Critical contribution of chemically diverse carbonyl molecules to the oxidative potential of atmospheric aerosols

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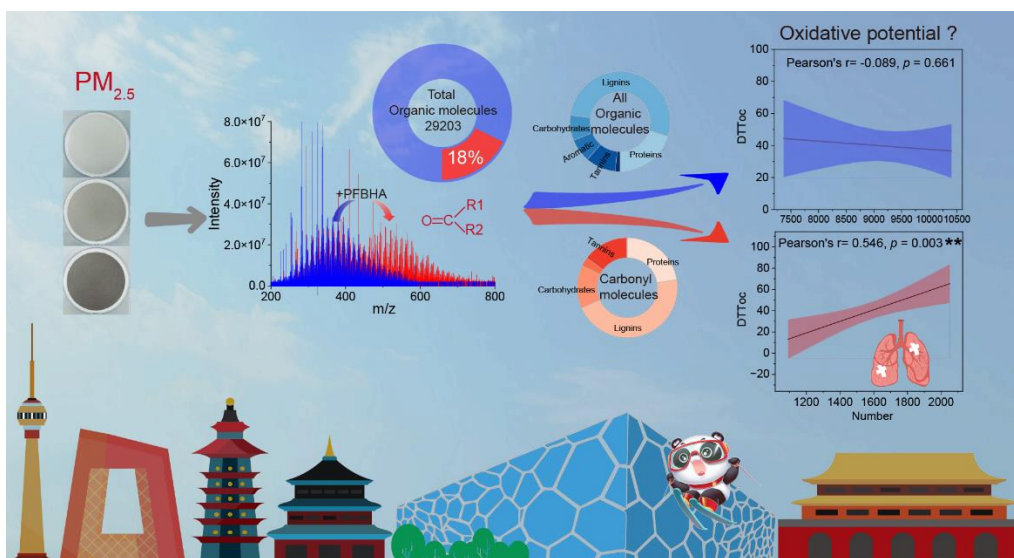
Abstract. Carbonyls have an important effect on atmospheric chemistry and human health because of their high electrophilicity. Here, high-throughput screening of carbonyl molecules in complex aerosol samples was achieved by combining targeted derivatization with non-targeted analysis using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Results showed that water-soluble organic matter (WSOM) in $PM_{2.5}$ contains a large variety of carbonyls (5147 in total), accounting for 17.6% of all identified organic molecules. Compared with non-carbonyl molecules, carbonyl molecules are more abundant in winter than in summer, and have unique molecular composition and chemical parameters. For the first time, a significant positive correlation was found between the abundance of carbonyl molecules and the dithiothreitol (DTT) activities of WSOM, and the elimination of the carbonyl group remarkably reduced the DTT activities, highlighting the pivotal role of carbonyls in determining the oxidative potential (OP) of organic aerosol. Among various molecules, oxidized aromatic compounds containing the carbonyl group produced in winter contributed more to the enhancement of DTT activity, which could be used as potential markers of atmospheric oxidative stress. This study improves our understanding of the chemical diversity and environmental health effects of atmospheric carbonyls, emphasizing the need for targeted strategies to mitigate the health risks associated with carbonyl-rich aerosols.

Graphical abstract

1 Introduction

40 Atmospheric carbonyls are important components of atmospheric organic compounds, forming not only from primary sources such as vehicle emissions, coal and biomass fuel combustion, and industrial emissions (Liu et al., 2022a), but also through secondary reactions between atmospheric oxidants and volatile organic compounds (VOCs) emitted from anthropogenic and biological sources (Claeys et al., 2004; Kalberer et al., 2004). Meanwhile, carbonyls are also involved in the formation of strong oxidative pollutants such as O_3 and peroxyacetyl nitrate (Liu et al., 2022a), as well as the formation

45 of secondary organic aerosols (Chen et al., 2023), thus playing a central role in atmospheric chemistry (Lary and Shallcross, 2000). Moreover, carbonyls are reactive and electrophilic compounds, which can react with nucleophilic sites in biomacromolecules, leading to biomacromolecular dysfunction and eventually cytotoxicity (Han et al., 2020; Kumagai et al., 2002; Rappaport et al., 2012).

Due to the key role of carbonyls in atmospheric chemical processes (Ji et al., 2020; Powelson et al., 2014) and its effects

50 on human health (Bora and Shankarrao Adole, 2021; Li et al., 2015), atmospheric carbonyls have received special attention. (Chen et al., 2023; Yang et al., 2023; Ye et al., 2023). Currently, high-performance liquid chromatography-ultraviolet/visible detection (HPLC-UV/Vis) (Qian et al., 2019a; Shen et al., 2018; Yu et al., 2023b) or gas chromatography-mass spectrometry (GC-MS) (Ho and Yu, 2004) coupled with carbonyl chemical derivatization are the dominant methods for the analysis of atmospheric carbonyls. These methods mainly focused on atmospheric VOCs such as formaldehyde, acetaldehyde, acetone,

55 keto acids, glyoxal, and methylglyoxal (Liu et al., 2022a). However, growing studies suggest that the concentration of carbonyls in the particulate phase was grossly underestimated and plenty of water-soluble and semi-volatile carbonyls with high molecular weight are also presented in the particulate phase (Shen et al., 2018; Wang et al., 2022; Tang et al., 2022). Recently, Xu et al. developed an enhanced method employing ultra-high-performance liquid chromatography and electrospray ionization tandem mass spectrometry (UHPLC-MS/MS) to simultaneously quantify 47 carbonyl compounds,

60 showing that carbonyl compounds missed by the traditional method have a critical contribution to atmospheric photochemical pollution (Xu et al., 2023). Until now, only a few numbers of carbonyls have been detected by target analysis, thus it is urgent to comprehensive identification of them in the atmosphere. In fact, this remains challenging due to the diversity and complexity of atmospheric chemical compositions.

In the past decade, non-targeted analysis methods based on ultra-high resolution mass spectrometry (UHRMS), such as

65 Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and Orbitrap mass spectrometry, have been widely used for molecular characterization of soluble components in atmospheric aerosols from different sources (Song et al., 2022, 2019; Bianco et al., 2018; Ma et al., 2022; Zeng et al., 2020; Yue et al., 2022). Based on non-targeted analysis, our understanding of the molecular composition and chemical diversity of atmospheric organic aerosols has greatly improved (Tang et al., 2022; Li et al., 2023a; Jiang et al., 2021). However, only molecular formulas in organic matter (OM) can be

70 obtained by direct UHRMS detection, and the assessment of molecular characteristic groups is empirically dependent on their elementary composition. Chemical derivatization is a common technique used in targeted analysis for carbonyl

compounds (Liu et al., 2020; Baluha et al., 2013). Recently, Wang et al. employed Girard's reagent T derivatization with +ESI Orbitrap MS analysis to detect the carbonyls in atmospheric fine particulate matter (PM$_{2.5}$) (Wang et al., 2022). However, all molecules containing three N atoms were assigned to derivative products, which may overestimate the contribution of carbonyls (Liu et al., 2020). In order to accurately and rapidly identify carbonyls from natural organic matter, we have recently developed a novel set of detection method and screening procedure based on O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine (PFBHA) derivatization and ESI FT-ICR MS analysis (Yu et al., 2023a). This method provides the opportunity to reveal the molecular composition and chemical diversity of atmospheric carbonyl molecules.

Oxidative potential (OP) is one of the most widely used indicators to assess the atmospheric health hazards of PM$_{2.5}$. Previous studies have reported the important role of water-soluble organic matter (WSOM), such as quinones and humic-like substances (HULIS), in determining the OP of atmospheric aerosols (Jiang and Jang, 2018; Verma et al., 2012). Due to the chemical diversity of WSOM, it is still unclear which fractions contributed to OP of atmospheric aerosols. Carbonyls are known as major electrophilic compounds in atmospheric WSOM (Huang et al., 2020; Graber and Rudich, 2006; Huo et al., 2021). Previous study have reported the correlation between the theoretical electrophilicity of model carbonyl compounds and dithiothreitol (DTT) activities (Chen et al., 2019a). Therefore, it is expected that atmospheric carbonyls may have an important contribution to the OP of WSOM in PM$_{2.5}$. However, until now, the relationship between carbonyls and DTT activities in actual atmospheric samples has not been addressed, mainly due to methodological limitations.

For the above reasons, in this study, we selected three stations in downtown, suburban, and mountainous sites of Beijing to collect atmospheric PM$_{2.5}$ samples for typical pollution processes in summer and winter. The carbonyl molecules and non-carbonyl molecules in WSOM extracted from PM$_{2.5}$ samples were studied by PFBHA derivatization and ESI FT-ICR MS analysis. DTT assay was employed to measure the OP of the collected samples, and the contribution of carbonyls to the OP of WSOM extracted from real atmospheric samples was investigated.

2 Methods and Materials

2.1 PM$_{2.5}$ sample collection and extraction

PM$_{2.5}$ samples were collected in 2022 during three periods: winter (January 19 to February 3), Winter Olympics (February 4 to February 20), and summer (July 10 to July 27). The sampling sites were the monitoring sites set up by Beijing Urban Ecosystem Research Station, including a downtown site at the Beijing Teaching Botanical Garden (39°88'N, 116°44'E), a suburban site at Caiyu Town, Daxing District (39°67'N, 116°71'E), and a mountainous site at Mangshan National Forest Park with altitude about 659 m (40°28'N, 116°29'E). Samples were collected on pre-baked (550 °C, 6 h) quartz filters (Pallflex, 90 mm diameter) using medium-volume samplers with PM$_{2.5}$ cutting heads (Qingdao Laoying Corp, Qingdao, China) at a 24-hour sampling period, and then stored in a refrigerator at -20 °C. Particulate matter concentrations and meteorological data during the sampling period were provided by Beijing Urban Ecosystem Research Station. Detailed sampling information is recorded in Table S1 of the Supporting Information (SI).

The water-soluble fractions were extracted from $PM_{2.5}$ samples (each 1/4 quartz filter membrane) twice with ultrapure water (10 mL) and sonicated for 30 min each time. Then the solution was filtered through the polytetrafluoroethylene syringe filter (PTFE, 0.22 μm, Jinteng, Tianjin, China). The filtrate was further purified and desalted by solid phase extraction (SPE, Varian Bond Elute PPL cartridges) to obtain WSOM (Li et al., 2023b). The quartz filters after water extraction were dried and extracted twice (30 min each) with 5 mL of methanol (MeOH) by ultrasonication. Since inorganic salts and metals were removed during ultrapure water extraction, the MeOH extracted fraction is considered water-insoluble organic matter (WISOM) (Yue et al., 2022). The same extraction operation was performed for the travel blank.

Detailed information on all chemicals used in the study is provided in Text S1 and more details about WSOM and WISOM extraction are provided in Text S2.

2.2 Derivatization of WSOM by PFBHA

Each WSOM sample was divided into three parts. One part was dried with N_2 and redissolved in ultrapure water for total organic carbon (TOC) analysis (Shimadzu 5000-A, Germany). Another part was dried with N_2 and redissolved in 50:50 MeOH /water (v/v) for FT-ICR MS analysis. The third part was used for PFBHA derivatization before FT-ICR MS analysis. Briefly, PFBHA (300 mg L^{-1}) and WSOM samples (100 mg L^{-1}) were dissolved in a mixture of acetonitrile (ACN) and water (70% and 30%, v/v) and then reacted in a shaker for 1 h and then incubated in a water bath at 50 ℃ for 12 h. Subsequently, the samples were blown dry with N_2 and the solvent was replaced with ACN and water (50% and 50%, v/v) and stored at -4°C. Here, ACN was used as a solvent to avoid the formation of potential solvent artifacts by reacting MeOH with conjugated carbonyl groups during the derivatization reaction (Chen et al., 2022). Furthermore, six model carbonyl molecules with different structures (including quinones, aldehydes, ketones, and acids with detailed information provided in Text S1) were employed to test the efficiencies of finding carbonyl compounds using the method used in this study. Six model compounds and their derivatized products can be detected in treatments, and derivatized products displayed considerable or higher S/N than original model carbonyls, indicating high derivatization and detection efficiencies of derivatized products using our method. (Figure S1 in SI).

2.3 ESI-FT-ICR MS analysis and carbonyl molecule identification

WSOM samples before and after derivatization were both detected using ESI-FT-ICR MS with the negative ion mode (15.0 T SolariX, Bruker. Billerica, MA, USA). The detection mass range was firstly set to m/z 99-2000, considering the mass range of all original and derived samples and the calibration range of sodium formate internal standard, the collected mass range was finally set to m/z 122-928. Molecular formulas were assigned to mass peaks with a signal-to-noise ratio (S/N) > 4 are considered valid. Detailed analysis methods are described in the Supporting Information (Text S3).

Molecular formula assignment in the original WSOM was conducted following our previous study (Tang et al., 2022; Li et al., 2023b). For carbonyl molecule identification, a new automatic screening procedure developed in our group was

employed (Yu et al., 2023a), and the detailed screening process was provided in Text S4. Briefly, the mass difference of the reactant-product ion pair formed by the PFBHA derivatization should be 195.01074 ($C_7H_2NF_5$) or its multiples ($C_{14}H_4N_2F_{10}$, $C_{21}H_6N_3F_{15}$) according to the reaction equation (Figure S2). The molecular formulas of carbonyls can be identified if the above mass difference was observed in the sample before and after PFBHA derivatization. As a result, carbonyl and non-carbonyl molecules in the original WSOM can be screened separately. Additionally, the molecular formulas of the control group (blank membrane samples) were subtracted for further analysis.

The molecular parameters such as double bond equivalence (DBE), modified aromaticity index (AImod), the nominal carbon oxidation states (NOSC) (Wang et al., 2021), and the average carbon oxidation state ($\overline{OS}_C$) (Kroll et al., 2011) of the identified molecular formulas were calculated as documented in Text S3. The magnitude-weighted average parameters (e.g., DBEw) are the average of that compositional value in all formulas weighted by the relative intensity of each formula (Lv et al., 2016). In the van Krevelen (VK) diagrams, all the detected molecular formulas were divided into five categories according to their the degree of aromatization and alkylation (Su et al., 2021; Jiang et al., 2022), which are polycyclic aromatic-like molecules (AImod > 0.67), highly aromatic-like molecules (0.5 < AImod ≤ 0.67), highly unsaturated-like molecules (AImod ≤ 0.5 and H/C < 1.5), unsaturated aliphatic-like molecules (1.5 ≤ H/C < 2.0), and saturated-like molecules (H/C ≥ 2.0 or O/C ≥ 0.8).

2.4 DTT activity assay

OP was assessed based on the DTT activity assay (Dou et al., 2015; Wang et al., 2018a; Lin and Yu, 2020). The DTT activity of the whole $PM_{2.5}$ samples was first assessed. The travel blanks and $PM_{2.5}$ samples (8 cm^2) were first ultrasonicated with 8 ml diethylenetriaminepentaacetic acid (DTPA, 1 mM, dissolved in 0.1 M phosphate buffer saline (PBS)) for 1 h, then the residual samples were added with 8 ml methanol for 1h. After filtering through 0.22μm PTFE membrane, PBS extract and methanol extract were each taken in a volume of 475 μL, mixed well, and then incubated with 50 μL DTT (2 mM, dissolved in 0.1 M PBS) in a cell incubator (37℃) for 0, 30, 60, 90, 120 min. Finally, 100 μL 5,5-dithiobis (2-nitrobenzoic acid) (DTNB, 1 mM, dissolved in 0.1 M PBS) was added and then the absorbance at 412 nm was measured by a microplate reader (SpectraMax iD3, Molecular Devices, USA).

For the WSOM and WISOM samples, 50uL of the samples were dissolved in 900uL of DTPA (1 mM, dissolved in 0.1 M PBS) and then incubated with 50 μL DTT and measured as described above. The whole experiment was conducted away from light and the consumption of DTT was controlled within 90%. Three repetitions were set for each sample and the experimental blank was deducted. As shown in Figure S3, the DTT concentrations varied linearly with time in this experiment, indicating a zero-level kinetic reaction, as reported in other studies (Ma et al., 2018; Chen et al., 2019b). As DTPA was added in this experiment to inhibit the consumption of DTT by metal ions, the measured values only reflect the response of OM to DTT (Lin and Yu, 2011). The volume-normalized DTT consumption rate (DTT_v), the mass-normalized

DTT consumption rate (DTT_m), and the TOC-normalized DTT consumption rate (DTT_{OC}) are calculated by the following equations.

$$\text{Volume} - \text{normalized DTT consumption rate } (DTT_v) = \frac{R_{DTT}(\%) \times n_{DTT}(pmol)}{t(min) \times \text{Air volumn}(m^3)}$$

where R_{DTT} (%) represents the ratio of DTT consumed in reaction time. n_{DTT} is the amount of initial DTT, t is the reaction time, and Air volume (m^3) is the sampling volume corresponding to the extracted $PM_{2.5}$ samples.

$$PM_{2.5} \text{ Mass} - \text{normalized DTT consumption rate } (DTT_m) = \frac{DTT_V(pmol\ min^{-1}\ m^{-3})}{PM_{2.5} \text{ mass concentration } (\mu g\ m^{-3})}$$

$$TOC - \text{normalized DTT consumption rate } (DTT_{oc}) = \frac{DTT_V(pmol\ min^{-1}\ m^{-3})}{TOC \text{ concentration } (\mu gC\ m^{-3})}$$

2.5 Reduction of the carbonyl group by Sodium borohydride (NaBH₄)

$NaBH_4$ has been reported to irreversibly reduce ketone, aldehyde, and quinone to alcohols (Baluha et al., 2013; Phillips and Smith, 2015). Therefore, carbonyl molecules in samples can be reduced by $NaBH_4$ treatment (Phillips and Smith, 2014; Baluha et al., 2013). Here, a standard humic substance Suwannee River natural organic matter (SRNOM) obtained from the International Humic Substances Society (IHSS) and a diesel soot sample collected from heavy-duty diesel vehicles were used to study the changes of carbonyls and DTT activity before and after $NaBH_4$ reduction. WSOM of diesel soot ($WSOM_{ds}$) was extracted with ultrapure water twice (10 ml, 30 min each) by ultrasonic extraction and filtered through the 0.22 µm filter membrane. Then the SRNOM and $WSOM_{ds}$ were treated by $NaBH_4$ according to previous studies with minor modifications (Phillips and Smith, 2014, 2015). Briefly, the samples were deoxidized with N_2 for 15 min, then 10 times the sample mass of $NaBH_4$ was added and the reaction was performed in the dark for 12h, and the specific steps were recorded in Text S5 and Figure S4. Afterward, the inorganic salts in the treated SRNOM and diesel soot samples, including unreacted $NaBH_4$ and the boron salts generated after the reaction, were removed by SPE (Text S2) (Lv et al., 2016). Then, the desalted samples of SRNOM and diesel soot were further subjected to carbonyl derivatization, FT-ICR MS analysis, and DTT activity assay.

2.6 Statistical Analysis

The Kruskal-Wallis tests in IBM SPSS Statistics 25 were used to perform the significance test of difference for more than two groups of samples. The pro-oxidative carbonyls were screened stepwise by Spearman correlation analysis, correcting false discovery rates (FDR), and partial least squares regression (PLSR) modeling (Zhang et al., 2023). Spearman correlation tests and FDR correction were performed using the packages "rcorr" and "fdrtool" in R v.3.6.2, respectively. The PLSR model, principal component analysis (PCA) model, and orthogonal partial least squares-discriminant analysis (OPLS-DA) model (Papazian et al., 2022) were performed and validated by SIMCA 14.1 software. Detailed description and model validation are recorded in Text S6 and Figure S5-7.

3 Results and discussion

 3.1 The organic molecular composition of WSOM in PM$_{2.5}$

According to the daily average PM$_{2.5}$ concentrations at each site during the sampling periods (Figure S8), air quality is worse in winter (3-146 µg m^{-3}) than in summer (2-64 µg m^{-3}). An obvious improvement in PM$_{2.5}$ pollution was observed during the Winter Olympics (5-43 µg m^{-3}), mainly due to the reduction of transportation and industrial emissions (Liu et al., 2022b). Based on the PM$_{2.5}$ concentration levels (> 80%, 40%-60%, and < 20%) in three periods, a total of 27 representative PM$_{2.5}$
200 samples (Table S1) were selected to further investigate the composition of organic molecules in WSOM by ESI FT-ICR MS. The number of identified molecules in single sample ranged from 7369 to 10401 (Table S2). It seems that even in very clean air, WSOM extracted from PM$_{2.5}$ contained more than 7000 molecules. Totally, 29,203 unique molecules were identified in all samples, of which 5,147 were carbonyl molecules and 24,056 were non-carbonyl molecules (Figure 1a). The number of carbonyls ranged from 11% to 22% in each sample, whereas the normalized molecular intensity of these carbonyls was
205 higher (20%-35%), likely due to the higher concentration levels of carbonyl molecules than non-carbonyl molecules. Significantly more carbonyl molecules were detected in winter than in summer (Kruskal-Wallis tests, $p < 0.05$), while non-carbonyl molecules detected in winter and summer showed no significant difference (Figure 1b), probably because more carbonyl compounds tended to be released into the gas phase in summer due to higher temperature (Qian et al., 2019b; Shen et al., 2018). At the same time, the fuel combustion emissions in winter may release more carbonyl molecules into the air
210 (Fu et al., 2008).

The magnitude-weighted average parameters such as molecular weight and elemental ratio of organic molecules in each sample are summarized in Figure 1c. Compared to non-carbonyl molecules, carbonyl molecules generally have a lower molecular weight (MW$_w$ = 374 ± 14), DBE$_w$ (6.63 ± 0.89), and AImod$_w$ (0.19 ± 0.08 values, but higher O/C$_w$ (0.60 ± 0.04), H/C$_w$ (1.36 ± 0.11) and NOSC$_w$ (-0.01 ± 0.04), indicating carbonyl group mainly presented in smaller organic molecules
215 with low aromaticity and high oxidation degree.

For all detected molecular formulas of five categories, the proportion of molecules in each group was estimated based on the molecular numbers (Figures S9 and S10). highly unsaturated-like and unsaturated aliphatic-like molecules are the most dominant components in both carbonyl and non-carbonyl molecules. Compared to non-carbonyl molecules, carbonyl molecules showed a significant decrease in polycyclic aromatic-like and highly aromatic-like molecules ($p < 0.01$), but a
220 significant increase in highly unsaturated-like, unsaturated aliphatic-like and saturated-like molecules ($p < 0.001$).

Additionally, molecular formulas can be categorized into four groups based on elemental composition and their proportions in carbonyls and non-carbonyls, and all molecules were estimated based on the molecular numbers (Figures S11 and S12). On average, CHON is the predominant element in both carbonyl and non-carbonyl molecules, but the percentage of CHON-containing carbonyls (38.5% ± 5.2%) is significantly lower than that of non-carbonyls (49.7% ± 4.2%) ($p < 0.001$).
225 Conversely, the percentages of CHO-containing carbonyls (27.7% ± 5.0%) are significantly higher than that of non-carbonyls (24.0% ± 3.4%) ($p < 0.01$). Particularly, the percentages of sulfur-containing molecules (CHOS) are significantly

higher in carbonyls (22.1% ± 4.5%) compared to non-carbonyls (11.8% ± 1.6%) ($p < 0.05$), as well as in CHONS, indicating a substantial contribution of carbonyl groups to sulfur-containing organic compounds.

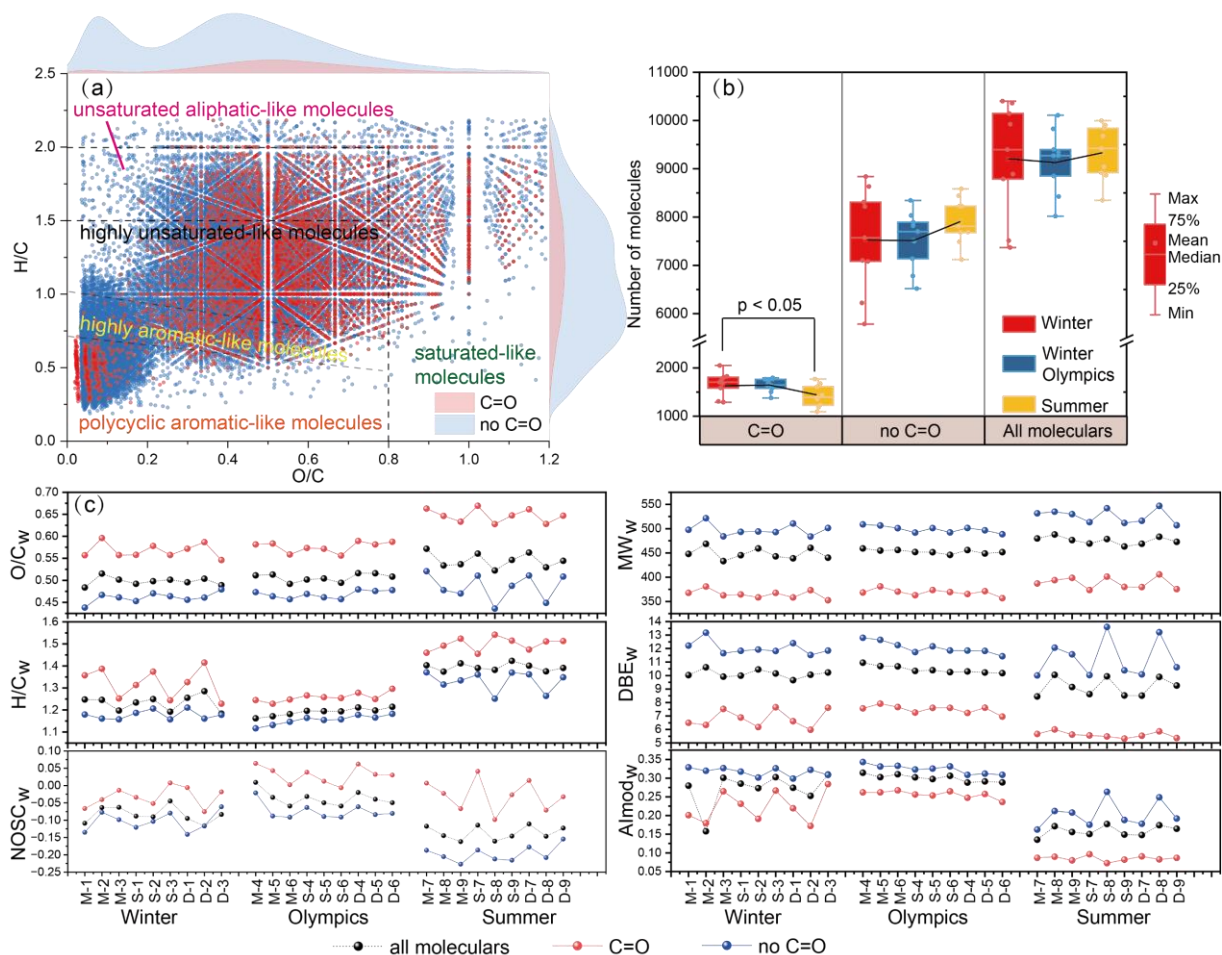



Figure 1: The molecular composition of WSOM in PM2.5 samples was analyzed by FT-ICR MS. (a) Van Krevelen (VK) diagram of carbonyl (C=O) and non-carbonyl (no C=O) molecules in all samples. (b) The distribution of total carbonyl and non-carbonyl molecules was detected in winter, Winter Olympics, and summer. (c) The magnitude-weighted average of O/C, H/C, the nominal oxidation states of carbon (NOSC), molecular weight (MW), double bond equivalence (DBE), and modified aromaticity index (AImod) of the samples. PM$_{2.5}$ samples were shown as from the mountainous (M), suburban (S), and downtown site (D) in the winter (1-3), Winter Olympics (4-6), and summer (7-9) samples.

3.2 Contributions of different organic fractions to the oxidative potential of PM$_{2.5}$

DTT activity is a commonly used cell-free assay to detect the OP of atmospheric samples (Bates et al., 2019; He and Zhang, 2022), wherein DTT$_v$ can reflect the DTT activity caused by PM$_{2.5}$ exposure, and DTT$_m$ can reflect the intrinsic DTT activity of the contaminants in PM$_{2.5}$ (Ma et al., 2018; Chen et al., 2019b; Daellenbach et al., 2020). Figure 2a illustrates the variation of OP levels of PM$_{2.5}$ samples. The average DTT$_v$ of PM$_{2.5}$ samples in this study was 164 ± 171 pmol min^{-1} m^{-3}, much lower than that reported for Tianjin (6.8 ± 3.4 nmol min^{-1} m^{-3}) (Liu et al., 2018), but in the same order of magnitude as the other Chinese cities (Shanghai: 0.13 nmol min^{-1} m^{-3}; Xi'an: 0.51 nmol min^{-1} m^{-3}; Hangzhou: 0.62 nmol min^{-1} m^{-3}) (Lyu et al., 2018; Chen et al., 2019b; Wang et al., 2019).

Samples collected in summer displayed the lowest DTT$_v$ (8-90 pmol min^{-1} m^{-3}), followed by Winter Olympics (32-660 pmol min^{-1} m^{-3}) and winter (43-741 pmol min^{-1} m^{-3}). Both DTT$_v$ and DTT$_m$ were significantly higher in winter than in summer ($p < 0.001$), indicating that both of the contributions of total organic aerosol and organic aerosol per unit mass to OP are higher in winter, and therefore the overall OP risk is higher in winter. Although the PM$_{2.5}$ pollution was significantly improved during the Winter Olympics, only a slight reduction of DTT$_v$ and DTT$_m$ values was observed in the Winter Olympics compared to other days in winter. During the Winter Olympics, transportation and industrial emissions have been successfully controlled (Liu et al., 2022b), but livelihood-related heating and household emissions remain unrestricted. In particular, this study observed a significantly lower DTT$_v$ level in 2022 compared to those reported in 2016 (1.9 ± 0.3 nmol min^{-1} m^{-3}) and 2017 (5.8 ± 7.1 nmol min^{-1} m^{-3}) for Beijing PM$_{2.5}$ samples (Yu et al., 2022; Campbell et al., 2021). This may be attributed to China's implementation of the "Three-Year Action Plan (2018-2020)", an energy policy that gradually shifted the use of coal to natural gas and electricity for cooking and heating in rural areas, leading to improved air quality for Beijing and its surroundings (Du et al., 2022; Li et al., 2023c). The results indicated that under the current air quality level in Beijing, livelihood-related emissions have an important contribution to atmospheric OP, thus the potential of regulating industrial and transportation emissions to improve atmospheric OP is less valid than energy upgrading. Hence winter heating and meteorological conditions may be the main influences on the OP of PM$_{2.5}$. As shown in Figure S13, no significant difference in DTT$_v$ was observed between regions. However, the DTT$_m$ of suburban sites is significantly higher than that of urban sites in winter, and the opposite is true in summer ($p < 0.05$). This is likely due to the differences in aerosol sources between different seasons (Steimer et al., 2020; Campbell et al., 2021). In winter, fossil fuel and biomass burning is a major local source of PM$_{2.5}$ in suburban sites, while this special combustion source aerosol in suburban sites was eliminated in summer. Detailed differences in carbonyl molecules in OA between winter and summer will be discussed later.

The DTT activities of WSOM and WISOM fractions for each sample were detected as well, results showed that the contribution of WSOM to DTT$_v$ (51%-84%) was much higher than that of WISOM (Figure 2b), indicating water extractable compounds have a greater contribution to the OP of PM$_{2.5}$. Meanwhile, we noticed that the seasonal variation of carbonyl molecules (Figure 1b) was consistent with the DTT$_{OC}$ (Figure 2c), which was higher in winter than in summer. Further, the correlation between the DTT$_{OC}$ and organic molecules was investigated (Figure 2d). Although an insignificant correlation

was observed between the normalized molecular intensities of all carbonyls and DTT$_{OC}$, a significant positive correlation was observed when S-containing molecules were excluded, (Figure S14), because unreasonably high intensities of sulfur-containing molecules in the samples due to their extremely high ionization efficiencies(Xie et al., 2022). In addition, both the number and the number proportion of carbonyl molecules were positively correlated with DTT$_{OC}$ (Pearson's r = 0.55, $p <$ 0.01 and Pearson's r = 0.63, $p <$ 0.001), whereas an insignificant or negative correlation was observed between those of non-carbonyls and DTT$_{OC}$ (Pearson's r = -0.26, $p =$ 0.185 and Pearson's r = -0.63, $p <$ 0.001) (Figure 2d and Figure S14). These results suggested carbonyl molecules played a more important role in OP generation than non-carbonyl molecules. By using simulated organic aerosol samples or model compounds, the contributions of carbonyl compounds with different structures to the oxidative potential of OA by a variety of cellular and acellular assays have been studied (Jiang and Jang, 2018; Han et al., 2020; Chen et al., 2019a; Wang et al., 2018b; Tuet et al., 2017; Bates et al., 2019). Conjugated carbonyls such as benzaldehyde, α,β-unsaturated carbonyl, aromatic aldehydes, and polycyclic aromatic hydrocarbon o-quinones, mainly belong to polycyclic aromatic-like carbonyl molecules and highly aromatic-like carbonyl molecules according to VK diagrams, are found to have high oxidative potential and may cause the toxicities of OA. Here, we observed the relationships between carbonyl molecules and DTT activities of real aerosol samples for the first time, providing further evidence for the health hazards of carbonyl molecules in atmospheric environments.

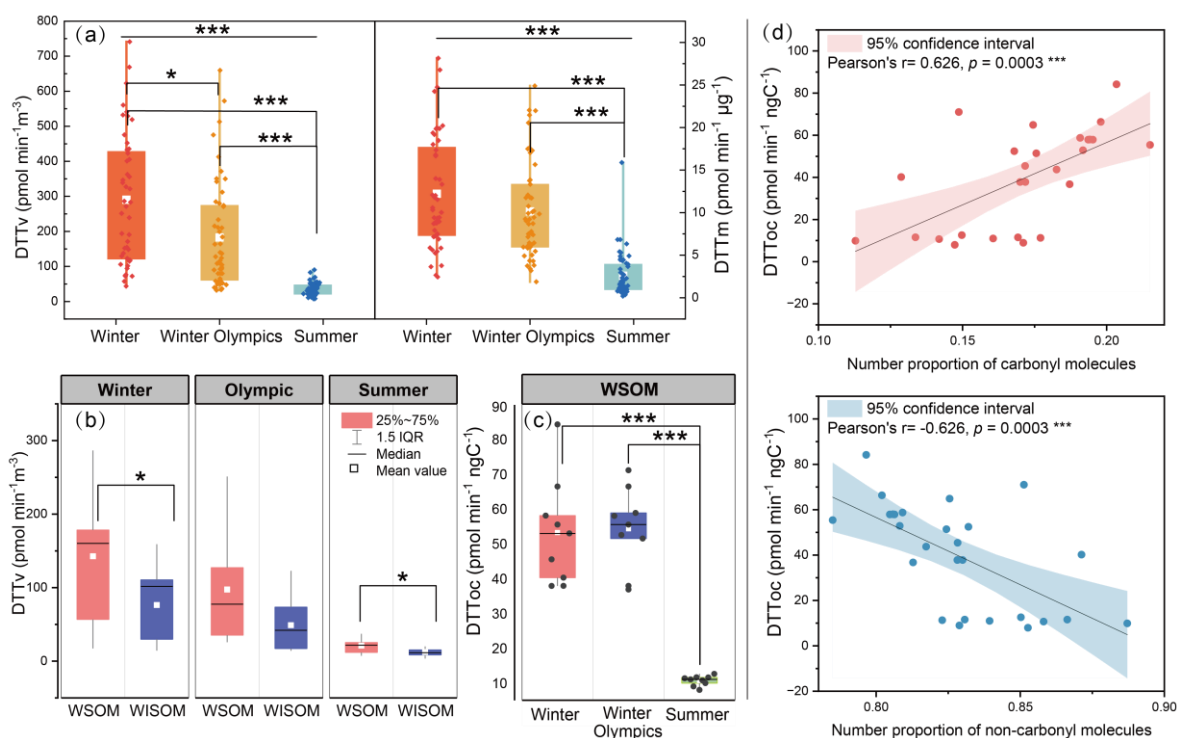



Figure 2: DTT consumption rates of different fractions in PM$_{2.5}$ and its correlation with organic molecules over Beijing in the winter, Winter Olympics, and summer (Kruskal-Wallis tests, differences between groups were considered statistically significant when $p < 0.05$, with $0.01 < p < 0.05$ marked by *; $p < 0.01$ marked by **; and $p < 0.001$ marked by *). (a) Volume-normalized DTT consumption rate (DTT$_v$) and mass-normalized DTT consumption rate (DTT$_m$) of organic matter in PM$_{2.5}$ of the sampling**

period. (b) DTT_v of water-soluble organic matter (WSOM) and water-insoluble organic matter (WISOM) for representative samples. (c) DTT consumption rate of WSOM normalized by TOC (DTT_{OC}). (d) Relationship between the number proportion of carbonyl and non-carbonyl molecules and oxidative potential of WSOM.

3.3 Verification of the contribution of carbonyl molecules to the oxidative potential of organic aerosol

$NaBH_4$ is a widely used reagent to irreversibly reduce ketone, aldehyde, and quinone to alcohols with high selectivity (Baluha et al., 2013; Phillips and Smith, 2015; Ma et al., 2010). To verify the contribution of carbonyl molecules to the OP of organic aerosol, $NaBH_4$ was employed to reduce carbonyls in WSOM to alcohols, and the changes in DTT activities before and after $NaBH_4$ treatment were investigated. Two OA model samples were chosen to perform $NaBH_4$ reduction, PFBHA derivatization, FT-ICR MS analysis, and DTT activity assay. One is SRNOM obtained from IHSS because it has the similar chemical composition to HULIS (Havers et al., 1998; Graber and Rudich, 2006); the other is WSOM extracted from diesel soot ($WSOM_{ds}$), as it is an important source of carbonyls in urban OA (Grosjean et al., 2001; Wang et al., 2023). FT-ICR MS results showed that SRNOM and $WSOM_{ds}$ contained 1367 and 1722 carbonyl molecules, respectively (Figure 3a, 3b). Unlike SRNOM, the carbonyl molecules of $WSOM_{ds}$ had a higher number of CHON (48.1%), likely due to the reaction between the high amount of nitrogen oxide (NOx) and VOC released from diesel vehicles. The original OP of SRNOM and $WSOM_{ds}$ were 23.83 ± 1.07 pmol min^{-1} μgC^{-1} and 57.28 ± 3.05 pmol min^{-1} μgC^{-1}. The higher OP of $WSOM_{ds}$ was attributed to its higher contents of carbonyl molecules. After $NaBH_4$ treatment, 62.9% (619) and 64.1% (1103) of carbonyl molecules in SRNOM and $WSOM_{ds}$ were removed respectively, leaving 24.5% (335) and 37.1% (619) of carbonyl molecules that cannot be removed (Figure 3c, 3d). This is the first time to evaluate the effect of $NaBH_4$ on the reduction of carbonyls in WSOM instead of model compounds because the new detection method was used. As predicted, DTT activities of the SRNOM and $WSOM_{ds}$ reduced 41.3% and 77.2% after $NaBH_4$ treatment (Figure 3e, 3f), which was consistent with the reduction of carbonyl molecules in two samples by $NaBH_4$ treatments. Moreover, an ambient-collected OA sample ($PM_{2.5} = 52.55$ μg m^{-3}) was used to verify the results obtained using model sample. As shown in Figure S15, after $NaBH_4$ treatment, the DTT activity of the real OA sample reduced by about 60%, which was consistent with the results using the model samples. These results further confirmed the important role of carbonyl molecules in determining the OP of organic aerosol.

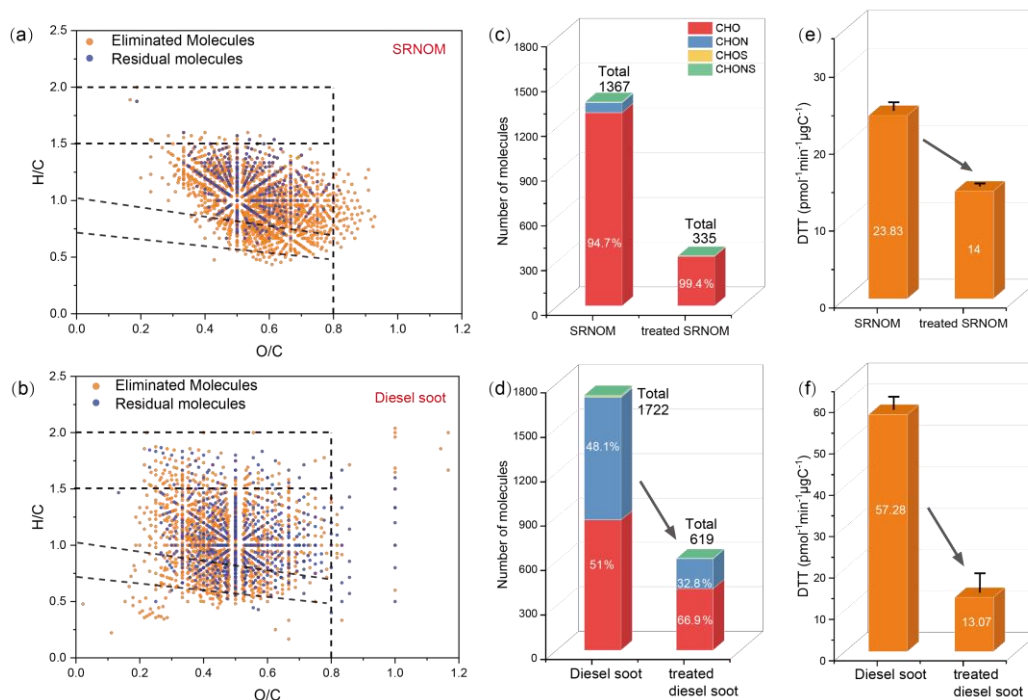



Figure 3: Van Krevelen diagrams of carbonyl molecules in SRNOM (a) and WSOM extracted from diesel soot (b), with orange points representing carbonyl molecules eliminated by NaBH$_4$ and blue points representing residual carbonyl molecules. Changes in carbonyl molecule composition of SRNOM (c) and WSOM extracted from diesel soot (d) before and after NaBH$_4$ treatment. Changes in DTT$_{OC}$ before and after NaBH$_4$ treatment of SRNOM (e) and WSOM extracted from diesel soot (f).

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3.4 Molecular composition of carbonyls in PM$_{2.5}$

320   Because of the importance of carbonyl molecules in determining the OP of PM$_{2.5}$, molecular characteristics for carbonyls were further studied. In general, the DBE$_w$ and AImod$_w$ values of carbonyl molecules detected in winter were higher than those in summer, while the MW$_w$, O/C$_w$, and H/C$_w$ values of carbonyl molecules detected in winter were lower (Figure S16). By using cluster analysis of the samples based on the composition of carbonyl molecules (Figure 4a), two distinct clusters of summer and winter samples were successfully obtained. In one of the clusters, the samples collected during the strict control

325   period of the Winter Olympics can be distinguished from the other winter samples. The proportions of carbonyl molecules in the five categories were estimated based on the molecular numbers. As shown in Figure S17, highly unsaturated-like molecules were the most abundant components during winter (62.3% ± 0.9%) and Winter Olympics (62.1% ± 1.1%), and their abundance was significantly higher than that in summer (58.2% ± 2.3%) ($p < 0.01$). In summer, besides highly unsaturated-like molecules, unsaturated aliphatic-like molecules (33.2% ± 2.2%) were also one of the most dominant

330   components. In addition, the abundance of highly aromatic-like molecules was significantly higher in winter (14.0% ± 1.5%) and Winter Olympics periods (14.0% ± 0.6%) than in summer (3.9% ± 1.0%) ($p < 0.05$).

The elementary composition of the carbonyl molecules was further analyzed. In general, the CHO-containing carbonyl molecules were distributed in regions with lower H/C values dominated by highly aromatic-like and highly unsaturated-like molecules, while the sulfur-containing carbonyl molecules (CHOS, CHONS) were distributed in the region with higher H/C

335   and O/C values dominated by unsaturated aliphatic-like and saturated-like molecules (Figure S18). Furthermore, CHON-containing carbonyl molecules comprised the highest proportion among all sampling seasons (Figure 4b). CHO-containing carbonyl molecules showed a higher proportion during winter and the Winter Olympics period compared to summer. In particular, carbonyl molecules containing sulfur (CHOS and CHONS) exhibit a lower proportion during the Winter Olympics period compared to winter and summer. This discrepancy may be attributed to control measures implemented

340   during the Winter Olympics, such as limiting the operations of high-emission and high-pollution enterprises, which potentially led to a reduction in sulfur-containing compounds. However, it is noteworthy that sulfur-containing carbonyls do not constitute the primary source of aerosol OP, as the DTT$_{OC}$ during the Winter Olympics remained comparable to that observed on other days (Figure 2d).
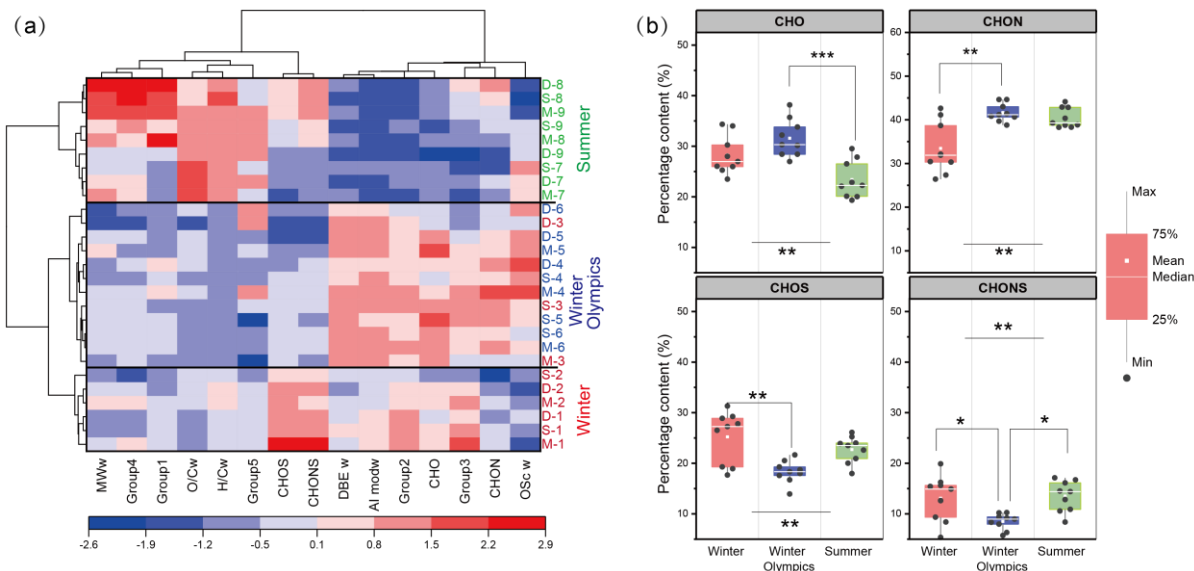
Figure 4: Molecular composition and distribution characteristics of carbonyl molecules in WSOM of PM2.5 samples. (a) The heatmap shows the correlation between the carbonyl molecular characteristics and the samples collected from the winter (1-3), Winter Olympics (4-6), and summer (7-9) in the mountainous (M), suburban (S), and downtown site (D) (Group1: polycyclic aromatic-like molecules, Group2: highly aromatic-like molecules, Group3: highly unsaturated-like molecules, Group4: unsaturated aliphatic-like molecules, Group5: saturated-like molecules). (b) The difference in the percentage distribution based on the molecular numbers of the elementary composition (CHO, CHON, CHOS, CHONS) of carbonyl molecules in winter, Winter Olympics, and summer samples.

3.5 Potential carbonyl markers of atmospheric oxidative stress

Carbonyl compounds with different structures should have different DTT activities. Spearman correlation matrix of the characteristic parameters of carbonyl molecules with DTT_{OC} revealed that DBE_w and $AImod_w$ were significantly positively correlated with DTT_{OC}, while MW_w, O/C_w, and H/C_w were significantly negatively correlated with DTT_{OC} (Figure S19). Thus, oligomers with high O/C ratios and a range of H/C ratios formed by atmospheric secondary oxidation (Nguyen et al., 2011; Kenseth et al., 2023), which are categorized as unsaturated aliphatic and saturated-like molecules, contribute weakly to oxidative potential. Conversely, the number of highly unsaturated and aromatic carbonyls (AImod > 0.5, classified as polycyclic aromatic-like, highly aromatic-like, and highly unsaturated-like molecules in the VK diagram) in the samples showed a higher correlation with the DTT_{OC} (Spearman's r = 0.779, $p < 0.001$), suggesting more attention should be paid to those carbonyl molecules.

In order to screen out potential carbonyl markers to indicate atmospheric oxidative stress (pro-oxidative carbonyls) from numerous carbonyl molecules, Spearman rank correlation and PLSR model analysis using the normalized intensities of carbonyl molecules with more than 50% detection rate and DTT_{OC} were performed. The results showed that 380 carbonyl molecules positively correlated with DTT_{OC} had a value of variable importance in projection scores (VIP) greater than 1.0, indicating these carbonyl molecules had greater DTT activity, thus can be considered as typical pro-oxidative carbonyls. As

shown in Figure 5a, these pro-oxidative carbonyls were mainly highly unsaturated-like (64%) and highly aromatic-like molecules (33%), and dominated by CHO (45.5%) and CHON (42.6%).

OPLS-DA model analysis was performed to further reveal the potential carbonyl markers in different seasons. Results showed that samples collected in winter and summer could be distinguished from each other by the pro-oxidative carbonyls (Figure S20). Then the molecules with VIP > 1 and had the highest model-correlation coefficients ($|p[corr]| > 0.5$) in the volcano plot were screened out as molecular markers in different seasons. Overall, 167 molecular markers in winter were found, which were mainly composed of CHO elements and had significantly higher aromaticity (DBE=11 ± 2, AImod=0.47 ± 0.16) and molecular weight (MW=368 ± 65) compared to other pro-oxidative carbonyls (DBE=9 ± 2, AImod=0.42 ± 0.19, MW=329 ± 65). However, no pro-oxidative carbonyls were found in summer (Figure 5b) due to the low DTT_{OC} of $PM_{2.5}$ collected in summer. Previous study also found that oxygenated OA containing carbon-oxygen double bonds connected to aromatic structures contribute to cellular oxidative stress, with a higher contribution observed during winter compared to summer (Liu et al., 2023). These results suggested that carbonyl-containing highly unsaturated and aromatic products serve as potential molecular markers for atmospheric oxidative stress, especially during periods of increased combustion by-products such as wintertime domestic heating season (Steimer et al., 2020; Huang et al., 2018; Huo et al., 2021).
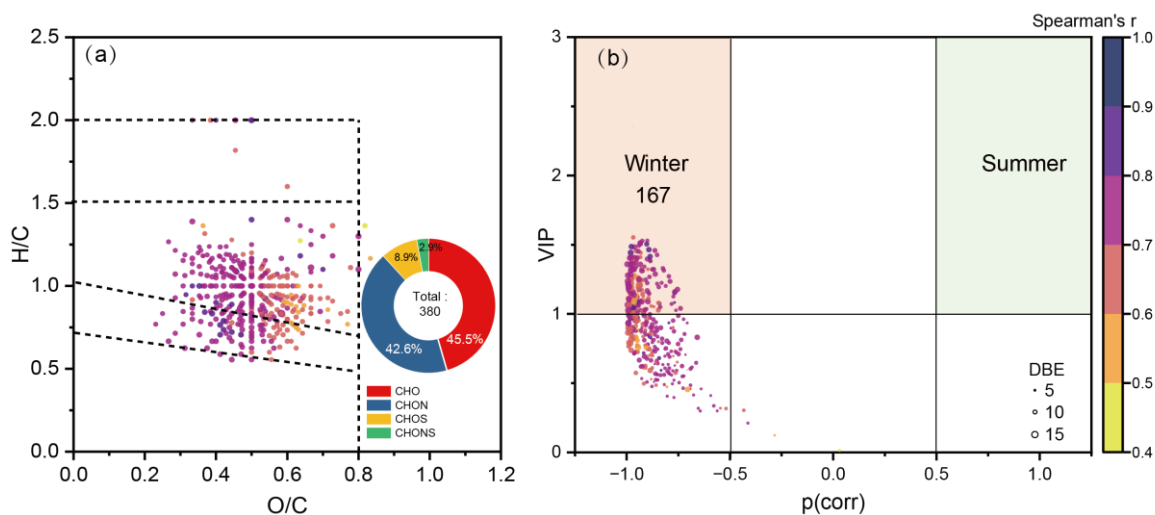
Figure 5: (a) Van Krevelen diagram of pro-oxidative carbonyls. (b) From the OPLS-DA model, the contribution of each pro-oxidative carbonyls to winter versus summer in the volcano plot, showing seasonal variation markers with the highest model-correlation coefficients ($|p[corr]| > 0.5$) and variable importance in projection scores (VIP > 1.0). Features are colored by their Spearman correlation coefficients.

4 Conclusions

$PM_{2.5}$ contains a large number of organic compounds, which have potential harm to the ecological environment and human health. In this study, we investigated the abundance and molecular diversity of carbonyl and non-carbonyl molecules in WSOM from $PM_{2.5}$ using FT-ICR MS analysis with chemical derivatization, taking Beijing as a research area. Carbonyl

molecules in these samples displayed high molecular diversity, accounting for 11%-22% of the total number of identified
organic molecules and 20%-35% of the total intensities of identified organic molecules. Compared with non-carbonyl molecules, more abundant carbonyl molecules are detected in winter than in summer, mainly due to the increasing fuel combustion emissions in winter. Through field sample analysis and simulation experiments, we found that carbonyl molecules played a pivotal role in determining the OP of organic aerosol. Among various carbonyl molecules, highly unsaturated and aromatic carbonyl molecules contributed more to atmospheric oxidative stress, suggesting more attention should be paid to the possible health hazards posed by atmospheric carbonyls. Highly unsaturated and aromatic carbonyl molecules are mainly sourced from fuel combustion and biomass burning processes such as wildfires, agricultural fires, and residential wood burning. In addition, although obvious improvement in $PM_{2.5}$ pollution was achieved, the OP and carbonyl molecules of atmospheric aerosols did not change significantly during the 2022 Beijing Winter Olympics. Therefore, livelihood-related heating and household emissions contribute significantly to the abundance of atmospheric carbonyl molecules, leading to elevated OP in atmospheric aerosols under the current air quality level in Beijing. As a result, the potential of regulating industrial and transportation emissions to improve atmospheric OP in Beijing will be decreased in the future. The control of atmospheric carbonyl pollution is a more challenging task than that of $PM_{2.5}$ pollution, and more scientific measures are needed to reduce the health hazards caused by atmospheric oxidation stress.

Data availability.

The data used in this study are available from the corresponding author upon request (jtlv@rcees.ac.cn).

Author contribution.

F. F. Li: methodology, formal analysis, investigation, visualization, writing – original graft. S. S. Tang: validation, investigation, methodology. J. T. Lv: conceptualization, methodology, formal analysis, writing - review & editing, supervision, funding acquisition. S. Y. Yu: methodology. X. Sun: investigation. D. Cao: methodology, validation. Y. W. Wang: conceptualization, writing – review & editing, supervision, funding acquisition. G. B. Jiang: supervision, validation.

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Competing interests.

The authors declare that they have no conflict of interest.

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