Dear ACP editor:

After reading the comments from you and the reviewers, we have carefully revised our manuscript. Our responses to the comments are itemized below.

Anything for our paper, please feel free to contact Prof. Gehui Wang via ghwang@geo.ecnu.edu.cn.

All the best

Can Wu

On behalf of Prof. Gehui Wang

Jun 26, 2024

Reviewer(s)' Comments to Author:

Reviewer 1

General Comments:

The vertical distribution of brown carbon is the crucial information to accurately assess its climate effects. The authors found significant amounts of secondary brown carbon in ascending air masses by the comprehensive field campaign performed at the mountain foot (MF) and mountain side (MS) of Mt. Hua, China. They attribute these findings to the formation of strong light-absorbing nitrogen-containing organic compounds (NOCs) leading to enhanced BrC absorption in the upper troposphere. Finally, the chemical element ratios obtained by AMS and isotopic results were proposed to further support that

such abundant NOCs were mainly formed via ammonia-induced aqueous reactions (e.g., Maillard reactions). The work is well-conducted and interesting, corresponding results are of importance to the field. However, pending the resolution of a few minor questions, it is recommended that this study undergoes minor revisions before its final publication.

Rely: We thank the reviewer's valuable comments. We have carefully revised our manuscript according to the comments. See details below.

(1) *Page 7, line 141-146: The chemical element ratio is the key evidence in this manuscript, thus, please provide more information of offline AMS analyses, such as the RIE values that would affect the calculation results and make AMS results unreliable.*

Rely: Thanks for your reminding. In this study, the HR-AMS was calibrated for the ionization efficiencies with 300 nm (D_m) ammonium nitrate and ammonium sulfate particle following the standard protocols; and the relative ionization efficiencies (RIEs) of 4.1 and 0.8 were used for ammonium and sulfate. While, the default RIEs were applied for organics, nitrate and chloride. Above discussions have been included in the method section. See page 8. line 173-177.

(2) *Page 10, line 215-216: The OSc value at MS site was merely ~0.06 higher than that at MF site, whether a significance test is conducted? This slight difference was farfetched to indicate a more oxidated atmosphere aloft; Thus, the authors should provide additional evidence to support hypothesis.*

Rely: Suggestion taken. A *T*-test has been conducted for OSc of two sites, of which result substantiated a significant discrepancy of OSc between two sites. This can be further verified by the BaP/BeP ratio, which can be employed to illustrate whether aerosols are freshly emitted (> 1) or aged (< 1). As shown in Figure 1, the averaged BaP/BeP ratio was 1.53±0.44 at MF site and 0.53±0.14, coincide with the OSc variation. All these evidences suggested that the aerosol aloft would be more aged compared to that at MF site. Above discussion has been added in the revised manuscript. See page 12, line 263-264.

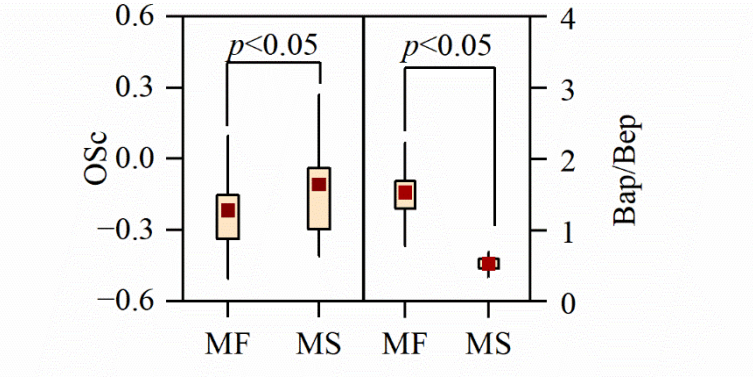

Figure 1 Comparison of OSc and BaP/BeP ratio among both sampling sites.

(3) *Any interpretation for these distinct relationship between Osc and abs365 nm at two sites shown in Figure 3a and 3c? And why would atmospheric oxidation cause photobleaching in MF and absorption enhancement in MS?*

Rely: As revealed by the temporal variation of abs $_{365\ nm}$ and Osc, daytime BrC at MF site did undergo significant photobleaching or oxidative whitening (Figure 2), thus reducing the brownness. This phenomenon may also occur in BrC aloft, which has whereas been disguised by a photoenhancement effect caused by dramatically secondary formation of NOCs. Furthermore, experimental results demonstrated that light-absorption of these NOCs formed via carbonyl/NH_4^+-mediated reactions could be moderately in within several hours of UV irradiation. As such, we think that significant formation of light-absorbing NOCs is crucial reason for the enhanced light-absorption of BrC aloft as aging proceeds.

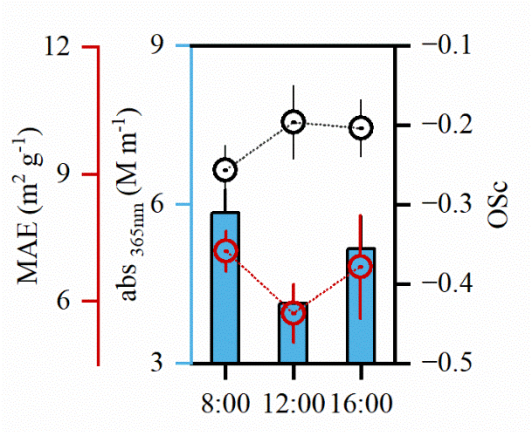

Figure 2 The temporal variation of daytime abs and Osc value at MF site.

(4) *In this work, the authors think that the aqueous reaction of dicarbonyl groups with NH_4^+/NH_3 can significantly promote absorbing NOCs formation in lifting air mass and lead to the enhanced light-absorption in the upper troposphere; However, why does the author think these reactions are not significant on the ground? And the surface NH4+ and other precursors concentration are more abundant compared to that aloft.*

Rely: The multiphase chemistry leading to absorbing NOCs was not only dependent on precursor concentration but only on reaction medium. As indicated by the laboratory measurements (Li, et al. 2021), methylglyoxal is more reactive than glyoxal, especially when exposed to $(NH_4)_2SO_4$ seeds. And more absorbing NOCs was generated by exposing $(NH_4)_2SO_4$ seeds to α-dicarbonyls vapor, but smaller yield occur on NH_4HSO_4 seeds. These experimental results demonstrated that NOCs formation was not only affected by precursor concentration but also by reaction medium. Whereas, the aerosol was dominated by $(NH_4)_2SO_4$ at MS site, and NH_4HSO_4 at MF site. Thus, the different chemical composition may be an important factor for the insignificant reactivity of those aqueous reactions.

(5) *Have the authors considered the time scales of vertical transport and chemical reactions mentioned in this work? The chemical-dynamic processes proposed in this work may be shorter than the transport time between the two sites.*

Rely: In our previous study at the same sites on Mt. Hua (Wu et al., 2022), we performed a WRF-Chem simulation of wind field and divergence, and found that the vertical motion of air parcel was fairly slow with an average vertical wind speed of < ~0.12 m s^{-1}. Given that, the air mass would take ~1.7 h to move up MS site from MF site, which was simply evaluated by using above wind speed. Whereas, the chemical reactions would be more rapid based on the smog chamber simulation conducted by Li et al. (2021), who found that the NOCs could be rapidly generated after corresponding reactants were introduced into the reaction chamber. As such, we think that the chemical-dynamic processes would be complete within the transport time between two sampling sites.

(6) *In Figure 4(d), the amount of isotopic data is seemly less than the total of the campaign; Please provide more details for the isotopic measurement.*

Rely: For sake of the analysis requirement of $\delta^{15}N\text{-}NH_4^+$, a merging pretreatment was applied for daily sample; Thus, there are only 21 isotopic data for daytime samples. And More description of the analytical method upon $\delta^{15}N\text{-}NH_4^+$ was also provide in the revised manuscript. See page 7, line 146-153.

(7) *Please unify the units of OC, EC and WSOC in Table 1.*

Reply: Suggestion taken. We unified the units of OC, WSOC and EC, and checked carefully throughout the manuscript.

Reviewer 2

General Comments:

This paper presents an interesting dataset to analyze the formation of tropospheric brown carbon on mountainous area from a field campaign performed at the mountain foot (MF) and mountain side (MS) of Mt. Hua, China. The in-depth analysis of this dataset provides some evidence of the formation of light-absorbing nitrogen-containing organic compounds at MS. However, from my point of view, there is a lack of information on dynamical circulation in the observation area. Moreover, it is not obvious for me that results obtained

on the ground at different altitudes can be related to vertical transport in the upper troposphere.

Overall recommendation:

I recommend that the paper should be accepted for publication in Atmospheric Chemistry and Physics after major and specific revisions listed below.

Reply: Thank you for your constructive comments. Regarding the reviewer's main concern, the details upon dynamical circulation have been supplied in the revision, more discussion can be seen in following section (Major Revisions); and other comments were also modified point by point.

Major Revisions:

(1) *My main concern is about the dynamics of the circulation of air masses on the mountainous aera of observations. In such a complex terrain, it is not obvious that both sites are dynamically connected all along the day especially since the two sites are 8 km apart.*

The present study presents results from observations at the ground. Even if one of the sites is 800 higher in altitude, I find it difficult to consider that the conclusions can be generalized to the upper troposphere.

Reply: In our previous study, divergence represented the expansion rate of the air mass in a unit of time was simulated by the WRF-Chem model over the whole observation. As depicted in Figure 3(a), southerly winds prevailed at mountain foot area, which can blow the pollutants into the valley. And the negative horizontal divergence at MS site and the decreasing vertical divergence indicated that the surface air parcel can be transported to the upper layer by the updrafts. Moreover, we also simply evaluated transport time by using the vertical wind speed at the layer blow 850 hpa, and found that the air parcel could move up to MS site from MF site within 2 hours. Thus, these simulation results have verified the

feasibility of vertical transport of air parcel during the daytime; and corresponding discussions were also included in the revision. See page 5, line 116-122.

Considering the elevation of MS site, we fully understand the reviewer's concern, and it was more appropriate to replace “upper troposphere” with “upper boundary layer” based on our observation.

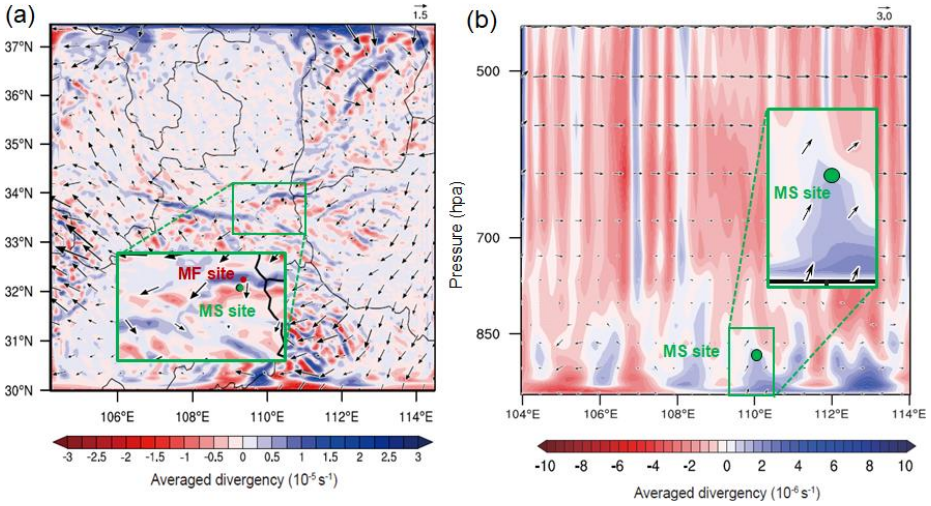

Figure 3 The distribution of daytime divergence and wind field over the whole campaign, (a) Horizontal distribution at surface. (b) Longitude–pressure cross-sections at 34°29′N. (Wu et al., 2022)

Specific Revisions:

(2) I recommend that all data used to discuss the formation of light absorbing NOCs during the air mass lifting process are limited to observations during the day when a circulation mainly driving by anabatic winds is established. I think results should be more significant in this way.

Please provide more details in legends of figures. No indications were given for the box plots on Figures 2 and 4, for the blue sky aera on Figure 4, etc.
Please re-read the text of the manuscript and its supplement carefully.

Reply: Thanks for your suggestion, but it’s unsuitable for nighttime data to discuss the NOCs formation and its optical properties in a lifting air mass. Because nocturnal boundary layer was usually below the MS site, of which nocturnal pollutants mainly were

the results of regional transport as indicated by the CWT analysis (Figure 4(a)). Given that, the emission sources at nighttime may be different among two sampling sites, causing disruption and inconvenience when discussing the NOCs formation. While, the indistinctive difference of diagnostic ratios and proportion upon organic tracers endorse insignificant change in the corresponding emission sources during the daytime transport (Figure 4(b and c)). Thus, the enhanced N:C and MAE of WOSM can be ascribed to secondary NOCs formation.

Sorry for our negligence of missing the legends in figure, we have modified and carefully scrutinized all the figure in the manuscript.

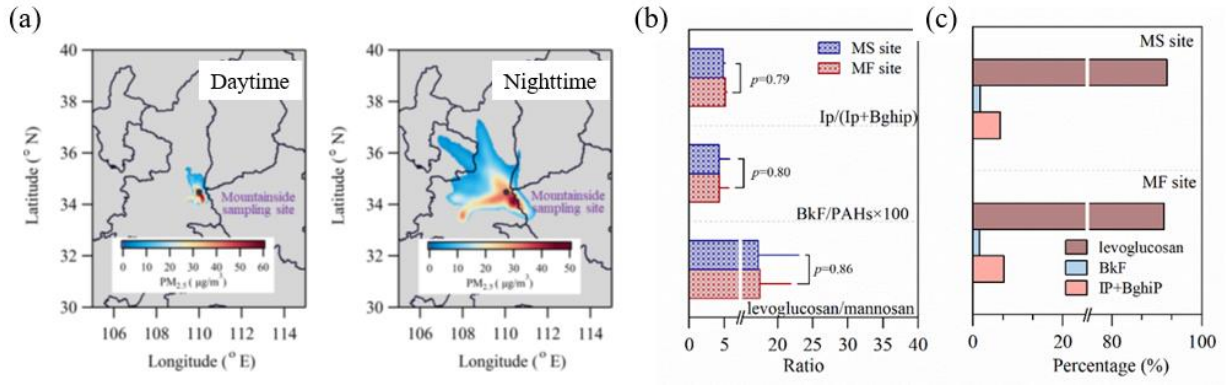

Figure 4 (a) Concentration-weighted trajectory (CWT) analyses of daytime $PM_{2.5}$ at MS site, (b) and (c) The mass ratio and proportion of organic tracers at two sampling sites.(Wu et al., 2022).

Comments:

Part 2:

• 2.1:

Comments:

(3) *Could you please indicate the altitude of both sites (line 111)?*

Reply: Suggestion taken. The location information including altitude has been improved in the revised manuscript. See page 5, line 112-113.

Comments:

(4) *If you precise the instrument used at MS, please do the same for MF.*

Reply: Suggestion taken. More details about the data and instrument used at MF site were provided in the revised manuscript. See page 6, line 126-128.

(5) *There is a contradiction: line 109 "$PM_{2.5}$ with 4-hour interval" and line 115 "Hourly concentrations of $PM_{2.5}$". Could you please clarify this?*

Reply: This is not contradictory. The offline $PM_{2.5}$ samples were merely used for chemical composition analysis, of which temporal interval was lower (4 hr). While, mass concentrations of pollutants (e.g., $PM_{2.5}$) were directly quantified by using online instruments possessed a higher time-resolution; and this is advantageous in accurately revealing the diel variation of pollutants as illustrated in our previous studies (Wu et al., 2022). To avoid ambiguity, we have rephrased the description in corresponding sentences.

Comments:

(6) *2.3: I do not understand how optical absorption of BrC was determined. Text S1 explained how the optical absorption is determine for WSOC. Did you assume that BrC is the light absorbing part of WSOC?*

Reply: As a complicated molecular composition of BrC, the bulk measurements were widely applied to characterize its optical properties; and WSOC was usually employed as a proxy for BrC in corresponding studies, albeit with some indeterminacy owing to the presence of non-absorbing components within WSOC.

Part 3

- *3.1:*

Comments:

(7) *I do not understand this sentence "Light absorption of BrC at the two sites markedly increased with a decrease in light wavelengths."*

Reply: The absorption spectrum that increases sharply from the vis to UV wavelengths is an inherent property of BrC (Figure 5), which was also found in field observations, such as in Xi'an (Wu et al., 2020), Seoul (Kim et al., 2016) and Los Angeles (Zhang et al., 2013).

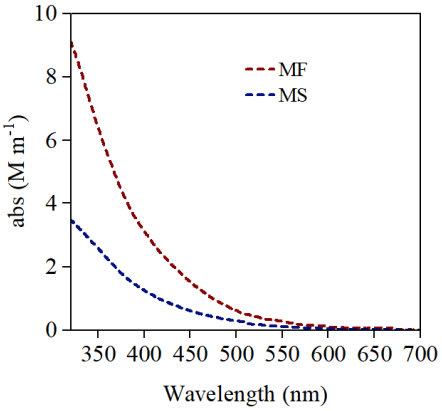

Figure 5 Averaged absorption spectra of BrC at both sampling sites.

Comments:

(8) *Figure 2d: It is explained in text S2 that the PMF was applied to "the daytime samples from both sites together as one data matrix". Could please tell me how sources appointment for the two sites were obtained?*

Reply: In our previous, the diagnostic ratios and proportion of these emission tracers from biomass burning, coal combustion and vehicle exhausts showed indistinctive divergences between two sites, thus, we supposed that the major emission sources were consistent at two sites. Given that, all the $abs_{356\ nm}$ and other tracers for different sources at two sites are regarded as input variables for PMF model that can output the result of each sample; and the source appointment results for MS and MF site can be separately calculated from the output data.

Comments:

(9) *Lines 233-237: I disagree with this sentence. In Yang et al. (2023), the authors did not arrive at the conclusions that "such a vertical profile of BrC is globally prevalent in the upper troposphere". Moreover, their vertical profiles shown in Fig. 7 were not in the upper troposphere. In the present study, measurements were obtained almost in boundary layer, thus it is not clear that the processes are similar than in Zhang et al. (2017) to reach such a conclusion.*

Reply: We agree with reviewer's concern, and the measurements conducted by Yang et al. (2023) and us indeed cannot draw above conclusion. Thus, we have rephrased this sentence as follows: "Similar vertical profile of BrC in the upper troposphere (5~12 km) of the continental US was also measured by in-situ aircraft measurements (Zhang et al., 2017)."

• 3.2:

Comments:

(10) *Line 246: "considerable" seems exaggerated, significant would be more accurate.*

Reply: Suggestion taken. See page 14, line 295.

Comments:

(11) *Lines 250-251: "indicating that additional NOCs were produced in the air mas lifting process." I find this sentence too affirmative with no information about the dynamical circulation of air masses.*

Reply: In our previous study (Wu et al., 2022), the model simulation results demonstrated a feasibility of vertical transport of air parcel from surface to upper layer, the related discussions were also added in the revised manuscript. See page 5, line 116-122.

Comments:

(12) *Lines 253-254 "20% higher than that at the MF site (Figure S5)": I do not see that on Fig. S5.*

Reply: Sorry for our carelessness. In the original manuscript, the 20% enhancement here refers to the fractional contribution of CHOxN fragments, rather than the total N-containing organic fragments. While, the fractional contribution of the total N-containing organic fragments increased by ~10% at MS site compared that at MF site, even up to ~25% at the day with low $PM_{2.5}$ load. Above results are still consistent with our conclusion. Corresponding discussion has been modified in the revision, see page 14, line 302-304.

Comments:

(13) *Lines 254-255: Information about the dynamical circulation is missing to be so affirmative.*

Reply: As previously answered, the related discussions have been added in the revision to address the reviewer's concern, these evidences manifest that the surface pollutants can be transported to the upper layer by the updrafts.

Comments:

(14) *Lines 256-259: Please nuance. The positive correlation (R^2=0.45) is not strong.*

Reply: Sorry for our inaccurate description. This has been corrected in the revised manuscript, and the t-test result (p<0.05) indicates that the linear relationship between WSON and abs $_{365nm}$ is significant. See page 14, line 306

• 3.3:

Comments:

(15) *Line 279: A R^2=0.57 is not a strong correlation.*

Reply: A t-test has been conducted, and revealed that this linear correlation between NO_2 and NACs is significant (p<0.01), albeit with a moderate correlation coefficient. Compared to the correlation analysis at MF site, thus, above results can also support the view that gas-

phase reaction is a dominant formation pathway for NACs aloft. Furthermore, the inappropriate description has been modified in undated version. See page 15, line 331.

(16) Line 297: the term "upper troposphere" is not correct.

Reply: Suggestion taken. We have replaced it with upper boundary layer, and carefully throughout manuscript.

Comments:

(17) *3.4: As WSON is higher at MF than at MS during the day, does this mean that the contribution of light absorbing NOC is very important at MS compared to MF?*

Reply: We fully endorse reviewer's conjecture. Notwithstanding lower load, NOCs account for a large proportion of OC at MS as indicated by a higher N:C ratio (Figure 6) at MS, of which contribution to light absorption was thus more important compared to that at MF site.

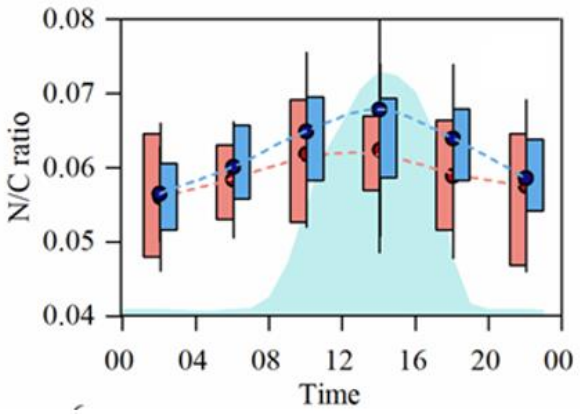

Figure 6 Diurnal variations of N:C ratio at both sampling sites.

Comments:

(17) *Part 4: conclusion should be revised according to my major concern above.*

Reply: Thanks for your kind suggestions, we have rephrased conclusion section. See page 20, line 428-445.

Reviewer 3

General Comments:

The manuscript by Wu et al. presents measurements of PM2.5 and some of its chemical constituents together with optical brown carbon measurements for two sites at different altitudes nearby Mt Hua, China. Generally, the manuscript is well-structured, reasonably well-written and the presented data is interesting and comprehensively discussed. My main concern is that major conclusions are based on the following two assumptions, which are not convincingly proven: 1) A direct connection of air masses between the two sites and 2) a lack of BrC sources in-between the sites. I give some details below, but these points need to be better addressed in a revision. In addition, some data analysis methods are not properly documented in the manuscript and need either be better explained or might even be removed, as further commented below. Overall, I recommend reconsideration after major revision.

Reply: Thank you for your rigorous comments. Regarding the reviewer's main concern, we have modified point by point in the revision, and more discussion can be seen in following section (Specific comments).

Specific comments:

(1) *Data from the mountain site are compared to another site at the mountain foot of Mt. Hua and any changes in chemical characteristics or BrC content are related to chemical processing taking place during the presumable quite short transport of air masses between the sites (8 km horizontally and 1 km vertically). No discussion, however, is provided to support the implicit assumption of connected air masses between the sites. What about wind direction for example? Was the mountain foot site indeed upwind of the mountain top site all the time? As for the anabatic valley breezes that are briefly mentioned: Is there any experimental evidence that such winds did indeed reach the mountain top site from the mountain foot site? And what about wind speeds and transport times? Could some of the*

observed differences in diurnal profiles be caused just by delayed arrival of valley pollution plumes at the mountain site?

Reply: Regarding the connection of air masses among two sites, the wind field and divergence simulated by WRF-Chem model are used here to elucidate it (Wu et al., 2022). As shown in following Figure 7(a), southerly winds prevailed over the observation period, and can blow the pollutants at MF into the valley; while, the upward vector of wind indicates that aerosol-rich air at the MF can be transported aloft by the prevailing valley breeze (Figure 7(b)). This can be also verified by the divergence that represents the expansion rate of the air mass in a unit of time. The positive values of vertical divergence among two sites decreased with enhanced elevation, suggesting that MS site is the sink for the surface the air pollutants (Figure (7b)). As for the transport time, we also simply evaluated by using the averaged vertical wind speed (~0.12 m/s) at the layer blow 850 hpa, and find that the surface air parcel may take approximately 1.7 hr to move up to MS site. All above discussions indicate a feasibility of vertical transport of air parcel among two sampling sites. Furthermore, as shown in Figure 7(c) and (d), the BrC in 29/8 and 30/8 exhibited different diurnal pattern, mainly due to the cloudy weather that may decelerate the transport of updrafts. However, these samples merely account for <10% of total, thus, with less influences on our conclusions. Above discussions have been included in the revision, see page 5, line 116-122.

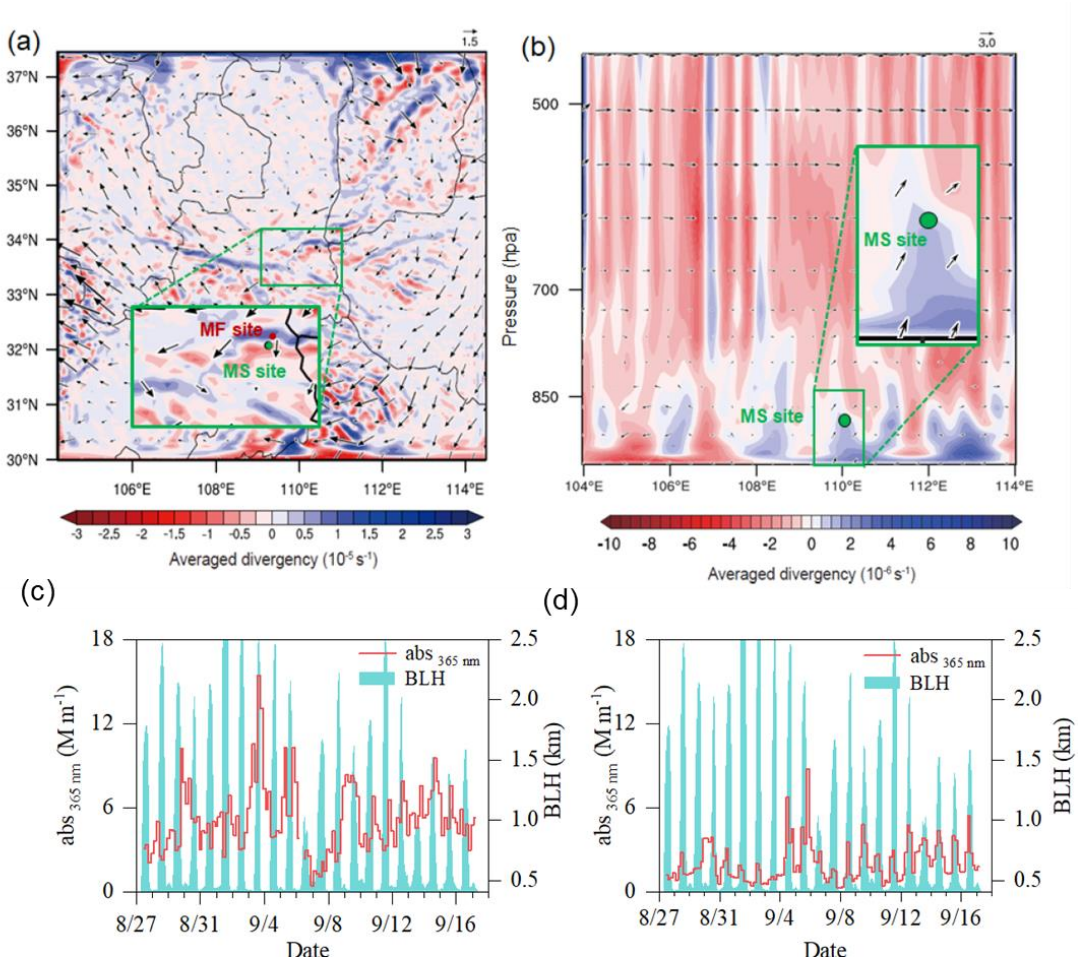

Figure 7 The distribution of daytime divergence and wind field over the whole campaign, (a) Horizontal distribution at surface. (b) Longitude–pressure cross-sections at 34°29′N. (Wu et al., 2022); Temporal variations of light absorption of BrC and the upper boundary layer (BLH) at MF (c) and MS (d) site.

Specific comments:

(2) *A second implicit assumption is the complete lack of any BrC sources between the sites. While this seems plausible for fossil sources, I wonder if it really holds for biomass burning sources as well? Are there no small villages along the path where people might burn wood or waste? What about agricultural fires or wild fires? Can these be ruled out as well for the campaign period in summer? In L220, the authors refer to their earlier Wu et al. 2020 study, but in this study, I could not find evidence for a lack of OA sources neither.*

In fact, in Fig. 8 of Wu et al. 2022, agricultural fires are included in the sketch as a possible source between the sites! Any biomass burning along the path would weaken the strong conclusion on chemical ageing between the sites.

Reply: Thanks for your comments. Actually, biomass burning was considered in the source apportionment of BrC (Figure 2d of manuscript), and accounted for 24% and 11% of total BrC at MF and MS, respectively. As indicated by the fire-spots map (Figure 8(a)), these biomass burnings were mainly domestic emissions rather than wildfires or agricultural fires. Moreover, the diagnostic ratios and proportion for these emission tracers from biomass burning, coal combustion and vehicle exhausts were also analyzed in our previous study (Wu et al., 2022), of which divergences among two sites were indistinctive (Figure 8 (b) and (c)). This can rule out the change of the corresponding emission sources during vertical transport. To further confirm this viewpoint, levoglucosan/galactosan ratio being a known proxy for identifying the different biomass fuels was statistically analyzed here showing an insignificant difference among two sites (Figure 9). Given all this, the new evidences can strongly endorse our conclusions that the major emission sources including biomass burning don't undergo significant change and the enhanced abs_{-BrC}/abs_{-BC} and MAE values in vertical transport process are mainly ascribed to secondary formation of BrC.

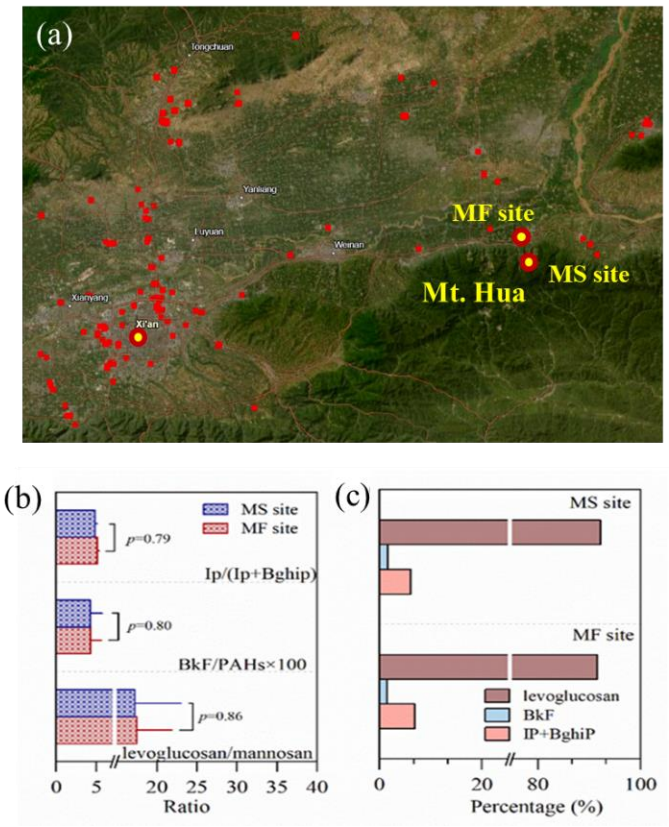

Figure 8 Fire spots during the whole campaign. (a) (The map was obtained from https://firms.modaps.eosdis.nasa.gov, last access: 16 Jun 2024); The mass ratio and proportion of organic tracers at two sampling sites. (b) and (c) (Wu et al., 2022).

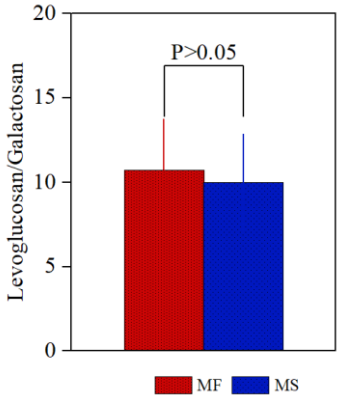

Figure 9 Comparison of levoglucosan/galactosan ratio among two sites.

Comments:

(3) *The application of the random forest analysis should be reconsidered. RF is a complex ML model typically applied for forecasting. While it can also be used to derive insight into*

data structure and relationship, there are quite some caveats that would need to be carefully addressed. First of all, care must be taken to not overfit the data and the exact model configuration would need to be documented (e.g. which RF implementation, which hyperparameter values and why they were chosen). Then, the method to interpret the RF model would need to be explained. Fig. 4b just says "RF analysis" and it remains completely unclear, what the given percentage values actually mean. There are a range of such interpretability methods and their outputs typically differ. On top of that, given the inherent randomness in RF, even the output from one and the same method can differ to some extent if repeatedly applied to the same data. Also, with correlated features – as in the given case – much care needs to be taken when interpreting the output of such methods. And lastly, the results shown do very likely just reflect the correlative structure of the data and this could much more easily be discussed by simple correlation coefficients. Another concern is that the authors might overinterpret the RF results in terms of causal dependence when in fact they just describes the statistical relationships between the variables.

Reply: We fully endorse above comments. The random forest is to a certain degree uncertain causing by inherent randomness, but it still widely employed in environmental pollution research. Given this, we did not merely rely on the RF results in this study, other important evidences, such as organic tracers and isotopic composition, were also applied to collectively corroborate our conclusions. Furthermore, the data was not overfitted here, and more detailed interpretations regarding model configuration were also replenished in the method section as suggested by the reviewer (See page 10, line 217-225). Finally, it is indeed not appropriate to interpret RF result as a causal quantitative contribution; Thus, we have rephased the title of Figure 4 as "Importance assessment for the key factors affecting the daytime WSON at MS site." And the corresponding contents were also modified in the revision. See page 16, line 347-349.

Comments:

(4) *PMF results are shown in Fig. 2d, but the experimental details are only partially given in Text S2. How was the uncertainty matrix constructed? Was bootstrap resampling performed to assess the robustness of the solution? Were all variables included as "strong" or were some downweighted? These experimental details should be included in the main manuscript, not SI. The assignment of the factors to atmospheric sources should also be justified, instead of just displayed in the SI. Conceptually, I wonder what it means to combine abs365 with the PM constituents. What is actually apportioned by the PMF, if concentrations and optical properties are mixed and analyzed together? A more appropriate reference to the PMF model should be given, not the website of the user guide.*

Reply: Thank you for reminding. The section of PMF interpretation has been transferred to the manuscript; detailed information upon uncertainty matrix and error fraction and references for PMF model were also provided in the revision. As revealed by the bootstrap analysis, the PMF solutions is robust, and reproducibility for each factor was larger than 80%. Furthermore, the accurate BrC content cannot be detected based on current technology, thus, abs_{365nm} largely dependent on aerosol source and composition is usually used as a proxy for BrC in PMF source apportionment; Such treatment was also find in the studies by Wang et al. (2020) and Zhang et al. (2010). See page 9, line 193-199, and line 203-207.

Comments:

(5) *The beginning of section 3.1 would benefit from some restructuring. It goes back and forth between discussing Figure 1 and Table 1 and is a bit difficult to follow.*

Reply: Suggestion taken. We have readjusted the beginning of 3.1 section, see page 11, line 233-236.

Comments:

(6) *Many results discussed throughout the paper are shown in the SI only, which sometimes makes it difficult to follow the reasoning without going back and forth between the paper and the SI. I recommend to critically assess which of this information is really*

needed. SI should not include entirely new data that is then still discussed as if it was part of the main manuscript.

Reply: Thanks for your advice. Appropriate adjustments have been conducted in the revision.

Further comments:

(7) *L31: Give reference for this earlier finding*

Reply: It is uncommon to cite reference in abstract; thus, we have cited this discovery multiple times in the manuscript (page 4, line 86; page 13, line 286; page 18, line 397).

Comments:

(8) *L81: Include reference for radiative forcing*

Reply: Suggestion taken.

Comments:

(9) *L122: Indicate the thermal protocol applied*

Reply: Suggestion taken. We have added the protocol in the revised manuscript. See page 6, line 132-134.

Comments:

(10) *L171: What is the difference between NH_4^+ and NH_3(aq)? How was the ladder measured?*

Reply: As shown in following chemical equations, NH_3(aq) is the undissociated form of ammonia in solution, which was simulated by the thermodynamic model (E-AIM (IV) as descripted in our previous study.

$NH_3(g) \rightleftarrows NH_3(aq)$

$NH_3(aq) + H_2O \rightleftarrows NH_4^+(aq) + OH^-(aq)$

Comments:

(11) *L176: R^2 would be the coefficient of determination, not correlation coefficient*

Reply: Sorry for our carelessness. We have corrected it. See page 10, line 223.

Comments:

(12) *L178: R^2 would need to have high values for good model performance, not small ones*

Reply: lt is really true as reviewer suggested that the coefficients of determination are close to unity (0.92 at MF site and 0.86 at MS site), and the small ones here refer to the error metrics.

Comments:

(13) *L197: If MAE at the two sites is really the same, does that not contradict the conclusion of higher BrC content at the mountain site?*

Reply: An equal MAE value further indicated that the light-absorptivity of BrC aloft could rival that at surface, despite more aged atmosphere aloft; Thus, it's uncontradicted. Additionally, our focus is the daytime BrC, of which MAE at MS site is increased as the air mass lifted, even higher than MF site at around noonday (Figure 2 in the manuscript). Such variation can support our conclusion of a significant formation of BrC during vertical transport. Based on our observations, we cannot draw above conclusion of higher BrC content at MS site due to oxidative whitening and the dilution effect with boundary layer variation.

Comments:

(14) *L275: Given the reported lack of correlation with NO_2, I cannot follow the suggestion of NACs deriving from combustion sources. All combustion sources emit NO_2.*

Reply: Apart from primary emission, NO_2 concentration can be significantly affected by photochemical reactions, especially in the daytime. Thus, we think that NO_2 is not suitable as a tracer for combustion sources. Moreover, CO that is a prevalent species in combustion emissions also exhibited a strong positive correlation with NACs at MF site (R^2=0.82,

Figure 10), further indicating that NACs at MF site was mainly derived from combustion emissions.

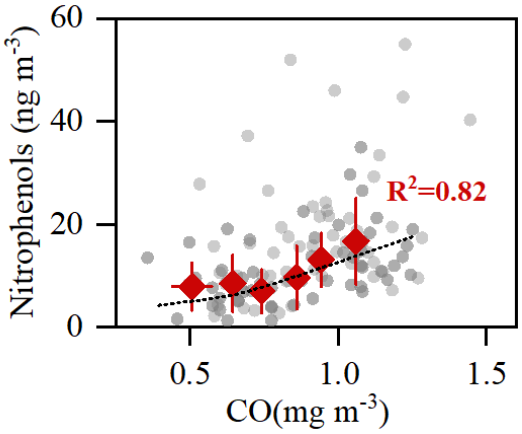

Figure 10 A correlation analysis of CO and NACs at MF site.

Comments:

(15) *L279f: Not sure I agree. I would expect all anthropogenic pollutants to co-correlate at the mountain site. It would help to show all correlations in the SI.*

Reply: Actually, it is not as reviewer suspects, and there are weak correlations between NACs and other anthropogenic pollutants (e.g., SO_2, hopanes and EC) at MS site as shown in Figure 11. These further indicate that NACs aloft are mainly derived from secondary formation.

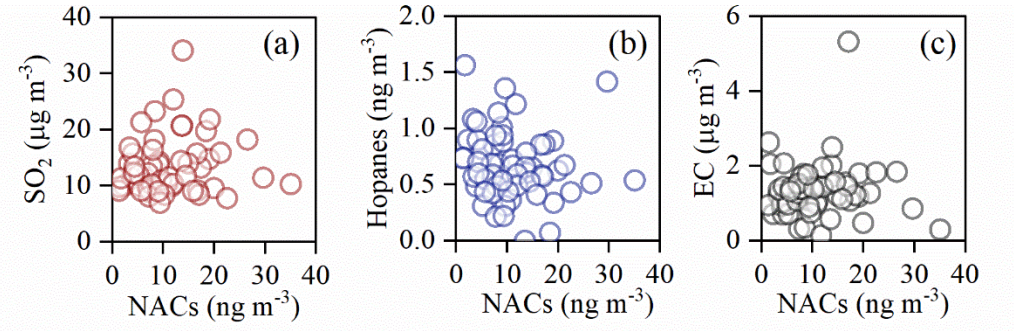

Figure 11 Correlation analysis between NACs and SO2, hopanes, EC at MS site.

Comments:

(16) *L283: A lack of correlation between NACs and ALWC does not necessarily indicate any specific formation mechanism. It also depends on the availability of precursors and whether the formation is volume-driven or concentration-driven. With low ALWC, aqueous concentrations might strongly increase.*

Reply: As revealed by the laboratory measurements (Li et al., 2023; Vione et al., 2004), photo-nitration of phenol in presence of HONO/·NO_2 is commonly believed to an important aqueous formation pathway of NACs; while, the particulate phenol poorly correlated with NACs (Figure 12), coincided with our findings. We added this evidence into the revised manuscript, and modified those unbecoming expression.

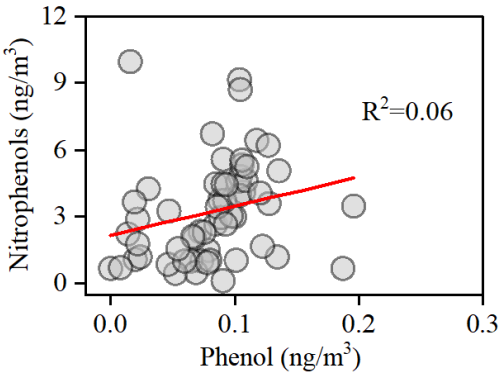

Figure 12 Scatter plots of nitrophenols (ng/m^3) versus phenol (ng/m^3) at MS site.

Comments:

(17) *L285ff: What is the relevance of protonation for the formation process discussed here?*

Reply: Sorry for our carelessness. We got the pH backwards among two sites, in fact aerosol acidity at MS site (3.4±2.2) moderately decreased compared to that at MF site (2.9±2.0). While, less acidic condition favors the dissociation of NACs into their ionized forms, and red-shifting their absorption spectra; thereby, ionized forms of NACs may play an important role in controlling their effect on BrC absorption, particularly in the visible range. But it is less relevance for the discussion of NACs formation process as suggested by reviewer, thus, this part has been deleted in the revised manuscript.

Comments:

(18) *L288: "explicit evidence" is quite a strong term for the discussed correlations, which might or might not be caused by the proposed processes.*

Reply: Suggestion taken. We have changed the inappropriate expression.

Comments:

(19) *L292: As detailed above, the RF does certainly not quantify the contributions of different influencing factors. I suppose the given percentages are just a metric for the degree of correlation in the data. They can certainly not be used as causal quantitative contributions.*

Reply: Suggestion taken. Based on reviewer's advice, the related description has been modified as "a random forest (RF) analysis being used as a metric for the degree of correlation between these influencing factors (ALWC, pH, T, NO_2, NH_4^+, etc.) and WSON". See page 16, line 345.

Comments:

(20) *L304: Experimental details of the isotopic analyses should briefly be included in the experimental section with reference to the earlier paper.*

Reply: Suggestion taken. More details of the analytical method upon nitrogen isotope are provide in the experimental section. See page 7, line 146-153.

Comments:

(21) *L355ff: In China, total PM loads have decreased. I would therefore expect that ALWC might have decreased as well, not increased, as the authors seem to suggest. Is there any reference for this statement? The following paragraph would hold only if ALWC has indeed increased.*

Reply: ALWC is theoretically driven by particulate hygroscopic components and meteorological factors; thus, we specifically emphasized that this comparison needs to be

conducted at a given RH and aerosol loading. In our previous study (Lv et al., 2023), a sensitivity test for ALWC change in different molar ratio of nitrate to sulfate ($R_{N/S}$) indicated that the ALWC increased with enhanced $R_{N/S}$ at a given RH (Figure 13 (a)); and the fractional contribution of WSOC to OC and partitioning coefficient of WSOC also showed similar trend with a change from sulfate-dominate region to nitrate-dominate region over the past 20 years. Given all that, we think that our conjectures are reasonable; and abundant nitrates that are more hygroscopic can form a liquid phase at a lower RH compared that of sulfate, therefore, which may promote aqueous formation of BrC.

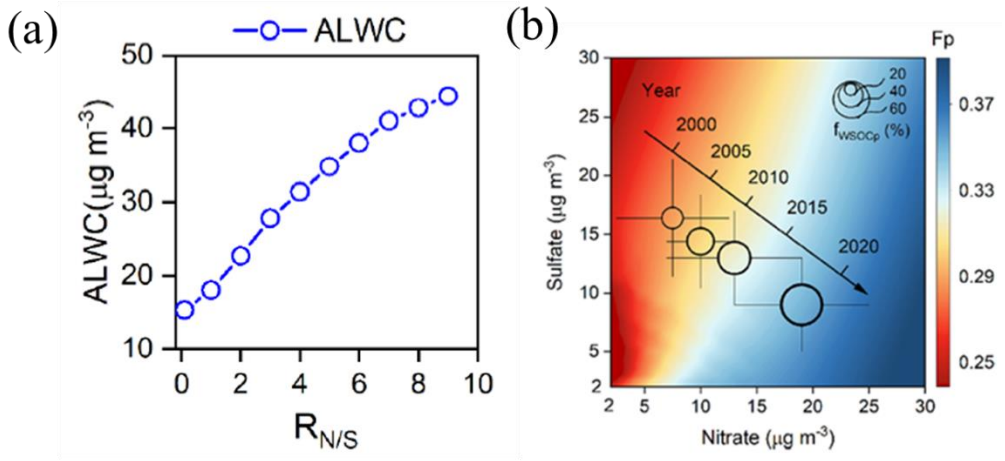

Figure 13 (a) Response of ALWC to the changes in the molar ratio of nitrate to sulfate ($R_{N/S}$) from 0.1 to 9.0 using the ISORROPIA-II thermodynamic model. (b) Contour plot of calculated partitioning coefficient as a function of nitrate and sulfate concentrations; Fp is the partitioning coefficient of WSOC, f_{WSOCp} is the relative abundance WSOC to OC. (Lv et al., 2023)

Comments:

(22) *Section 4: It is uncommon to refer to and discuss new Figures in the Conclusions section. Maybe consider to split "atmospheric implications" and "conclusions" into separate sections.*

Reply: Suggestion taken. We have separated the two parts in the revision.

Comments:

(23) *Is it r or R2 that is plotted in the Figure?*

Reply: It's R^2 in the Figure.

Comments:

(24) *S4: What about bootstrap uncertainty of the factor profiles?*

Reply: Suggestion taken. The reproducibility of factors was over 80%, indicating that the bootstrap uncertainties can be interpreted and the PMF solution is appropriate and robust.

Reference

Kim, H., Kim, J. Y., Jin, H. C., Lee, J. Y., and Lee, S. P.: Seasonal variations in the light-absorbing properties of water-soluble and insoluble organic aerosols in Seoul, Korea, Atmos. Environ., 129, 234-242, 10.1016/j.atmosenv.2016.01.042, 2016.

Li, F., Zhou, S., Du, L., Zhao, J., Hang, J., and Wang, X.: Aqueous-phase chemistry of atmospheric phenolic compounds: A critical review of laboratory studies, Sci. Total Environ., 856, 10.1016/j.scitotenv.2022.158895, 2023.

Lv, S., Wu, C., Wang, F., Liu, X., Zhang, S., Chen, Y., Zhang, F., Yang, Y., Wang, H., Huang, C., Fu, Q., Duan, Y., and Wang, G.: Nitrate-Enhanced Gas-to-Particle-Phase Partitioning of Water- Soluble Organic Compounds in Chinese Urban Atmosphere: Implications for Secondary Organic Aerosol Formation, Environmental Science & Technology Letters, 10, 14-20, 10.1021/acs.estlett.2c00894, 2023.

Vione, D., Maurino, V., Minero, C., Lucchiari, M., and Pelizzetti, E.: Nitration and hydroxylation of benzene in the presence of nitrite/nitrous acid in aqueous solution, Chemosphere, 56, 1049-1059, 10.1016/j.chemosphere.2004.05.027, 2004.

Wang, Q., Liu, H., Wang, P., Dai, W., Zhang, T., Zhao, Y., Tian, J., Zhang, W., Han, Y., and Cao, J.: Optical source apportionment and radiative effect of light-absorbing carbonaceous aerosols in a tropical marine monsoon climate zone: the importance of ship emissions, Atmos. Chem. Phys., 20, 15537-15549, 10.5194/acp-20-15537-2020, 2020.

Wu, C., Cao, C., Li, J., Lv, S., Li, J., Liu, X., Zhang, S., Liu, S., Zhang, F., Meng, J., and Wang, G.: Different physicochemical behaviors of nitrate and ammonium duringtransport: a case study on Mt. Hua, China, Atmos. Chem. Phys., 22, 15621-15635, 10.5194/acp-22-15621-2022, 2022.

Wu, C., Wang, G., Li, J., Li, J., Cao, C., Ge, S., Xie, Y., Chen, J., Li, X., Xue, G., Wang, X., Zhao, Z., and Cao, F.: The characteristics of atmospheric brown carbon in Xi'an, inland China: sources, size distributions and optical properties, Atmos. Chem. Phys., 20, 2017-2030, 10.5194/acp-20-2017-2020, 2020.

Zhang, X., Lin, Y.-H., Surratt, J. D., and Weber, R. J.: Sources, Composition and Absorption Angstrom Exponent of Light-absorbing Organic Components in Aerosol Extracts from the Los Angeles Basin, Environ. Sci. Technol., 47, 3685-3693, 10.1021/es305047b, 2013.

Zhang, X., Hecobian, A., Zheng, M., Frank, N. H., and Weber, R. J.: Biomass burning impact on PM_{2.5} over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis, Atmos. Chem. Phys., 10, 6839-6853, 10.5194/acp-10-6839-2010, 2010.

Zhang, Y., Forrister, H., Liu, J., Dibb, J., Anderson, B., Schwarz, J. P., Perring, A. E., Jimenez, J. L., Campuzano-Jost, P., Wang, Y., Nenes, A., and Weber, R. J.: Top-of-atmosphere radiative forcing affected by brown carbon in the upper troposphere, Nat. Geosci., 10, 486-489, 10.1038/ngeo2960, 2017.