels (Ramanathan and Carmichael, 2008), and can exert significant impacts on global and regional climate, planetary boundary layer height (PBLH), air quality and human health, etc. (Lee et al., 2017; Bond et al., 2013; Ding et al., 2016). BC can strongly absorb solar radiation and warm up the atmosphere directly. By internally or externally mix with non-BC materials (coatings, including co-emitted primary organics/inorganics and secondary materials that associate with BC) (Chen et al., 2016a; Lee et al., 2017; Wang et al., 2017a), the properties and morphologies of BC might be altered greatly (Liu et al., 2013; Liu et al., 2017; Liu et al., 2015; Cappa et al., 2012; Peng et al., 2016; Wang et al., 2017c; Li et al., 2016). Thick coating can increase the mass absorption cross section of BC, thus enhance the light absorption of BC core via "lensing effect" (Jacobson, 2011; Liu et al., 2015; Pokhrel et al., 2017). However, coating thickness of BC-containing particles significantly depends on ~~their~~ sources/chemical ~~composition~~compositions and aging processes, thus there are great uncertainties on light absorption enhancement (E_{abs}) of BC as well as its global radiative forcing (Cappa et al., 2012; Liu et al., 2017; Cui et al., 2016; Liu et al., 2015). For instance, the mass ratio of coatings to BC core (R_{BC}, an analog of coating thickness) from biomass burning is usually greater than 3 (Liu et al., 2017) and can be larger than 10 in remote sites (Wang et al., 2017a). Normally, when R_{BC} is less than 1.5, it is probably from traffic sources, whereas secondary organic aerosol (SOA) dominated BC-containing particles is usually with a R_{BC} greater than 4 (Lee et al., 2017). Moreover, the coating species can modify the hygroscopicity of BC-containing particles (Liu et al., 2013) when associated with hydrophilic materials, and some of them can ~~serve as~~activated into cloud condensation nuclei (CCN), therefore alter the albedo and precipitation of clouds indirectly (Dusek et al., 2010; Dusek et al., 2006).

In the past decades, a number of field studies on BC have been conducted in the winter of Beijing, and mainly focused on BC mass loadings, mixing states, optical properties, human health impacts and sources (coal combustion, biomass burning and vehicles, etc.) (Wu et al., 2017; Cheng et al., 2017; Ji et al., 2017; Wang et al., 2017b; Wu et al., 2016; Chen et al., 2016b; Meng et al., 2016; Wang et al., 2016b; Liu et al., 2016; Yang et al., 2014; Schleicher et al., 2013a; Schleicher et al., 2013b; Song et al., 2013; Zhang et al., 2017). There were real-time studies on BC, and on the chemical characteristics of total fine particles (including particles with and without BC) in Beijing. However, to the best of our knowledge, no study was conducted in real-time to characterize the chemical compositions exclusively

~~only~~of BC-containing particles in Beijing despite the important effects of coating materials on BC properties aforementioned. Currently, a few studies have explored BC-containing particles in other locations, e.g., Toronto (Willis et al., 2016; Lee et al., 2015), California (Lee et al., 2017; Massoli et al., 2015; Cappa et al., 2012), London (Liu et al., 2015) and Tibet (Wang et al., 2017a) by using the Aerodyne soot-particle Aerosol Mass Spectrometer (SP-AMS) (Onasch et al., 2012; Lee et al., 2015; Wang et al., 2016a; Ge et al., 2017b). The SP-AMS physically combines the 1064 nm laser vaporizer of single particle soot photometer (SP2) into a high-resolution aerosol mass spectrometer (HR-AMS~~)~~ ~~(Onasch et al., 2012;Canagaratna et al., 2007).~~). After removal of the AMS tungsten vaporizer and by operating the instrument with ~~the~~ laser vaporizer only, refractory BC as well as its associated coating can be evaporated since the 1064 nm laser can selectively heat the BC (Massoli et al., 2015). In other words, ~~the~~ laser-only SP-AMS can exclusively measure BC cores and the species coated on BC cores. This unique technique allows us to explore in details the characteristics of BC-coating species with no perturbations from other co-existing non-BC containing particles in ambient air.

Beijing, as the most reprehensive megacity with a large population in developing countries, the BC-containing particles may have specific source profiles and physiochemical properties, therefore elucidation of its characteristics is important to understand the haze formation and improve air quality in such regions. ~~In this work,~~In this work, as a part of the UK-China Air Pollution and Human Health (APHH) study (Shi et al., 2018), we report for the first time the real-time measurement results on the chemical composition, mass loading, size distribution, and sources/processes of ~~the~~ BC-containing particles during wintertime of 2016 in urban Beijing ~~by using the laser-only SP-AMS.~~ Results regarding ~~mixing states~~ physical properties and optical properties are presented in ~~other publications in~~Liu et al. (2018) and Xie et al. (2018) of this special issue~~.~~, respectively.

2. Experiments

2.1 Sampling site and instrumentation

As a part of the ~~UK-CHINA-Air Pollution & Human Health (~~APHH~~)~~ winter campaign, we conducted measurements at the Tower Division of Institute of Atmospheric Physics (IAP), Chinese Academy of Science (39°58′N, 116°22′E) in Beijing (Figure S1 in the supplement), from 15 November to 13 December of 2016. The site was surrounded by residential infrastructures and a freeway in the east (360m).

The SP-AMS was deployed on the rooftop of Herong Building (~8m above the ground), with a $PM_{2.5}$ cyclone (Model URG-2000-30EN) and a diffusion dryer in front of the inlet. The single particle soot photometer (SP2, Droplet Measurement Technology, Inc., Boulder, CO, USA) was operated simultaneously ~~nearby~~ inside another container nearby (~20 m away) on the ground. The SP2 incandescence signal was calibrated for BC mass by using Aquadag® black carbon standard (Aqueous Deflocculated Acheson Graphite, Acheson Inc., USA) (Laborde et al., 2012). For the SP-AMS, since the filament that ejects electrons can still heat the tungsten vaporizer up to ~200 °C (Willis et al., 2014) even it is turned off, the tungsten vaporizer was thus physically removed to make sure only BC and its associates were vaporized by the laser, and to eliminate influences from species uncoated on ~~the~~ BC cores.

The tuning and calibration procedures of ~~the~~ SP-AMS followed the procedures described previously (Lee et al., 2015; Willis et al., 2016; Massoli et al., 2015; Wang et al., 2017a). During the campaign, the SP-AMS was run with a 10-minutes cycle: one W mode with high chemical resolution (2.5 min) and two mass sensitive V modes including one with particle time of flight (PToF) mode (2.5 min) and another one (5 min) with ~~the measured~~ a large mass-to-charge (*m/z*~~-~~) range (up to 2000~~ to investigate fullerene-like carbon clusters~~) (Wang et al., 2016a). The filtered air measurement was performed for a day to determine the detection limits (DLs) of various aerosol species and to adjust the fragmentation table. The ionization efficiency (IE) and relative ionization efficiency (RIE) of sulfate and nitrate were calibrated by using pure ammonium nitrate and ammonium sulfate according to Jayne et al. (2000), respectively. RIE of BC was calibrated by using Regal Black (RB, REGAL 400R pigment black, Cabot Corp.) (Onasch et al., 2012), and the average ratio of C_1^+ to C_3^+ was determined to be 0.53 to minimize the influence of C_1^+ from non-refractory organics. However, it should be aware that laser-only SP-AMS cannot vaporize ammonium nitrate/sulfate if they do not coat on BC, thus the IE and RIE calibrations were done before removal of the tungsten vaporizer and the values were assumed to be unchanged after the tungsten heater's removal (Willis et al., 2016). Note the RIE of BC was calibrated before the campaign and was repeated in the middle and end of the campaign. RIEs of nitrate, ammonium, sulfate and BC were determined to be 1.1, 3.82, 0.82, and 0.17, respectively. The default value of 1.4 was used as RIE of organics (Canagaratna et al., 2007). Polystyrene latex (PSL) spheres (100-700 nm) (Duke Scientific Corp., Palo Alto, CA) were used to calibrate the size before the campaign (Canagaratna et al., 2007) .

2.3 Data Analysis

Standard AMS data analysis software (Squirrel and Pika) based on Igor Pro 6.37 (Wavemetrixs, Lake Oswego, OR, USA) were used to obtain the concentrations, mass spectra and size distributions of BC and its coating species. All data were calculated based on high-resolution fitting results. Due to different vaporization schemes between the SP-AMS and HR -AMS, mass spectra from these two instruments even for the same population of particles are not entirely the same. Laser-only SP-AMS can result in overall less fragmentation, therefore the mass profile may contain more large *m/z* fragments and less small *m/z* fragments compared with that from HR-AMS (Massoli et al., 2015). Therefore, here the elemental ratios of organics, i.e., oxygen-to-carbon, hydrogen-to-carbon and nitrogen-to-carbon ratios (O/C, H/C and N/C) were determined by the Aiken approach first (Aiken et al., 2008), and then O/C and H/C were corrected by using factors of 0.83 and 1.16, respectively (Canagaratna et al., 2015).

Source apportionment for organics coated on BC was conducted by using Positive matrix factorization (PMF) (Paatero and Tapper, 1994) Evaluation Tool written in Igor (Ulbrich et al., 2009). In this study, high-resolution mass spectra (HR-MS) of organic (including BC) and inorganic species were combined together to perform the PMF analyses (Sun et al., 2012; Wang et al., 2017a; Wang et al., 2018). It should be noticed that, only fragment ions from polycyclic aromatic hydrocarbons (PAHs) were included for *m/z* range of ~150 to ~250 in the PMF analysis because of the limited mass resolution of SP-AMS. All PMF solutions were evaluated following the standard instruction (Zhang et al., 2011). Finally, four types of organic aerosol (OA) associated with BC were determined eventually, including a fossil fuel combustion OA (FFOA), a biomass burning OA (BBOA) and two oxygenated OA (OOA1 and OOA2~~).~~) (a diagnostic plot was provided in Fig. S2).

Supporting data such as meteorological parameters including relative humidity (RH), wind speed (WS), wind direction (WD) and temperature (T), as well as concentrations of gaseous species such as O_3, SO_2, NO, NO_2, NO_x, NO_y, NO_z, and CO were measured in parallel simultaneously. All data reported here were at local time (Beijing Time, UTC+8).

3. Results and ~~discussions~~discussion

3.1 Overview of BC-containing aerosol characteristics

Figs. 1 and 2 show the temporal variations of meteorology parameters, mass loadings of gaseous

pollutants (CO, NO_x, SO_2 and O_3), BC and its associated coating components (sulfate, nitrate, ammonium, chloride, total OA and ~~the~~ four PMF-resolved OA factors). The campaign-averaged composition of BC-containing particles and mass contributions of the four OA factors to total OA were also displayed in Fig. 2. Overall, wind directions and speeds had close associations with ~~the~~ overall mass loadings of BC-containing particles. The pollution periods (characterized by concentrations of BC-containing particles above 10 μg m^{-3}) were accompanied by relatively low wind speeds (<4 m s^{-1}) and in a relatively large part from southern air masses since Beijing is at the foot of the mountains which facilitate the accumulation of pollutants from southern North China Plain (NCP). The clean periods (characterized by the concentrations of BC-containing particles below 10 μg m^{-3}) were mainly under the control of northwest strong winds (>4 m s^{-1}) ~~from the northwest.~~(Fig. S3). During the campaign, the mass loadings of BC cores and BC-containing particles ranged from 0.11 ~26.54 μg m^{-3} and 0.71~174.40 μg m^{-3}, with an average of 4.9 μg m^{-3} and 29.4 μg m^{-3}, respectively. We also compared BC concentrations determined by the SP-AMS with those from SP2, and they correlated quite well with each other (r^2 of 0.93; Fig. ~~S3~~S4), indicating the quantification of BC by the SP-AMS is reliable.

The coating species occupied on average about 83.4% of the mass of BC-containing particles, indicating BC was generally thickly coated throughout the whole campaign, with an average mass ratio of coatings to BC (R_{BC}) of ~5.0. Organic aerosol (OA) was the most abundant coating component, taking up to 59.4% of the total mass, followed by nitrate~~,~~ (8.8%), sulfate~~,~~ (6.5%), ammonium (4.7%) and chloride (~~8.8%, 6.5%, 4.7% and~~ 4.0~~%, respectively).~~%). OA correlated quite well with BC (r^2 of 0.97), suggesting that many OA species were co-emitted and mixed with BC, and indeed, primary OA (POA=FFOA+BBOA) was found to dominate the OA mass (66.3%=43.9%+22.4%). Chloride (Cl^-) had a great correlation with BC (r^2 of 0.94), suggesting it was mainly associated with primary emissions, for example, gasoline, diesel and coal combustion during wintertime in urban Beijing. Sulfate and nitrate are typically secondarily formed, therefore their correlations with BC were relatively weak (r^2 of 0.64 for SO_4^{2-} *vs.* BC, and 0.60 for NO_3^- *vs.* BC). Their properties are discussed in ~~more~~ details in the following sections.

3.2 Chemically-resolved size distributions of BC-containing particles

Fig. 3a shows the campaign-averaged mass-based size distributions of major BC-coating species,

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including organics (BC-Org), sulfate (BC-Sulfate), nitrate (BC-Nitrate), chloride (BC-Chl) and BC core itself. It should be noticed that the size distribution of BC was scaled from that of *m/z* 24 (C_2^+), as other major carbon cluster ions might be significantly affected by other ions, for example, C_1^+ at *m/z* 12 can be influenced by fragments from non-BC organics, C_3^+ at *m/z* 36 by HCl^+, C_4^+ at *m/z* 48 by SO^+, and C_5^+ at *m/z* 60 by $C_2H_4O_2^+$ etc. Similarly, the size distribution of BC-Chl was scaled from Cl^+ signal at *m/z* 35. As shown in Fig. 3a, on average, size distributions of BC-Sulfate, BC-Nitrate and BC-Org displayed a similar pattern with a major peak at ~550 nm (vacuum aerodynamic diameter, D_{va}), suggesting that they were relatively well internally mixed. However, the BC presented a remarkably different pattern with a much broader distribution and smaller peak sizes than its coating species, and in particular, relatively small particles tended to have thin coatings.

Figs. 3b-f further present image plots of size distributions of the major aerosol components as a function of R_{BC} (~~as~~ a surrogate ~~for~~of coating thickness). Different from the average data shown in Fig. 3a, the coating species can be roughly classified into two modes separated by R_{BC} of ~4.5. Most sulfate and nitrate concentrated at R_{BC}>4.5 (Figs. 3b and 3c): Sulfate peaked in a narrow R_{BC} range of 5.5~6.5, while significant nitrate mass could distribute across a wider R_{BC} range (even to R_{BC} of ~8.0). Only organics and chloride had a significant portion of mass distributed on relatively thinly coated BC-containing particles at R_{BC}<4.5 (Figs. 3e and 3f). Specifically, they both showed a sub-mode locating in the regime with R_{BC} of ~3.5-4.5 and D_{va} of ~200-700nm. These sub-modes suggest that organics or chloride are partially from primary sources as freshly emitted BC are more likely thinly coated. This is consistent with that organics included species from fossil fuel and biomass burning combustion revealed by the PMF analysis. Similarly, coal burning might contribute to chloride during wintertime in Beijing (Sun et al., 2016). As for sulfate and nitrate, since they are predominantly secondary species, they would coat on BC cores due to chemical aging therefore mostly distributed at higher R_{BC}.

3.3 Sources of organic coating species

The ~~high-resolution mass spectra (~~HRMS~~)~~ of different factors of the organic coating resolved from PMF analyses, their relative contributions and diurnal cycles of temporal variations relative to BC are shown in Fig. 4. Fig. 4a illustrates the mass profile of the fossil fuel combustion OA with BC carbon clusters (FFOA + BC). This factor had a low O/C ratio of 0.16. In this work, this factor might include emissions from both traffic and coal combustion, as it contained a series of significant PAHs ion

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fragments in the mass spectrum (PAHs fragments are negligible in other factors) indicative of coal burning (Sun et al., 2014; Sun et al., 2016), and presented a good correlation with $C_4H_9^+$ (r^2 of 0.72) ~~which is~~ a AMS tracer ion of vehicle emissions (Zhang et al., 2005). Temporal variations of FFOA also correlated well with $C_9H_7^+$ (*m/z* 115, r^2 of 0.92) and Cl^- (r^2 of 0.60), which have been proposed as possible coal combustion tracer species (Yan et al., 2018; Sun et al., 2014). The FFOA/BC (Fig. 4f) appeared to be higher during nighttime than that during daytime. Note the diurnal pattern of BC itself (Fig. 5c) was similar as that of FFOA/BC. The diurnal variations of BC might be influenced by both fossil fuel combustion activities and relatively low PBLH during nighttime. The fossil fuel combustion included coal burning and vehicle emissions (gasoline cars, and the heavy-duty diesel vehicles that are only allowed to enter the city during later night). The mass ratios of different factors to BC shall have less influences from PBLH, therefore high levels of FFOA/BC strongly indicate that co-emitted organic species with BC from fossil fuel combustion were enhanced during nighttime.

Figure 4b shows the mass spectrum of BBOA and related BC clusters. One feature of this factor is that it had relatively high fractional contributions of $C_2H_4O_2^+$ (1.47% of total) and $C_3H_5O_2^+$ (0.95%), which are often regarded as AMS marker ions from biomass burning emitted levoglucosan (Cubison et al., 2011; Mohr et al., 2009). Note the FFOA also contained appreciable $C_2H_4O_2^+$ and $C_3H_5O_2^+$ signals, partially due to that coal burning (such as lignite) can emit some levoglucosan as well (Yan et al., 2018). Nevertheless, mass fractions of $C_2H_4O_2^+$ and $C_3H_5O_2^+$ in FFOA were less than those in BBOA, and they correlated much better with BBOA than those with FFOA (for examples, r^2 of 0.90 for BBOA *vs.* $C_2H_4O_2^+$, and 0.72 for FFOA *vs.* $C_2H_4O_2^+$). The BBOA correlated very well with another biomass burning tracer - K^+ (r^2 of 0.90). In addition, BBOA had negligible PAHs ion fragments while the FFOA contained remarkably high PAHs signals. Such characteristics are generally in agreement with previous AMS findings in the same location during wintertime in Beijing (Sun et al., 2016). For these reasons, the second factor was identified as BBOA. The diurnal pattern of BBOA/BC reached minimum during afternoon and was overall high during nighttime, similar as FFOA/BC, indicating the nighttime enhancement of BB-related organics emissions in wintertime Beijing.

Besides the two POA factors, we also identified two secondary OA factors (OOA1 and OOA2), whose O/C ratios were 0.45 and 0.28, respectively. OOA1 was the most oxidized OA factor that had a higher $CO_2^+/C_2H_3O^+$ ratio than that of OOA2. The correlation between OOA1 and sulfate was better than it with nitrate (r^2 of 0.99 *vs.* 0.86). As a comparison, the less oxygenated OOA2 correlated better

with nitrate than it with sulfate (r^2 of 0.59 *vs.* 0.34). These characteristics are consistent with previous AMS-PMF results (Zhang et al., 2011). Opposite to the diurnal cycles of FFOA and BBOA, the OOA2/BC ratio arose significantly from early morning and peaked in the afternoon (~3pm). The diurnal pattern of OOA1/BC presented a similar peak at ~3pm. This result demonstrates a clear evidence and important role of afternoon photochemical reactions to the formation of secondary organic species. However, the precursors leading to the formations of OOA1 and OOA2 remain to be elucidated. Interestingly, for OOA1/BC, in addition to the peak during afternoon, ~~the ratio~~it increased during early evening and remained at high levels until early morning. This result indicates that nighttime aqueous-phase processing (high levels of RH during nighttime shown in Fig. 5a) can also contribute to OOA1 production. As such behavior was not observed for OOA2/BC, it agrees with previous field and laboratory findings that aqueous-phase reactions tend to produce more highly oxygenated species (Ervens et al., 2011; Ge et al., 2012; Herrmann et al., 2015; Xu et al., 2017).

Overall, the mass fractions of BC cores that were associated with fossil fuel combustion, biomass burning, less and more oxygenated secondary processes were 32.7%, 31.8%, 18~~,~~.7% and 16.9%, respectively (Fig. 4e). The organic coating of BC was predominantly ~~coated by~~ primary species.

3.4. Diurnal patterns of BC and coating species

Fig. 5 presents the diurnal cycles of meteorological parameters (T, RH, WS and WD), BC concentrations and R_{BC}, mass ratios of major species to BC, gaseous species (CO, SO_2 and NO_x), O/C and OS_c (oxidation state, defined as 2*O/C-H/C)(Kroll et al., 2011). Note BC did not present a peak at 8:00 am, yet $R_{BC,}$ Org/BC, SO_4^{2-}/BC, NO_3^-/BC and Cl^-/BC were all low at ~8:00 am. This was likely attributed to increase of the mass fractions of fresh and barely coated BC-containing particles (rather than the increase of absolute concentrations of fresh BC-containing particles) emitted during morning rush hours from traffic emissions, etc. This was consistent with the decreases of O/C and OS_c and increases of CO and NO_2 at 8:00 am of the day. On the contrary, the R_{BC} drop at ~4:00 pm was unlikely due to influences of afternoon rush hours, as there were no increases of CO, NO_2, and both O/C and OS_c were at high levels. In fact, the 4:00pm R_{BC} drop was mainly caused by the large decrease of ~~organics coating concentration~~Org/BC (as SO_4^{2-}/BC, NO_3^-/BC and Cl^-/BC did not decrease at 4:00pm, Fig. 5d) - mainly the portions of fossil fuel and biomass burning OA (Fig. 4f).

The diurnal variation of NO_3^-/BC peaked at ~3-4 pm, consistent with the variation of T, and similar

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as those in the previous reports during wintertime in Beijing (Ge et al., 2017a; Sun et al., 2016), reflecting the dominated contribution of photochemical formation of nitrate. SO_4^{2-}/BC showed a relatively small afternoon increase, indicating partial sulfate was produced from photochemical activities; it also presented a nighttime enhancement, similar as OOA1/BC, suggesting the sulfate formation in aqueous-phase, consistent with the nighttime increase of RH and decrease of temperature (Fig. 5a). Due to increases of FFOA/BC, BBOA/BC and OOA1/BC (the portion likely from aqueous-phase production), Org/BC remained at high levels during nighttime. All these increases added together, leading to the high R_{BC} during nighttime. In addition, Cl^-/BC varied generally similar to those of FFOA/BC and BBOA/BC, again indicating its strong association with primary emissions.

3.5 Characteristics of coating species during different periods

3.5.1 Coating compositions ~~at~~during clean and pollution periods

Fig. 6 shows the variations of BC-coating compositions as a function of ~~coating thickness~~R_{BC} during clean (CP) and pollution periods (PP) (~~separated~~divided by the concentration of 10 μg/m^3), respectively. Contrasting difference of the coating composition during these two cases was observed: primary OA (especially FFOA) appeared to be the most abundant component during CP while mass contributions of secondary organic and inorganic species were remarkably high during PP (Figs. 6a and b), and the average R_{BC} during PP (~5.1) was also higher than that during CP (~4.5) (Fig. 6f). These results again reinforce the importance of secondarily formed species to the heavy haze pollution in urban Beijing (Huang et al., 2014). Furthermore, the BC coating composition as well as OS_c during CP were both relatively stable against R_{BC} (Fig. 6c). On the contrary, during PP, with the increase of R_{BC}, the mass fractions of secondary species (OOA1, nitrate and sulfate) increased clearly, especially at R_{BC}>5; consistently, OS_c of organic coating increased from ~-0.85 to >-0.70. Such behavior again highlights the contribution of chemical aging process to the heavy haze pollution.

Relative to other observations (Wang et al., 2017a; Massoli et al., 2015; Cappa et al., 2012), the levels of R_{BC} during both CP and PP are much smaller than those for highly aged BC, which might have R_{BC}>10. ~~This can~~As BC-containing particle in urban Beijing were influenced by multiple local/regional primary sources, relative amount of secondarily formed coating species would be less than those of highly aged BC, therefore this lower R_{BC} is expected ~~for urban aerosols.~~ On the other hand, the R_{BC} levels ~~here~~ are ~~also~~ generally higher than those found for the BC-containing particles in

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Los Angeles where the average R_{BC} was typically smaller than 4 due to ~~predominant~~direct and prominent influence of vehicle emissions (Lee et al., 2017). Regarding the variations of coating composition *vs.* R_{BC}, the behavior during PP is in fact consistent with a few previous field measurement results in American or European urban locations (Massoli et al., 2015; Liu et al., 2017; Lee et al., 2017; Cappa et al., 2012; Collier et al., 2018), indicating a general behavior for BC-containing particles in urban area that more aged BC tends to have thicker coating. Yet this property can be altered if significant POA emissions exist, such as the case during CP in this work, and a case with heavy BBOA influences observed in Tibet Plateau (Wang et al., 2017a).

3.5.2 Coating compositions ~~at~~during two different episodes

Although we demonstrated in Section 3.5.1, the heavy pollution of BC-containing particles was on average associated with more secondary species, the underlying governing factors of individual pollution events might vary from each other. Here we investigated the characteristics of BC-containing particles in two most polluted episodes occurring during the campaign. The first episode (FE) was accompanied with relatively high RH (from 6:00 pm of 3 Dec. to 8:00 am of 4 Dec., 2016), while the second episode (SE) was dominated by primary emissions (from 0:00 am to 6:00 am of 11 Dec., 2016). The average mass loadings of BC cores and BC-containing particles were 18.1 μg m^{-3} and 123.1 μg m^{-3} during FE, 14.4 μg m^{-3} and 80.0 μg m^{-3} during SE, respectively - both were much higher than the campaign-averaged BC of 4.9 μg m^{-3} and BC-containing particles of 29.4 μg m^{-3}. Back trajectories, wind rose plots and distributions of the wind speeds/directions of these two episodes were provide in Fig. S5, showing that these two episodes had remarkably different air mass origins and sources.

For FE, the average T and RH were ~4.2 °C and ~78%, respectively. The average T was close to the campaign-average value of 4.8ºC, but the air was more humid than the campaign-average RH of ~50%. Correspondingly, we observed ~~clear increases~~remarkable elevations of the mass contributions of sulfate from 6.5% to 10.3%, nitrate from 8.8% to 10.2%, OOA1 from 7.5% to 11.5% (Figs. 7a and 7c). Such enhancements were very likely linked with the aqueous-phase processing as this episode occurred during nighttime and was characterized with high RH conditions. During FE, nitrate and sulfate also correlated very well (r^2 of 0.94; Fig. ~~S4~~S6), therefore formation of nitrate would also relate with aqueous-phase processing in this episode. Consistently, nitrate and sulfate formations driven by high RH in North China Plain have been proved previously (Kuang et al., 2016; Sun et al., 2018; Wu

et al., 2018). As a comparison, the mass fraction of photochemical-relevant OOA2 decreased significantly from campaign-average 13.3% to 9.8%. In addition, mass fraction of Cl^- also increased from campaign-average 4.0% to 5.3%; meanwhile, we found that relative to the campaign-average values, the KCl^+/BC ratio decreased 14%, the $K_3SO_4^+$/BC ratio increased 28%, possibly indicating that the heterogeneous replacement reactions of coal-burning related Cl^- by SO_4^{2-} during FE (Fig. ~~S4~~S6). Overall, due to mainly the aqueous-phase production of secondary coating components, comparing to campaign-average values, the average R_{BC} during FE became larger (5.5 *vs.* 5.0), ~~the~~ OA became more oxygenated (O/C of 0.18 *vs.* 0.15), and size distributions of OA, sulfate and nitrate all shifted to larger peak sizes (Fig. ~~S5a~~S7a).

On the other hand, for SE, even though it also occurred during nighttime, the average RH was significantly low (~47%), and it was overwhelmingly dominated by primary species (50.6% of FFOA, 15.2% of BBOA and 18% of BC). Secondary sulfate and nitrate only ~~occupied~~took up 2.5% and 2.2% of the total mass of BC-containing particles. Nighttime aqueous-phase related OOA1 contribution was nearly negligible (only 0.8%), which in another way, manifests that during nighttime ~~efficient~~ OOA1 production was strongly associated with high RH conditions. Due to the contribution of fresh primary emissions, the coating OA was less oxygenated than that of campaign-averaged OA (O/C of 0.12 *vs.* 0.15), and the average R_{BC} during ~~PE~~SE was consistently smaller (4.5 *vs.* 5.0). Mass spectrum of BC-Org (Fig. 7b) also contained significant PAHs fragments, in line with the large contribution from FFOA (mainly coal combustion). Average size distribution of OA during SE was broader and peaked in a smaller diameter (<500 nm D_{va}) (Fig. ~~S5b~~S7b), in response to the dominance of POA. Occurrence of the highly polluted SE demonstrates that even though the pollutions of BC-containing particles in urban Beijing during winter are on average governed by secondary species, local primary emissions sometimes can lead to serious and short-term pollution events as well.

4. Conclusions

As part of the UK-China 2016 APHH winter campaign, for the first time, an Aerodyne SP-AMS was introduced to exclusively determine the chemical compositions of BC-containing particles in urban Beijing. We found the average concentrations of BC and its coating species were 4.9 and 24.5 μg m^{-3}, ~~namely~~therefore the R_{BC} (mass ratio of coating to BC) was ~5.0. The coating was dominated by organics (59.4% of total mass of BC-containing particles), followed by nitrate and sulfate (15.3%

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together). Size distribution data ~~demonstrate~~demonstrates that larger BC-containing particles tend to have thicker coating, more secondary species and more internally mixed coating components. PMF analyses of organic coating further identified two POA factors ~~related~~relevant with fossil fuel and biomass burning, respectively, which dominated the total OA mass. Two SOA factors were also separated, and both of them were found to be mainly contributed by photochemical activities, besides a fraction of the highly oxidized OA factor could be produced by nighttime aqueous-phase reactions. In addition, significant photochemical formation of nitrate rather than sulfate in the afternoon was observed.

Comparisons of the coating compositions between clean and pollution periods shows the critically important role of chemical aging for the pollution of BC-containing particles in urban Beijing. We also found that in one case, aqueous-phase production might lead to serious pollution under high RH conditions, while in another case, fossil fuel combustion could cause extreme and short-term heavy pollution. Comparisons between the BC-containing particles and the total submicron aerosol particles during this campaign will be presented in details in near future.

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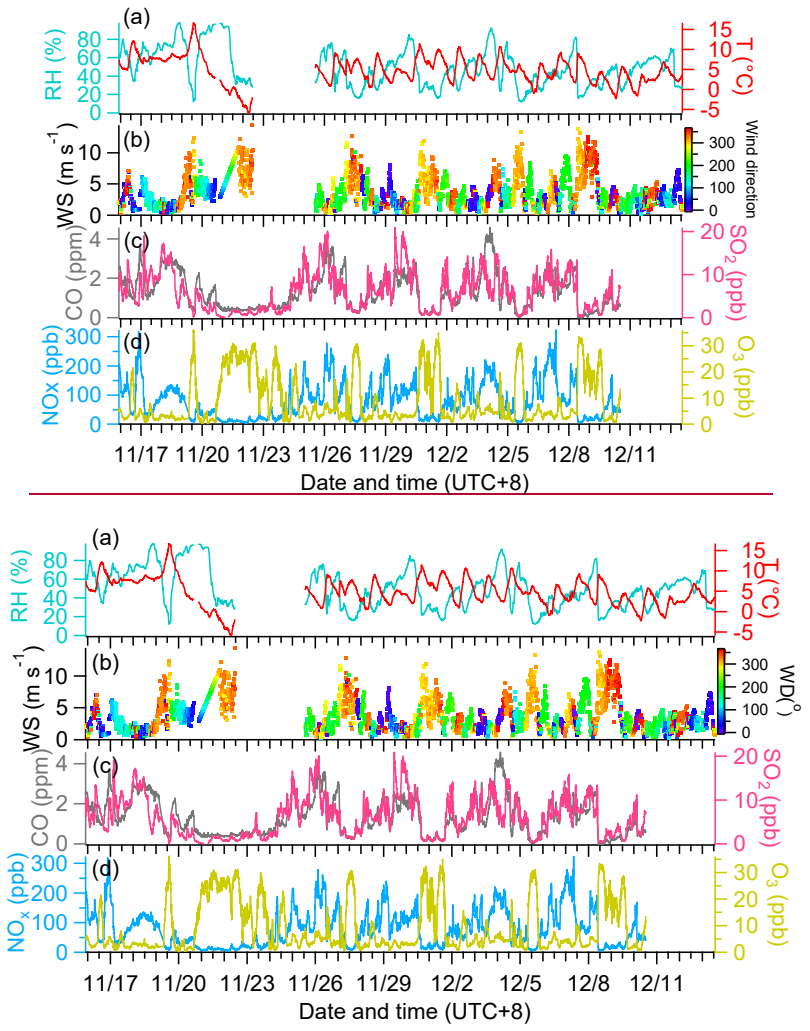


Figure 1. Temporal variation of (a) relative humidity (RH) and temperature (T, °C), (b) wind speed (WS, m s^{-1}) and wind direction (WD), and (c)(d) mass loadings of CO, SO_2, NO_x and O_3.

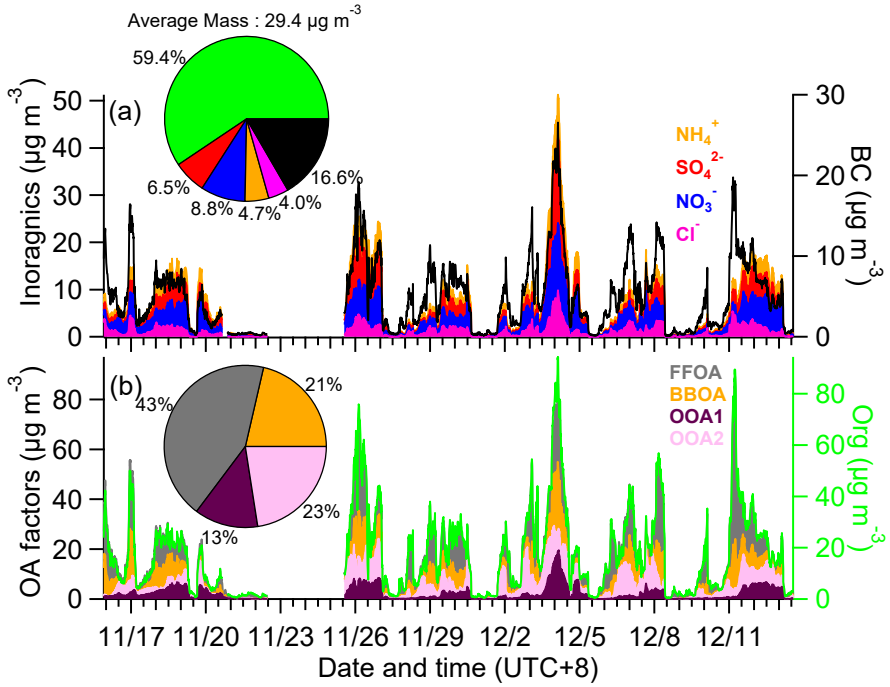


Figure 2. (a) Temporal variations of mass loadings of inorganic coating components (sulfate, nitrate, ammonium and chloride) and BC cores, and (b) temporal variations of mass loadings of organic coating (Org) and PMF separated OA factors (inset pie charts show the average composition of total BC-containing particles~~,~~ and organics, respectively).

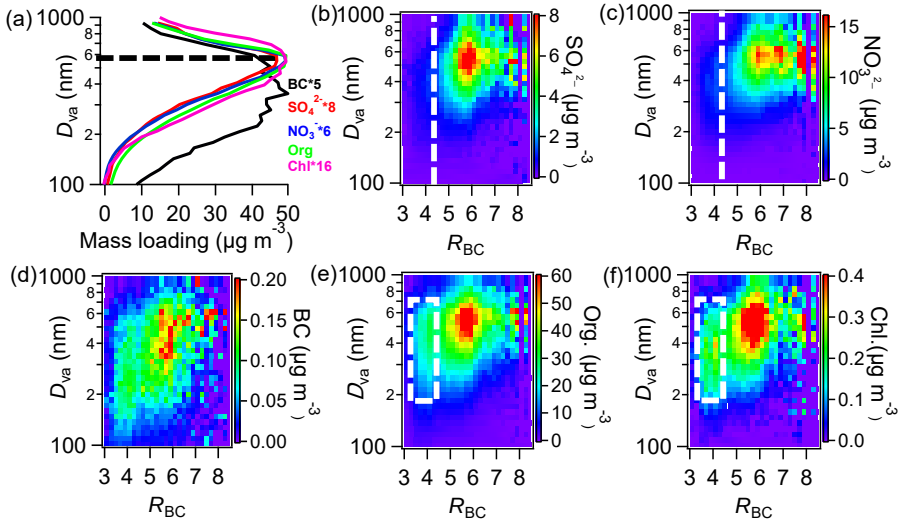
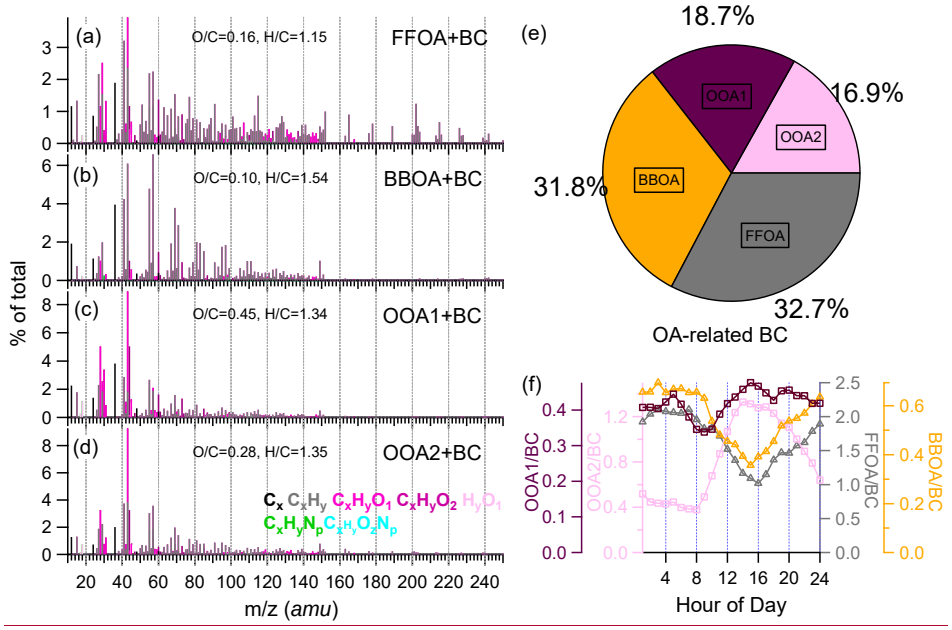


Figure 3. Mass-based campaign-averaged size distributions: (a) major coating components and BC cores, and (b-f) image plots of size distributions of sulfate, nitrate, BC, organics, and chloride as a function of R_{BC} (mass ratio of coating-to-*BC*) (Note size distributions of BC and chloride were scaled from those of *m/z* 24 and *m/z* 35, respectively)



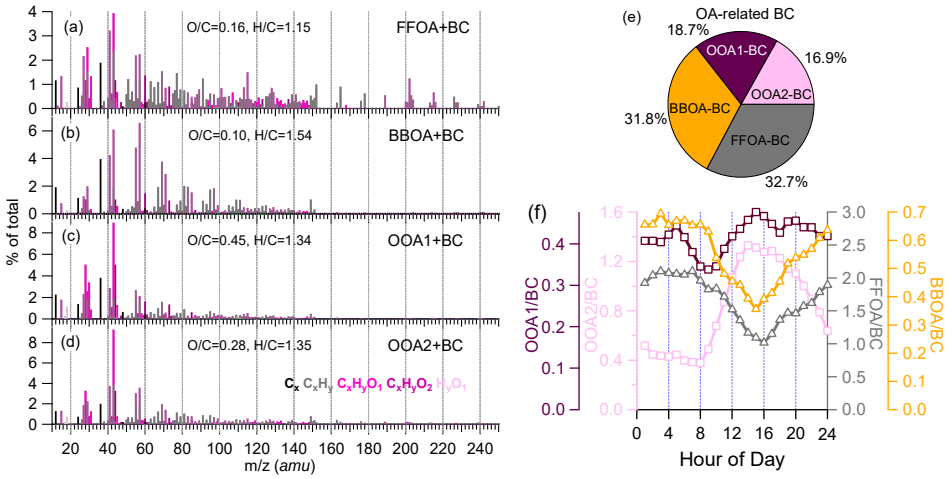
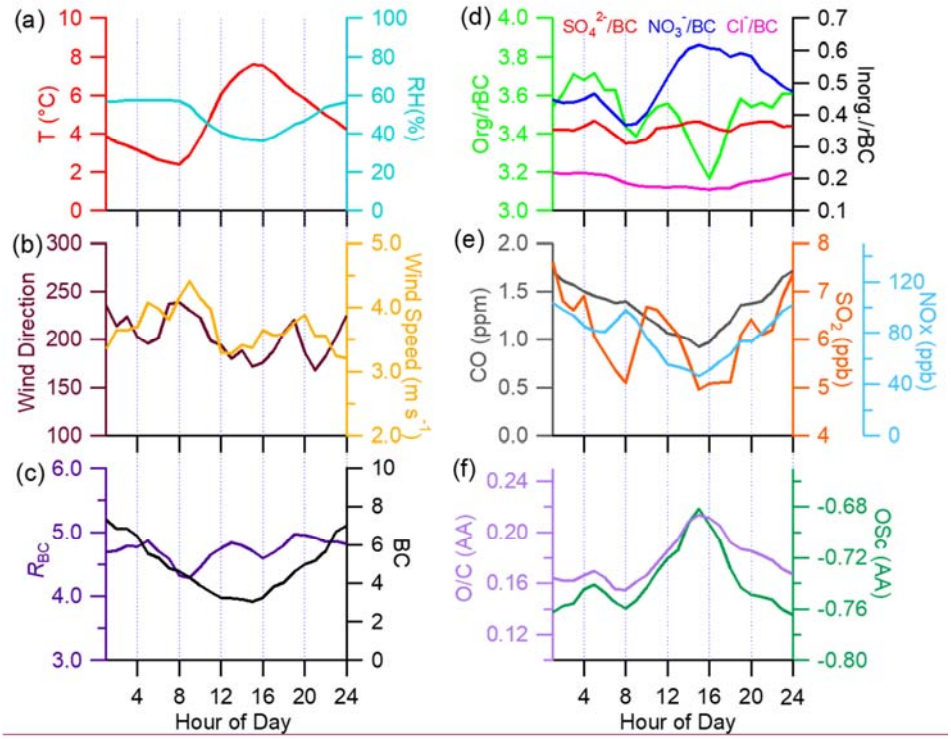


Figure 4. High-resolution mass spectra of (a) fossil fuel combustion OA (FFOA + BC), (b) biomass burning OA (BBOA + BC), (c) OOA1 + BC, (d) OOA2 + BC, (e) Mass fractions of the BC fragments apportioned in different OA factors, and (f) diurnal cycles of the four OA factors relative to BC.


(a)
T (°C)
RH(%)
(b)
Wind Direction
Wind Speed (m s-1)
(c)
RBC
BC
(d)
SO4 2-/BC
NO3-/BC
Cl-/BC
Org/BC
Inorg./BC
(e)
CO (ppm)
SO2 (ppb)
NOx (ppb)
(f)
O/C (AA)
OSc (AA)
4 8 12 16 20 24
Hour of Day
4 8 12 16 20 24
Hour of Day

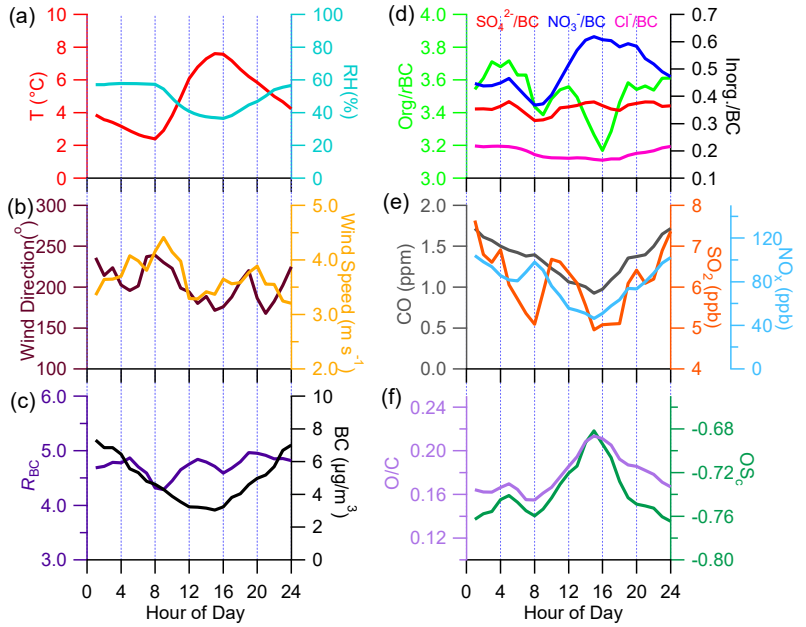


Figure 5. Diurnal cycles of (a) T and RH, (b) wind direction and wind speed, (c) mass ratio of coatings to BC (R_{BC}) and BC, (d) Org/BC, SO_4^{2-}/BC, NO_3^-/BC and Cl^-/*BC*, (e) mass ~~loading~~loadings of gaseous species (CO, SO_2, NO_x), and (f) O/C and oxidation state (OS_c=2*O/C-H/C).

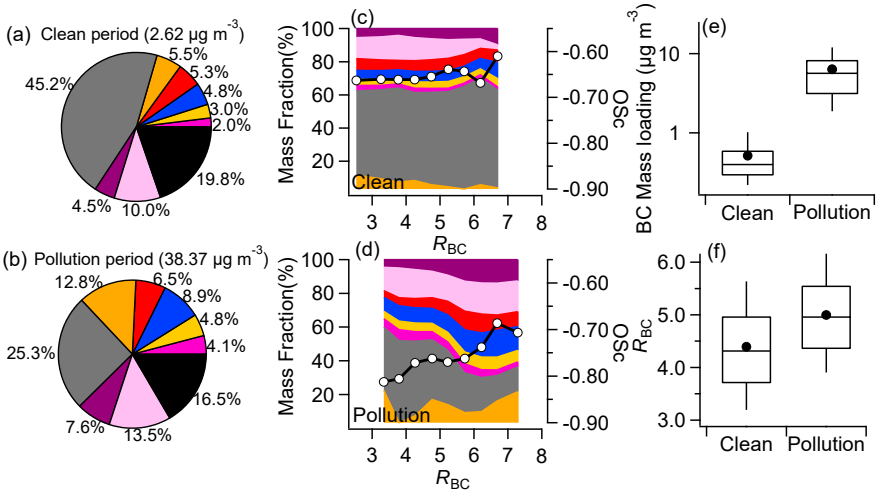
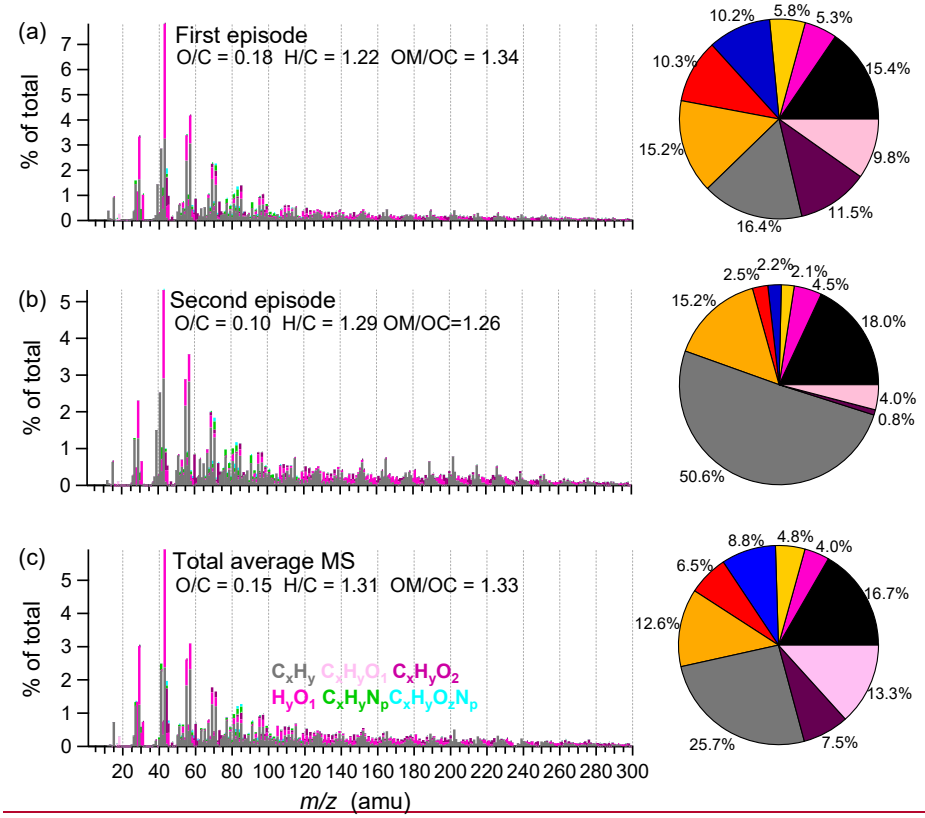


Figure 6. (a)(b) Average compositions of BC-containing particles during clean and pollution periods, (c)(d) mass fractions of the non-BC coating components (left *y*-axis) and OS_c (right *y*-axis) during clean and pollution periods as a function of R_{BC}, box plots of BC mass loadings (e) and R_{BC} during clean and pollution periods (colors of the components are consistent with those in Fig. 2).


(a)
First episode
O/C = 0.18 H/C = 1.22 OM/OC = 1.34
% of total
10.2%
5.8%
5.3%
15.4%
10.3%
15.2%
9.8%
16.4%
11.5%
(b)
Second episode
O/C = 0.10 H/C = 1.29 OM/OC=1.26
% of total
2.5%
2.2%
2.1%
4.5%
15.2%
18.0%
4.0%
0.8%
50.6%
(c)
Total average MS
O/C = 0.15 H/C = 1.31 OM/OC = 1.33
% of total
8.8%
4.8%
4.0%
6.5%
16.7%
12.6%
13.3%
25.7%
7.5%
CxHy CxHyO1 CxHyO2
HyO1 CxHyNp CxHyOzNp
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
m/z (amu)

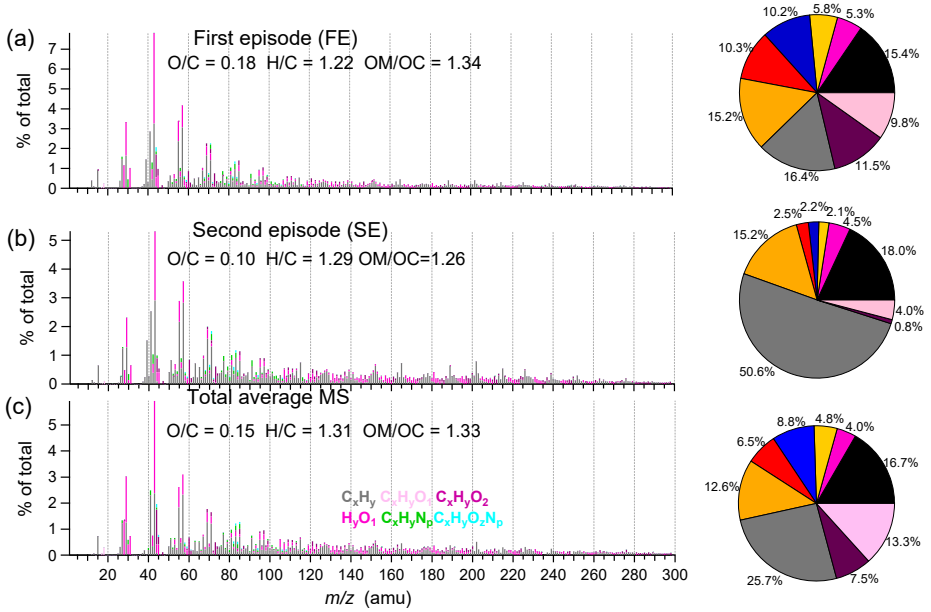


Figure 7. High-resolution mass spectra of the average OA at different episodes: (a) first episode (FE), (b) second episode (SE) and (c) whole campaign (inset pies show the average compositions during corresponding episodes; colors of different components are consistent with those in Fig. 2).