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Organosulfur Compounds: A Non-Negligible Component Affecting the Light Absorption of Brown Carbon During North China Haze Events

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Key Points:

- Sulfur contents affected the BrC absorption, and OSCs contributed ~20% of the total identified chromophores in the haze event
- Coal combustion emission and its secondary process are the main sources of OSCs with aromatic OSCs dominated the molecular composition
- The transformation of OSCs may potentially impact the changes in BrC light-absorption capacity

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract

The roles of organosulfur compounds (OSCs), an important component in organic matter, in brown carbon (BrC) aerosol absorption is often overlooked. Here, the molecular composition of OSCs and its associations with methanol-soluble BrC (MS-BrC) absorption during a haze event in North China were revealed using a Fourier transform ion cyclotron resonance mass spectrometry analysis. By combining aggregated boosted tree model and partial least squares regression estimation, our results suggested that OSCs were mainly composed of potential aromatic structures, and the MS-BrC absorption was closely related to OSCs. Specifically, OSCs contribute a notable 26% of the total potential BrC molecular number and an upper limit of 10.4% of total MS-BrC absorption. Furthermore, we found that OSCs were mainly influenced by coal combustion, and the potential desulfurization reactions showed associations with the variations of MS-BrC absorption. Since the residential coal combustion (an important primary source of OSs) was the major energy in North China, our research underscores the potential of aromatic OSCs as tracers for assessing the impact of fossil fuel combustion on BrC and highlights the important atmospheric influences of OSCs (e.g., light absorption and health), which need more works to uncover the origins, fates, and environmental effects of OSCs.

Plain Language Summary

Organosulfur compounds (OSCs) constitute a significant component of atmospheric organic matter, with their sources, formation mechanisms, and environmental impacts having been extensively studied. Nevertheless, the relationship between OSCs and brown carbon (BrC) absorption in environmental samples remains largely unexplored to date. Notably, OSCs were found abundant in fossil fuel combustion emissions, particularly for residential coal combustions, which are a widely used energy supply in North China. Here, we collected hourly $PM_{2.5}$ samples during a haze event in North China and characterized the molecular composition of OSCs using high-resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Through statistical analyses, including the aggregated boosted tree (ABT) model and partial least squares regression (PLSR), we found that BrC absorption during the haze event was influenced by OSCs emitted from coal combustions. Furthermore, the secondary transformation of OSCs may be associated with changes in MS-BrC light-absorbing capacity. Our findings underscore the crucial role of OSCs to BrC during winter haze in North China particularly in haze events dominated by coal combustion. Findings from this study is of great significance for understanding the environmental effects of OSCs and provides further insights into the source and atmospheric transformations of atmospheric BrC.

1. Introduction

Organosulfur compounds (OSCs) constitute an important fraction of organic matter masses (up to 50%) (Jiang, Li, Tang, Cui, et al., 2022; Luk´acs et al., 2009; Surratt et al., 2008; Tolocka & Turpin, 2012) and have critical influences on the physicochemical properties of aerosols, such as hygroscopicity (Hansen et al., 2015; Peng et al., 2021), acidity (Rudzi´nski et al., 2009), and volatility (Fan et al., 2022). Numerous studies have observed

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elevated levels of particulate OSCs during haze events (Cai et al., 2020; Han et al., 2023; Huang, Cao, et al., 2018; Wei et al., 2020), highlighting the potential importance of OSCs in haze formation.

Generally, atmospheric OSCs are mainly formed via the secondary reactions of volatile organic compounds (VOCs) with inorganic sulfur (Bruggemann et al., 2020; Gao & Zhu, 2021). Various formation mechanisms of small molecular weight and biogenic VOCs-derived organosulfates have been extensively investigated, as they usually showed higher concentrations in atmosphere particularly in Europe (Brüggemann et al., 2017; Luk´acs et al., 2009; Surratt et al., 2008) and North America (Chen et al., 2021; Hughes et al., 2021; Vandergrift et al., 2022). However, in China, anthropogenic emissions remain at high levels (Fan et al., 2022), and a high fraction of aromatic OSCs (~50% of total) was observed (Jiang, Li, Tang, Cui, et al., 2022). The sources and formations of these anthropogenic-related OSCs are not well studied. In addition to secondary oxidations (Riva et al., 2015), researches based on Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) have shown that it can be emitted directly from the fossil fuel combustion and biomass burning (Cui et al., 2019; Song et al., 2018).

Atmospheric brown carbon (BrC) is an important type of light-absorbing organic matter showing importance for climate and radiative forcing (Laskin et al., 2015). The complex and changeable molecular composition of BrC hinder the estimation of its light absorption properties and radiative forcing accurately. A large number of chromophores, including nitro-aromatics and polycyclic aromatic hydrocarbons (PAHs), have been identified in biomass burning and ambient samples using high-resolution mass spectrometry (HR-MS) interfaced to optical detectors (Huang et al., 2021; Lin et al., 2017, 2018). Factors including nitrogen contents, aromaticity, and molecular weight as well as environmental variables (e.g., emissions, relative humidity, and UV radiation) have been found to affect the light absorption capacity of BrC(Jiang et al., 2021). However, the light absorption of OSCs (particularly aromatic OSCs) has rarely been reported, and the importance of OSCs to BrC absorption is often overlooked. To our knowledge, only several laboratory simulation experiments have shown that the formations of OSCs could lead the enhance of BrC absorption (Fleming et al., 2019; Nguyen et al., 2012). Recently, some studies have reported that OSCs could contributed 3.9%–41% of total soluble BrC absorption in winter samples at North China and costal city in China, where coal and liquid fossil combustion were important to ambient aerosols (Bai et al., 2020; Zeng et al., 2020, 2021). In fact, aromatic OSCs were found being abundant in humic-like substances (a major BrC fraction) of fresh source samples (Cui et al., 2019; Song et al., 2018) and therefore may have contributions on atmospheric BrC absorption in the fossil combustion influenced ambient.

FT-ICR MS combined with negative electrospray ionization (ESI) is an effective method for analyzing the molecular composition of OSCs(Gao & Zhu, 2021; Jiang, Li, Tang, Zhang, et al., 2022). Despite the shortcomings of this method in quantifying OSCs and identifying chromophores compared to HPLC-UV/HRMS platform, a useful method to identify and quantify some BrC chromophores and OSCs, FT-ICR MS analysis can provide sufficiently rich molecular compositional information to reveal the relationship between the molecular composition of OSCs and BrC absorption due to its higher resolution. For example, many previous studies have linked the molecular formulas obtained from FT-ICR MS analysis and optical properties and used statistical analysis to find structural features of chromophores (Kellerman et al., 2015; Stubbins et al., 2014). More recently, some studies have also been trying to quantify the BrC absorption contributed by OA components using the rich FT-ICR MS data (Zeng et al., 2020, 2021).

North China Plain (NCP) often experiences severe haze pollution during winter due to anthropogenic emissions such as residential biomass burning and coal combustion (Zhang et al., 2019). Especially, the intense domestic coal combustion has been considered a major source of BrC and OSCs. Here, we used FT-ICR MS to characterize the molecular composition of OSCs during a haze event in North China and explored their relations to BrC absorption. Moreover, the effect of potential source and transformation of OSCs on BrC absorption based on the FT-ICR MS data analysis were evaluated, which provided further understanding on BrC.

2. Materials and Methods

2.1. Sample Collection and Chemical Analysis

Hourly resolution $PM_{2.5}$ samples were collected on quartz fiber filters (QFFs, Whatman) using a high-volume sampler (TE-6070, TISCH, U.S., 1.13 $m^3 \cdot min^{-1}$) during a severe haze event that occurred between 2^{nd}–5th January 2020 at Wangdu County, Hebei Province (38.72°N, 115.12°E). The QFFs were prebaked and packed with aluminum foil, and the QFFs carrying $PM_{2.5}$ was then stored in a refrigerator (−20°C) and took back to laboratory for further analysis. The measured parameters include chemical species (organic carbon: OC; NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, oxalate, levoglucosan, polycyclic aromatic hydrocarbons, phthalic acid) (Feng et al., 2021, 2022; Jiang et al., 2023a) and the light-absorption coefficients at 365 nm (Abs_{365}) for methanol-soluble BrC (MS-BrC) (Jiang et al., 2023b). Twenty-nine selected $PM_{2.5}$ samples were used for FT-ICR MS analysis to investigate molecular composition changes during the haze event. Details about the sampling information, sample selection, and chemical species analysis were presented in Text S1 in Supporting Information S1 and our previous studies (Jiang et al., 2023a, 2023b).

2.2. FT-ICR MS Analysis

The molecular composition of methanol-soluble OC (MSOC) was analyzed using a 9.4 T solariX XR FT-ICR MS (Bruker Daltonik GmbH, Bremen, Germany) (Jiang et al., 2022a, 2022b, 2023a). To minimize to influence of "matrix effects" which is a well-known drawback in MS analysis, a portion of the quartz filters with similar organics concentrations (∼30 μg of C) were punched according to previous studies (Herzsprung et al., 2020; Jiang et al., 2021). Furthermore, ESI- has been reported performing very efficiently and reproducibly for polar compounds of OSCs (Jiang, Li, Tang, Cui, et al., 2022; Lin et al., 2012). Filters punched with a stainless puncher were put into prebaked glass bottles, and MSOC was extracted with 2 mL (×3 times) methanol in a cold-water bath (30 min). After filtering through a 0.22 μm PTFE filter membrane, the extracts were concentrated into 1 mL and injected to FT-ICR MS for molecular composition analysis. Peak collection was performed in negative ESI mode with the detection mass range set at 100–800 Da. A custom software was used for formula assignments and the identified formulas were roughly categorized into four main groups according to their elemental composition: CHO, CHON, CHOS, and CHONS. Several parameters that widely used for characterizing the chemical structures of the identified compounds were calculated, including the elemental ratios (e.g., H/C, O/C, N/C, S/C, N/S), double bond equivalent (DBE), aromaticity equivalent (Xc) (Jiang, Li, Tang, Cui, et al., 2022; Yassine et al., 2014), and carbon-oxidation state ($\overline{OS}$) (Kroll et al., 2011).

$$\mathrm{DBE} = (2c + 2 - h + n)/2$$

$$Xc = (3[DBE - 0.5 \times (o - 4)] - 2)/(DBE - 0.5 \times (o - 4))$$

$$\overline{\mathrm{OS}} \approx 2\mathrm{O/C} - \mathrm{H/C} - 5\mathrm{N/C}$$

2.3. Statistical Analysis

Here, an aggregated boosted tree (ABT) approach was applied to determine the importance of chemical parameters to BrC(De'ath, 2007). Compared to traditional methods such as linear correlation or multiple linear regression, the ABT model is better at handling the nonlinearity and interaction between variables and can quantitatively evaluate the relative impact of each explanatory variable on the response variable. The ABT model used here was constructed in *R* (v2.07) using the "gbmplus" package. Detailed chemical characteristic used for the ABT model fitting were presented in Table S1 in Supporting Information S1. A 500 trees with fivefold cross-validation were used. Spearman rank correlation between the intensity of each molecule and Abs_{365} was performed in the open-source *R* software to identify the compounds that having associations with MS-BrC absorption (Jiang et al., 2021; Kellerman et al., 2014). The potential contributions of each compound to MS-BrC absorption were further estimated using a partial least squares regression (PLSR) model (Text S2) (Zeng et al., 2020, 2021). The PLSR regression can decompose the large molecular data set into several the most important factors with the orthogonal scores and loading being available, and therefore, it has been widely used in determining the coefficients of organic functional groups and BrC absorption quantification (Weakley et al., 2016; Zeng et al., 2020). The uncertainty of this method was described in Text S2 in Supporting Information S1. We further applied the nonmetric multidimensional scaling (NMDS) analysis to qualify the factors that associated with the distribution of OSCs using the *R* package of "vegan" (Jiang et al., 2021, 2022a).

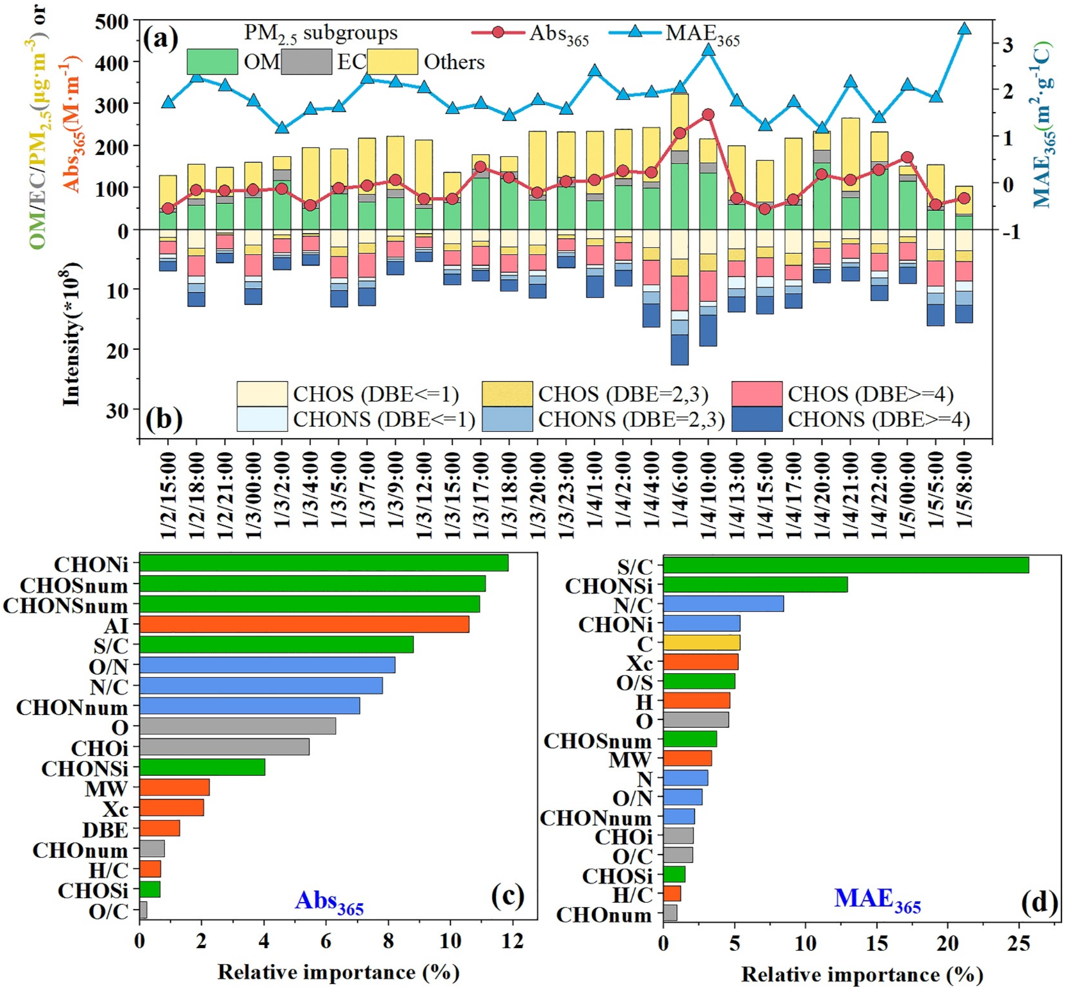

Figure 1. (a) Temporal variations of $PM_{2.5}$, Abs_{365}, MAE_{365} during the sampling period. (b) Formulas intensity of OSCs compounds in different DBE groups. (c) and (d) Relative importance of chemical parameters to the variations of Abs_{365} and MAE_{365} estimated by the ABT model.

3. Results and Discussion

3.1. General Relations Between OSCs and BrC Absorption

The light-absorption properties of MS-BrC for the samples, which are also used for FT-ICR MS analysis in this study, are shown in Figure 1a. The measured Abs_{365} (47.9–273 $M{\cdot}m^{-1}$) showed moderate positive correlation with the $PM_{2.5}$ mass concentrations ($r = 0.51$, $p < 0.05$) and EC ($r = 0.68$, $p < 0.01$) but have strong positive correlation with the OC concentrations ($r = 0.80$, $p < 0.01$). This suggested that the MS-BrC absorption showed a more close association with the OC concentrations than $PM_{2.5}$, and with the increase in $PM_{2.5}$ pollution, the MS-BrC absorption may not necessarily significantly increase. Furthermore, the lower correlation coefficients between the Abs_{365} and EC may also suggest that the primary emissions were not the sole dominant factor causing changes in MS-BrC absorption during the haze event. These results not only indicated the nonlinear relationship between MS-BrC and $PM_{2.5}$ pollution but also highlighted the nonuniqueness of MS-BrC sources, that is, the secondary formation of OC may also be an important factor affecting the changes in MS-BrC absorption. After normalizing of Abs_{365} to the OC concentrations, the mass absorption efficiency of MS-BrC at 365 nm (MAE_{365}) was obtained with values falling within the reported range for fresh coal combustion organic aerosols (CCOA) (Chen & Bond, 2010; Li et al., 2019; Tang et al., 2020; Xie, Hays, & Holder, 2017). In fact, the sources of MS-BrC during the whole sampling campaign (67 samples) were revealed in our a recent study using a tracer-based positive matrix factorization (PMF) model, and our results demonstrated that primary fossil fuels combustion (mainly coal combustion), along with their aqueous-phase secondary organic aerosol (SOA) formation processes, predominantly contributed to MS-BrC absorption as illustrated in Figure S1 in Supporting Information S1 (Jiang et al., 2023b).

As we all known, light-absorption properties of brown carbon (BrC) are intimately tied to its chemical structures (instinct reason, e.g., nitrogen contents, unsaturated degree, aromaticity, and molecular weight) and influenced by source emissions and atmospheric processes (external reason). High-resolution FT-ICR MS analysis serves as a powerful tool in elucidating the molecular composition of MSOC, enabling us to delve into the nexus between MS-BrC absorption and its chemical composition. Given the variations in molecular composition across different environmental conditions, the primary driven factors influencing BrC absorption vary accordingly. Here, we employ the ABT model to quantify the significance of chemical properties contributing to BrC absorption variations during a haze event in the NCP. As shown in Figure 1c, except the intensity fraction of CHON compounds, the number fractions of OSCs emerge as pivotal factors influencing Abs_{365} variations. However, as for the mass absorption capacity, the sulfur to carbon ratio (S/C) showed the highest relative influence on the variations of MAE_{365} (Figure 1d). It should be mentioned that our ABT analysis results did not mean other factors such as nitrogen contents or aromaticity were not important for the MS-BrC absorption during the haze event, but the OSCs may have larger impacts on the variations of MS-BrC absorption than others. In fact, both the ABT model and our PLSR analysis (Section 3.3) showed that CHON compounds may have significant impacts on the MS-BrC absorption during the haze event. In this study, the relative high importance of S/C ratio to MAE_{365} could be related to the specificity of the sampling activity. As mentioned above, fossil combustion sources such as domestic coal combustion, which are major primary emission sources of OSCs(Cui et al., 2019; Song et al., 2018), significantly influenced the particulate pollution during our sampling campaign. Similar temporal trends are discernible between Abs_{365} (also for MAE_{365}) and the total intensity of OSCs (CHOS + CHONS) accompanied by significant positive correlations (Figure S2 in Supporting Information S1). Furthermore, the S/C ratio demonstrated noteworthy correlations with both Abs_{365} ($r = 0.48$, $p < 0.01$) and MAE_{365} ($r = 0.42$, $p < 0.05$) (Table S1 in Supporting Information S1). Although these correlations are moderate, given that the intricacies of BrC molecular chemistry and chemical transformations, these findings collectively suggested that the OSCs and BrC may be affected by similar sources and atmospheric processes during the haze event in this study and highlight the potential importance of studying OSCs for understanding MS-BrC absorption changes.

3.2. Molecular Composition of OSCs and Its Associations to BrC Absorption

In this study, 306–769 (357 ± 81) and 174–403 (250 ± 61) of CHOS and CHONS compounds were detected with their relative intensity of 7.8%–15% (10 ± 1.7%) and 3.8%–13% (7.0 ± 1.9%) to the total formulas (Figure 1b and Figure S3 in Supporting Information S1). Overall, the average number fractions of CHOS compounds with potential aliphatic (DBE ≤ 1), olefinic (DBE = 2,3), and aromatic (DBE ≥ 4) structures to the total CHOS compounds were 33 ± 7.0%, 19 ± 3.4%, and 48 ± 9.5%, respectively (Jiang et al., 2016; Lin et al., 2012). Even when we used the Xc index to reduce the uncertainty in estimating the potential aromatic structures in CHOS compounds (Yassine et al., 2014), the average proportions of both formular number and intensity of aromatic CHOS (Xc ≥ 2.5) exceed 40% of total CHOS, suggesting the dominance of potential aromatic CHOS compounds in the detected formular set. Similar results were found for CHONS compounds that more than half of them can be attributed to aromatic OSCs using both the DBE and Xc criteria. This result was similar to a recent field observation conducted in Xi'an, a big city in North China (Han et al., 2023). It should be noted that the aromatic OSCs were mainly derived from the primary combustion sources, especially the fossil fuel combustion such as residential coal combustion and non-road vehicle emissions (Cui et al., 2019; Song et al., 2018). Although previous study has also shown that the aromatic sulfonates can be formed in atmosphere via the gas-phase oxidations of PAHs in the presence of sulfate aerosols (Riva et al., 2015), there is no doubt that the high fractions of aromatic OSCs detected in these samples indicated the importance of anthropogenic emissions for atmospheric OSCs during the haze event. Several classes of intense common-aromatic OSCs (appeared in >50% of samples) were detected, such as $C_nH_{2n-6}SO_5$ (DBE = 4), $C_nH_{n-2}SO_5$ (DBE = 6), $C_nH_{2n-5}NSO_4$ (DBE = 4), and $C_nH_{2n-7}NSO_7$ (DBE = 5) (Figure 2). Since the S-containing functional group itself is not chromophoric, OSCs with low DBE values are usually not considered as BrC chromophores (Nakayama et al., 2015). However, the OSCs with DBE values higher than 4 have benzene-ring structures, making them potential BrC chromophores due to their ability to form conjugated structures (e.g., π-π, σ-π) (Laskin et al., 2015). For example, as shown in Figure S4 in Supporting Information S1, the UV-vis spectrum of two typical OSCs ($C_6H_5NSO_7$ and $C_6H_6SO_5$) with one of its possible structures were

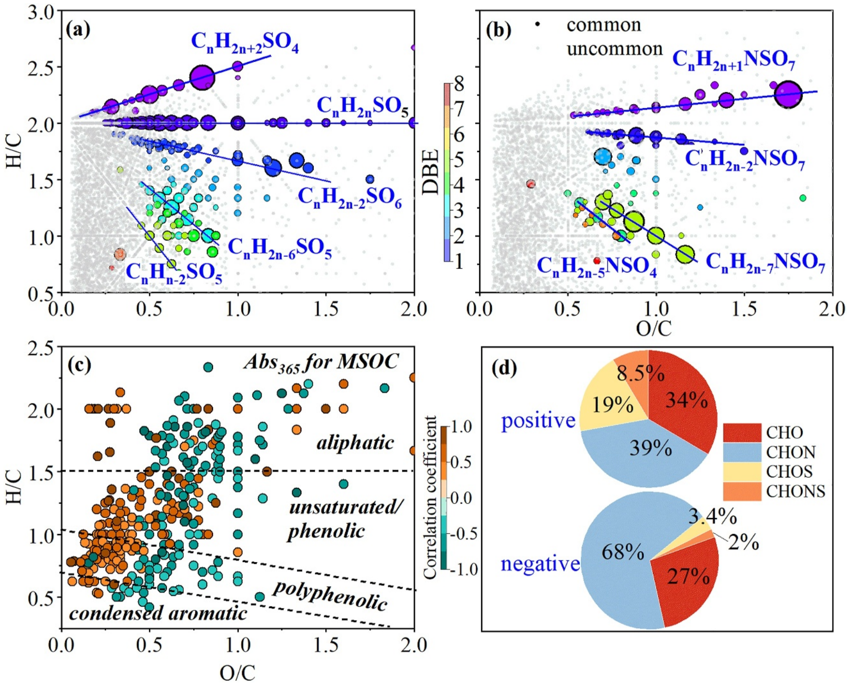

Figure 2. Van-Krevlen diagrams of (a) CHOS and (b) CHONS compounds detected in this study. Circle size denotes the average intensity of each formula, and the color gradient denotes the formulas having different DBE values. Several homologous with high average intensity are marked in the figure. Van-Krevlen diagram (c) showing the compounds that having significant Spearman correlations with the MS-BrC absorption (Abs_{365}), and (d) the two pie charts presented the formular number fractions of the positive and negative molecule pools in (c).

calculated using the Gaussian software, and they all showed light absorption at the wavelength of 200–500 nm, especially for $C_6H_5NSO_7$ as it may contained a nitro function group. Moreover, a recent study has reported that the light-absorption contribution by $C_nH_{2n-6}SO_3$ (DBE = 4) compounds could reach 12% in ambient samples (Bai et al., 2020).

To further understand the molecular associations of OSCs related to BrC absorption, a Van-Krevlen plot was employed to visually present the Spearman correlation analysis results between Abs_{365} and the intensity of individual formula detected by FT-ICR MS. This approach is an effective method for elucidating changes in molecular composition in response to environmental variables (Jiang et al., 2021; Kellerman et al., 2014). As shown in Figure 2c, the molecules exhibiting significantly positive correlations with Abs_{365} clustered in the left corner (red points), primarily comprising unsaturated and polycyclic aromatic hydrocarbon (PAH)-like substances with lower oxygen-to-carbon (O/C) ratios. The number fractions of CHO, CHON, and OSCs compounds to total molecules were all close to 1/3 (Figure 2d). Conversely, compounds showing negative correlations with Abs_{365} (blue points) have higher O/C ratios, with CHON compounds dominating over 70% of the total molecular formulas, whereas OSCs only accounted for 3%. It should be noted that those molecules having positive correlation with Abs_{365} may not necessarily be true BrC molecules but showed similar variation trend with BrC absorption. Additionally, these molecules only accounted a small fraction of the total compound set, and the majority of detected compounds showed no significant association with the variations of BrC absorption. Hence, the molecular pattern presented in Figure 2c suggested that the hourly variation in BrC absorption during the haze event was characterized by different variations in OSCs and CHON compounds, and the changes in relative abundance of OSCs was one of the main reasons that lead to the variations of BrC absorption. With the increase in BrC absorption, the abundance of more unsaturated OSCs may increase, while accompanied by the decrease in abundance for the molecules dominated by CHON compounds. It is crucial to note that correlation analysis does not establish causal relationships. Hence, we cannot definitively attribute the enhanced BrC absorption solely to the transformation of CHON into OSCs, as elevated coal combustion emissions can also alter the abundance of OSCs, contributing to this observed molecular distribution (Jiang et al., 2021).

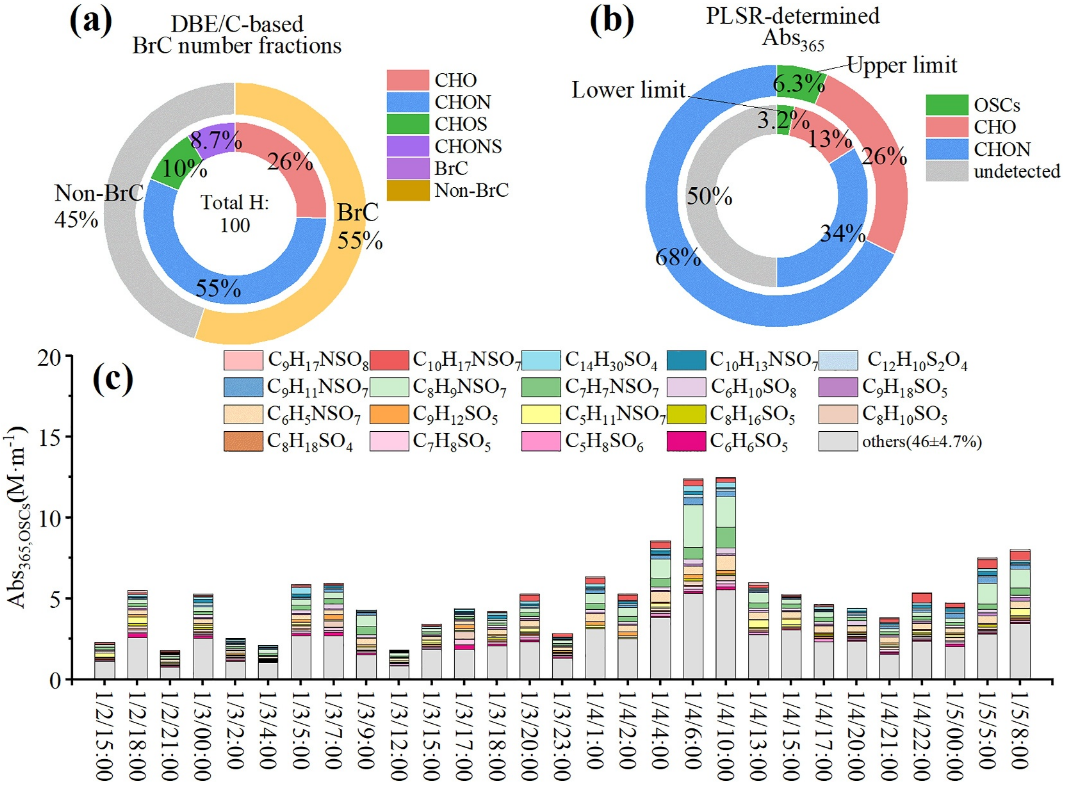

Figure 3. The proportions of potential BrC chromophore groups estimated using (a) DBE/C criteria and (b) PLSR method, respectively. (c) Temporal variations of top BrC molecule estimated by PLSR analysis with the assumption that 50% of MS-BrC absorption contributed by ESI- FT-ICR MS detected molecules.

3.3. The Light Absorption Contributions of OSCs

As mentioned above, although FT-ICR MS cannot provide spectroscopic information that we therefore were unable to accurately identify chromophores and their contribution to MS-BrC absorption, the empirical criteria of $0.5 \leq \text{DBE/C} \leq 0.9$ proposed in a previous study (Lin et al., 2018) can serve as a valuable tool to filter potential chromophores within FT-ICR MS molecules. Despite some low absorption molecules with DBE/C values outside this range may not include and therefore introducing uncertainty, our analysis yielded a substantial range of 847–2002 potential chromophores, with CHON compounds comprising over 50% (Figure 3a). This is a foreseeable outcome, which aligned with numerous previous studies that N-containing component was the major chromophores in organic aerosols (Jiang et al., 2021; Lin et al., 2017; Xie, Chen, et al., 2017). Nevertheless, a non-negligible fraction of potential OSC chromophores (CHOS + CHONS compounds) was found among the total identified chromophores (19 ± 2.9%), contributing to 10 ± 1.9% and 6.0 ± 1.9% of the total detected compound number and intensity, respectively. These results support our above findings and also emphasize the importance of OSCs in BrC absorption during the haze event in this study.

The contribution of OSCs to BrC absorption ($\text{Abs}_{365,\ \text{OSCs}}$) was further quantified using a PLSR model, which has been successfully employed in recent studies to estimate the contribution of each FT-ICR MS-detected molecule to BrC absorption (Zeng et al., 2020, 2021). Details on the calculation of $\text{Abs}_{365,\ \text{OSCs}}$ using PLSR method were presented in the Text S2 in Supporting Information S1. Results from PLSR analysis showed that the BrC absorption attributed to OSCs accounted for 3.2 ± 0.9% (2.0%–5.2%) of the total MS-BrC absorption, assumption that the compounds detected via ESI- FT-ICR MS contributed 50% of MS-BrC absorption at the lower limit (Figure 3b). The detailed description about the assumption that the compounds detected via ESI- FT-ICR MS contributed at least 50% of MS-BrC absorption were presented in Text S2 in Supporting Information S1. This absorption proportion is comparable to that of those strong light-absorbing chromophores such as PAHs (1.7%–3.7%) (Huang, Yang, et al., 2018) and several nitro-aromatic compounds (~4%) (Mohr et al., 2013; Teich et al., 2017; Zhang et al., 2013). However, it significantly lower than that reported in recent studies in Xi'an using the same method (Zeng et al., 2020, 2021), where CHONS compounds were observed to play a dominant role in organic aerosols. The absolute BrC absorption contributed by OSCs was estimated to range from 1.8 to 12 $M{\cdot}m^{-1}$ with an average value of 5.2 $M{\cdot}m^{-1}$. This value was comparable to or higher than that of bulk BrC components observed in some major cities in China and Western countries (see table summarized in Wang et al. (2022)). If we assumed that all MS-BrC absorption was contributed by the compounds detected by our ESI- FT-ICR MS, the BrC absorption attributed to OSCs would increase to 6.2 ± 0.9% (ranging from 4% to 10%), and the absolute BrC absorption contributed by OSCs could reach up to 25 $M{\cdot}m^{-1}$.

As shown in Figure 3c, the aromatic classes of $C_nH_{2n\text{-}7}NSO_7$ (e.g., $C_7H_7NSO_7$) and $C_nH_{2n\text{-}6}SO_5$ (e.g., $C_6H_7SO_5$) contributed the highest BrC absorption among the OSCs. These compound showing strong light absorption was due to their benzene-ring structure and/or additional N-containing function group. In addition, our analysis revealed that $C_{10}H_{17}NSO_7$ (DBE = 3), derived from biogenic VOCs, also made a notable contribution to BrC absorption (0%–0.3%), which aligns with previous reports by Bai et al. (2020). This suggested that biogenic OSCs with lower DBE values, while exhibiting lower absorption compared to aromatic and nitrogen-containing OSCs, are also potential BrC chromophores (Fleming et al., 2019; Nguyen et al., 2012). In summary, despite the different methods were applied here to estimate the importance of OSCs to MS-BrC absorption during the haze event and large uncertainties may arise from these estimations, the collective results emphasized that the contribution of OSCs to atmospheric BrC absorption might not be ignored.

3.4. Sources and Potential Transformation of OSCs

OSCs were considered mainly originated from the primary emissions of fossil fuels combustion and secondary reactions of VOCs with inorganic sulfur species (Jiang, Li, Tang, Cui, et al., 2022). As indicated in Figure S6 in Supporting Information S1, both the formular number and intensity of OSCs exhibited significant correlations with chemical tracers such as Cl^- and SO_4^{2-}, implying the influence of primary coal combustion and its subsequent secondary processes. Notably, in contrast to aromatic OSCs, non-aromatic OSCs not only significantly correlated with Cl^- and SO_4^{2-} but also displayed positive correlations with SOR (sulfur oxidation ratio, defined as the mole ratio of $[SO_4^{2-}]/([SO_4^{2-}] + [SO_2])$) and negative correlations with o-phthalic acid, an organic tracer indicative of secondary oxidation processes from anthropogenic emissions (Kawamura et al., 2005; Seinfeld & Pankow, 2003). Regarding the $Abs_{365,OSCs}$, we observed significant positive correlations with the MS-BrC absorption ($r = 0.65$, $p < 0.01$, Figure 4a), suggesting that OSC chromophores may share similar sources with the bulk MS-BrC fraction. Also, to remove the influence of meteorology and transport, we normalized the $Abs_{365,OSCs}$ by the OSCs contributed OC (estimated using the FT-ICR MS data: $OC_{OSCs} = OC \times (intensity_{CHOS} + intensity_{CHONS})/Total\ Intensity$) and found the mass absorption efficients of OSCs also showed a positive correlation with the MAE_{365} of bulk MS-BrC fraction ($r = 0.50$, $p < 0.05$). As mentioned earlier, our tracer-based PMF model results have demonstrated that MS-BrC absorption was mainly influenced by primary fossil fuels combustion. In addition, positive correlations were also observed between $Abs_{365,OSCs}$ and the fossil source related chemicals of Cl^- and SO_4^{2-}. More directly, the $Abs_{365,OSCs}$ were positively correlated to the fossil combustion related BrC absorption ($r = 0.58$, $p < 0.01$, Figure 4b). It should be mentioned that the BrC absorption contributed by fossil fuel combustion were estimated in our PMF analysis results (Jiang et al., 2023b). All these results collectively supported that primary coal combustion might be a major source of OSC chromophores. Furthermore, numerous studies have suggested that the presence of sulfuric acid seeds can facilitate the secondary formation of OSCs and enhance BrC absorption (Fleming et al., 2019; Laskin et al., 2015). The positive correlations observed between $Abs_{365,OSCs}$, SO_4^{2-} and SOR likely support this hypothesis but require further investigations for confirmation.

Our previous studies have also suggested that secondary processes have significant influences on BrC absorption and molecular composition during the sampling campaign (Jiang et al., 2023a, 2023b). Consequently, the transformation of OSCs may impact BrC absorption. However, the current comprehension of the atmospheric transformation of OSCs remains controversial, as both production and transformation often occur concurrently in the atmosphere (Bruggemann et al., 2020), hindering the estimation of the potential effects of OSC transformation on BrC absorption. Generally, there are two reported pathways for the transformation of OSCs: hydrolysis and heterogeneous oxidation pathway. Several studies have indicated that the hydrolysis of OSCs is relatively slow on the SOA timescales, with hydrolysis rates highly dependent on molecular structures (Hu et al., 2011; Mael et al., 2015). For example, studies have shown that the hydrolysis lifetimes of some primary OSs could reach hundreds to thousand hours at acid conditions (Darer et al., 2011; Hu et al., 2011; Mael et al., 2015). However, in

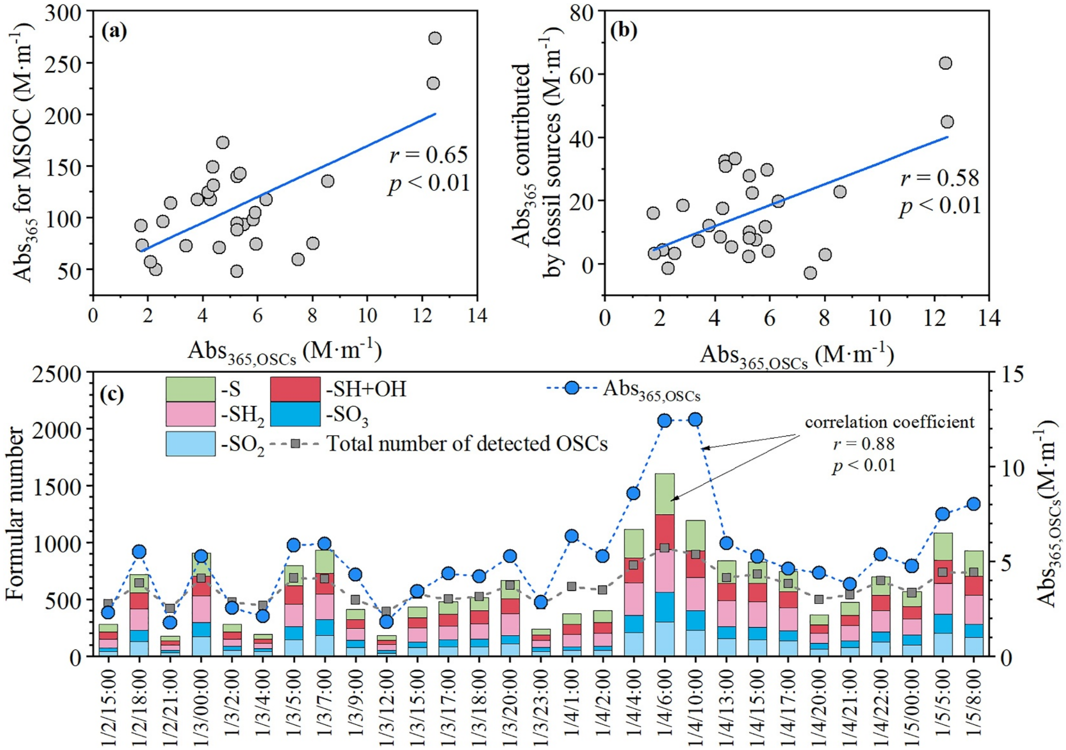

Figure 4. Correlations between the PLSR-estimated $\mathrm{Abs}_{365,\mathrm{OSCs}}$ and (a) the bulk MS-BrC absorption (Abs_{365}) as well as (b) the BrC absorption contributed by fossil sources. (c) Formular number of the precursor-product pairs for the 5 typical sulfur-related transformation reactions in atmosphere. The sum number of detected OSCs and $\mathrm{Abs}_{365,\mathrm{OSCs}}$ is also presented here for comparison use.

laboratory simulation experiments, some tertiary OSs can be rapidly hydrolyzed with a chemical lifetime of only 2.5 hr (Hu et al., 2011). Bruggemann et al. (2020) believed that hydrolysis could play a crucial role in the atmospheric removal of certain OSCs, and they also proposed that OSs should not always be seen as permanent SOA constituents. Though the heterogeneous oxidation of OSCs is also not well-understood, a recent study has revealed that small alkyl-sulfates can undergo efficient oxidation through heterogeneous OH reactions (Kwong et al., 2018). Field observation have further showed that some alkylbenzene OSCs displayed short apparent half-life times as low as 1.2 hr (Siemens et al., 2023), suggesting rapid transformation rates of OSCs in atmosphere. In fact, in this study, results from non-metric multidimensional scaling (NMSD) analysis suggested the photooxidation processes (corresponding to *o*-phthalic acid) emerged as one of important factors driving the molecular distribution of OSCs (Figure S7 in Supporting Information S1), although other factors that related to primary emissions such as biomass burning, fossil fuel combustion, and SO_2 were also important driven factors. Also, the SO_4^{2-} that related to the secondary processes of fossil combustion was another important driven factor. These results indicated that secondary oxidation processes may have potential influences on the distribution of OSCs, which may further affect the BrC absorption properties during the haze event.

It was assumed that atmospheric oxidation processes tend to result in the loss of sulfur-containing groups for OSCs, as the OSCs in the haze atmosphere were mainly by primary emissions. The precursor-product pairs of 5 typical sulfur-related transformation reactions were searched in the FT-ICR MS molecule pool (Bruggemann et al., 2020; Chen et al., 2022). Figure S8 in Supporting Information S1 presented the proposed transformation reactions for the reduced S compounds (Berndt et al., 2023) and organosulfates (Bruggemann et al., 2020)/organosulfonates (Riva et al., 2015) from experimental studies. To find the potential precursor-product pairs, we compared the differences in the atom number between different molecules, and those molecular pairs that meet the criteria were thus considered as precursor-product pairs. Although this is a rough estimation method, many studies have shown that it can provide a reliable understanding of molecular transformation mechanisms (Chen et al., 2022; Jiang, Li, Tang, Zhao et al., 2022). The identified OSC pairs accounted for 13 ± 5.7% to 25 ± 8.4% of the total detected OSC numbers and was significantly correlated with the estimated $\mathrm{Abs}_{365,\mathrm{OSCs}}$ ($r = 0.88$,

$p < 0.01$, Figure 4c), suggesting the potential association between $\mathrm{Abs}_{365,\mathrm{OSCs}}$ and the transformation of OSCs. Additionally, these OSC pairs showed a moderate correlation with bulk MS-BrC absorption ($r = 0.42$, $p < 0.05$), further indicating a potential linkage between desulfurization reactions and bulk MS-BrC light-absorption properties. The intensity ratios of products to precursor could further indicate the possibility of desulfurization reactions occurring in the atmosphere. As shown in Figure S9 in Supporting Information S1, we found that the intensity ratios of products to precursor for some desulfurization reactions, such as the loss of -SO_2 and -SH_2, showed negative correlations with the decrease ratios of MAE_{365} of MS-BrC caused by secondary processes. Noted that the decrease ratios of MAE_{365} of MS-BrC caused by secondary processes were calculated using a deweathered random forest model, and the details were presented in our previous study (Jiang et al., 2023b). Our findings probably implied that desulphurization processes in OSCs would be accompanied by a reduction in MS-BrC light-absorbing capacity. However, given the intricate nature of atmospheric chemical processes, the precise impact of OSC transformations on BrC absorption in the atmosphere requires further investigation to fully elucidate the underlying mechanisms.

4. Conclusions

In this study, we investigated the molecular composition of OSCs and its associations with MS-BrC absorption during a haze event in North China using high-resolution FT-ICR MS and a series of statistical analysis. Both ABT and correlation analysis suggested the aerosol sulfur contents showed close relationships with the variations of BrC during the haze event influenced by residential coal combustion. The measured OSCs were mainly composed of potential aromatic structures, with the upper limit contribution contributed by OSCs to the total estimated to be as high as 25 $\mathrm{M{\cdot}m^{-1}}$, accounting for approximately 10.4% of the total BrC based on the PLSR estimation. Further investigations suggested that the OSCs were also mainly derived from coal combustion, but the potential desulphurization processes of OSCs may result to a decrease of BrC absorption capacity, with the variations of OSCs absorption may explain 14% of the MAE_{365} variance caused by secondary processes.

Coal combustion has been widely reported as an important sources of BrC in North China (Sun et al., 2017; Yan et al., 2017), yet limited attention has been paid to the evolution of BrC from freshly emitted CCOA. As an important component of CCOA, OSCs played an important role in the haze formation in North China (Han et al., 2023; Song et al., 2018). Our results, based on FT-ICR MS analysis, emphasize the importance of anthropogenic emitted OSCs, especially CCOA, in contributing to BrC absorption during haze events. Thus, it is necessary to study the BrC absorption properties of CCOA and the impacts of aging on the molecular composition and BrC absorption. Furthermore, it should be noted that non-road diesel and heavy fuel oil combustion (e.g., ship emissions) are also main sources of aromatic OSCs in atmosphere (Bai et al., 2020; Cui et al., 2019). Therefore, the importance of OSCs on atmospheric BrC in coastal and port cities in the world should be also concerned. Although the total absorption attributed to OSCs constituted only a small fraction of the bulk MS-BrC absorption, the significant associations between aromatic OSCs and coal combustion suggested their potential as tracers for the impact of fossil fuel combustion on BrC. Furthermore, given that aromatic OSCs are abundant in fresh emissions but tend to be less prevalent in environmental samples, the potential transformations of OSCs in the environment could lead to changes in BrC absorption properties.

As the transformations of OSCs could yield SO_4^{2-}, which is of great significance for particle generation and sulfur cycling, elucidating the transformation mechanisms of OSCs across different time periods and regions in the environment is crucial for comprehensively understanding the impact of anthropogenic OSCs on environmental pollution and human health.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The authors comply with AGU's data policy, and the data supporting this paper was uploaded on Zenodo and can be found by Jiang et al. (2024), which includes the original data for the FT-ICR MSs, chemical species, and BrC absorption. The ABT model, PLSR model, and other statistical analysis were all achieved in the open-source software *R* (R_Core_Team, 2022) and is available from https://www.r-project.org.

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