Characteristics and Sources of Environmentally Persistent Free Radicals in PM$_{2.5}$ in Dalian: Important Role of Polycyclic Aromatic Hydrocarbons

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Abstract

Environmentally persistent free radicals (EPFRs) are an emerging class of environmental hazardous contaminants that extensively, stably exist in airborne particulate matter and pose harmful effects on human health. However, there was little research about the sources of EPFRs in actual atmospheric conditions. This study reported the occurrence, characteristics and sources of EPFRs and polycyclic aromatic hydrocarbons (PAHs) in PM$_{2.5}$ collected in Dalian, China. The concentrations of PM$_{2.5}$-bound EPFRs ranged from $1.13 \times 10^{13}$ to $8.97 \times 10^{15}$ spins/m$^3$ (mean value: $1.14 \times 10^{15}$ spins/m$^3$). Carbon-centered radicals and carbon-centered radicals with adjacent oxygen atoms were detected. The concentration of $\sum$PAHs ranged from 1.09 to 76.24 ng/m$^3$ and PAHs with high molecular weight (HMW) were predominant species in PM$_{2.5}$. The correlation analysis and PMF result showed that coal and biomass combustion are the top contributors to EPFR, followed by vehicle emission. The secondary sources to EFPRs was negligible. The finding of present study provides an important evidence for further study on the formation mechanism of EPFRs in actual atmospheric to control the air pollution.

1 Introduction

Environmentally persistent free radicals (EPFRs), present within fine atmospheric particulate matter, have caused concern because they are demonstrated to be detrimental to human health (Chen et al., 2018a; Fahmy et al., 2010; Reed et al., 2015). EPFRs, in contrast to common short lifetime radicals (superoxide radicals and hydroxyl radicals for instance), have longer lifetimes up to months or years (Chen et al., 2019a; Gehling and Dellinger, 2013). Toxicological studies have confirmed that EPFRs can generate reactive oxygen species (ROS) in different media, which lead to oxidative stress on cells (Gehling et al., 2014; Khachatryan and Dellinger, 2011; Khachatryan et al., 2014; Khachatryan et al., 2011; Wang et al., 2020). Thus, investigation on the occurrence, characteristics and sources of particulate EPFRs will be of great importance for assessing their potential health risks.

Studies have shown that ambient particulate matters with different sizes could contain large amounts of EPFRs with different characteristics (Arangio et al., 2016; Chen et al., 2020; Shaltout et al., 2015; Yang et al., 2017b). For example, Yang et al. (2017b) detected the EPFRs in different size of fine particulate matter during haze days in winter in Beijing with concentration ranging from $1.49 \times 10^{20}$ to $1.95 \times 10^{20}$ spins/g, and found the particulate matter with aerodynamic diameters < 1 µm had a highest EPFRs level. Chen et al. (2020) also found the level and type of EPFRs in fine particulate matter (< 2.1 µm) are different with those in coarse particles (2.1–10 µm). Other studies also found the EPFR levels in airborne particulate matter in different cities, such as Taif, Saudi Arabia, Denver, United States and Xuanwei, China (Runberg et al., 2020; Shaltout et al., 2015; Wang et al., 2018). Till now, a few researches have been published on evaluating the concentrations and sources of EPFRs, but information are merely limited to several cities with limited samples. Furthermore, atmospheric particulate matter may contain different kinds of EPFRs according to the $g$ factor ($g > 2.004$, oxygen-centered radicals; $2.003 < g < 2.004$, carbon-centered radicals with adjacent oxygen; $g < 2.003$, carbon-centered radicals) in different regions and in different seasons.
(Chen et al., 2018b; Ruan et al., 2019). Thus, further investigations on the characteristics of EPFRs in different regions are still necessary.

Currently, sufficient investigation on the formation mechanism and the sources of particulate matter-bound EPFRs is still lack. Many studies have reported that particulate matter bound EPFRs were related to formation and adsorption of substituted aromatic molecules and transitional metal oxide (such as copper oxides, ferric oxides) on the particle formed in thermal or combustion process (Gehling and Dellinger, 2013; Reed et al., 2014; Vejerano et al., 2012; Yang et al., 2017a). In addition, EPFRs could also be formed during the photochemical decomposition process of organic pollutants, indicating that burning process was not the sole source of EPFRs (Borrowman et al., 2016; Chen et al., 2019b; Jia et al., 2019b; Zhu et al., 2019). Furthermore, the sources of PM$_{2.5}$-bound EPFRs are different in different cities with different meteorological conditions, which need further exploration (Chen et al., 2018b; Shaltout et al., 2015; Wang et al., 2019a). PAHs, an important precursor of EPFRs, is a typical class of organic species released into atmospheric environment from different sources resulting ubiquitous presence in atmospheric environment (Jia et al., 2016; Jia et al., 2017; Jia et al., 2018). PAHs are regarded as “seasonal contaminants” because of the variations of concentrations and composition between different seasons (Ravindra et al., 2008). The variations are caused not only by the different meteorological conditions (e.g., humidity, temperature) but also by the presence of different sources (Ravindra et al., 2008; Tian et al., 2009). Although previous studies have confirmed that PAHs can form EPFRs during photochemical reaction or oxidation by O$_3$ in laboratory condition, the relationship between EPFRs and PAHs in actual atmospheric is still unknown (Borrowman et al., 2016; D’Arienzo et al., 2017; Jia et al., 2016; Jia et al., 2017; Jia et al., 2019b; Jia et al., 2018; Yang et al., 2017a). Moreover, PAHs from different sources have different congener compositions which is also a key factor in the relationships. In addition, criteria pollutants (e.g., ozone, sulfur dioxide, carbon monoxide, nitric oxide and PM) in atmospheric environment are typical pollutants that may also play an important role during the formation process of EPFRs (Borrowman et al., 2016; Chen et al., 2018b; Wang et al., 2019a). However, information on the source apportionment of EPFRs by the precursors-PAHs and criteria pollutants in actual atmospheric condition is still missing.

The motivation for the present work was an interest in the sources of PM$_{2.5}$-bound EPFRs in Dalian. In present study, the concentrations and characteristics of PM$_{2.5}$-bound EPFRs and PAHs samples collected in non-heating and heating periods were investigated. In addition, the statistic correlation between the concentrations of PAH, six kinds of criteria pollutants and EPFRs and the positive matrix factor (PMF) model was also performed. Based on the results of this work, the dominant source of EPFRs in PM$_{2.5}$ in Dalian was identified.

2 Materials And Methods

2.1 Chemicals and reagents
The details of the chemicals and reagents and their supplier was shown in the Supplementary Material.

### 2.2 Sampling Information

PM$_{2.5}$ samples were collected for 48 h in quartz filter at a flow rate 100 L/min by a low-volume air sampler (Zhongrui, ZR-3920C, China). The filter was baked at 400 °C and stored in valve bag at -20 °C before the sampling. A total of 46 PM$_{2.5}$ samples were collected during heating and non-heating period from November 2018 to May 2019. The site was located west of the Dalian University of Technology campus in Dalian, a northeast city in China. All filters were wrapped with aluminized paper, and stored at -20 °C until pretreatment. The concentrations of six conventional atmospheric pollutants, namely CO, NO$_2$, PM$_{2.5}$, PM$_{10}$, SO$_2$, and O$_3$ were recorded from the daily report according to local environmental monitoring stations during sampling period.

### 2.3 EPFRs analysis

The PM$_{2.5}$-bound EPFRs were measured with a Bruker EXM A-200 spectrometer (Bruker, Bermen, Germany). The experiment was performed based on the method of previous report (Yang et al., 2017b). The filters with collected PM$_{2.5}$ were cut into pieces and steeped in 20 ml dichloromethane (DCM) for 12 h in dark environment. And then use ultrasonic extraction to extract for 30 min. After transfer the supernatant to another sample bottle, the filter pieces were rinsed in triplicate. The supernatant liquid and rinse solutions were fully mixed and then evaporated to approximately 100 μL with a nitrogen blower. The typical operation parameters of EPR were set as follows: scan width, 100 Gauss; center field, 3400 G; microwave frequency, 9.84 GHz, detection time 178 s, number of detections, 5; modulation amplitude, 0.20 mT; microwave power, 8.0 mW. Radical quantification for PM$_{2.5}$-bound EPFRs was calculated by comparing the DI/N, as calculated from double integration of the first derivative signal divided by normalized constant, to a 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard, and the concentrations were normalized to the volume of air. The calibration of DPPH was shown in Fig. S2. The final result was given in spins/m$^3$ which means the radical concentration per m$^3$ of air. The value of g factor was estimated using Bruker's WINEPR software. All measurements were performed at room temperature.

The spin number is calculated using equation (1):

$$S_{EPFR} = S_{DPH} \times \frac{(DI/N)_{EPFRs}}{(DI/N)_{DPH}}$$  \hspace{1cm} (1)

Here $S_{DPH}$ is the total number of DPPH spin. DI/N$_{EPFRs}$ and DI/N$_{DPH}$ were obtained by double integration of the first derivative signal divided by normalized constant.
2.4 PAHs analysis

Briefly, half of the filter samples were cut into pieces, spiked with five labelled PAHs (Chrysene-D12, Perylene-D12, Acenaphthene-D10, Naphthalene-D8, Phenanthrene-D10), and placed in dark environment for 12 h subsequently, finally extracted twice with n-hexane: Dichloromethane (DCM) (1:1, v/v) using ultrasonic. The extract solutions were condensed to ~0.5 mL with nitrogen blower and then cleaned up by a multilayer column filled with 1 cm anhydrous sodium sulfate and 4 cm neutral silica gel from top to bottom. PAH congeners were eluted with 20 mL mixture (DCM: n-hexane=1:1, V/V). The eluate was concentrated to about 0.3 mL with nitrogen blower. Before GC/MS analysis, a known amount hexamethylbenzene as the internal standard was added in the samples for quantification (Wang et al., 2019b).

PAHs were determined by GC-MS (Shimadzu, GCMS-QP2020, Japan) with electron ionization (EI) in SIM model. The 15 kinds of PAH congeners were separated in a DB5-MS capillary column (0.25 mm i.d. × 30 m, 0.25 μm film thickness). 1 μL sample was injected in the splitless mode. The helium carrier gas was at a flow rate of 1 mL/min. The oven temperature started at 80 °C for 3 min, increased to 300 °C at 6 °C/min, and then held for 3 min. The temperature of transfer line was 300 °C and that of ion source was 250 °C.

2.5 Quality assurance and quality control (QA/QC)

The limit of quantification (LOQ) and the limit of detection (LOD) were defined as ten and three times of the ratio of single to noise. The LOD and LOQ were in range of 0.32-16 pg/m³ and 1.08-53.6 pg/m³ (Table S1). Target compounds in samples with concentration below the LOQ were assigned a value of non-detected (n. d.). The recoveries of surrogate standards of PYR-d12, CHR-d12, PHE-d10, ACE-d10, NAP-d8, and were 97.2%, 108.9%, 84.6%, 67.6%, and 53.5%, respectively. The result was corrected by the surrogate recoveries.

2.6 Statistical analysis

Person' correlation analysis was performed between the concentrations of EPFRs, conventional pollutants (CO, SO₂, PM₂.₅, PM₁₀, NO₂ and O₃) and PAH congeners for investigating the potential sources of PM2.5-bound EPFRs in Dalian. Statistically significant correlation was set at a p < 0.05. The concentration of some PAH congeners below the LOQs, were set as half the LOQ for statistical analysis. All statistical analyses were conducted with IBM SPSS Statistics 24.

Furthermore, the EPA PMF 5.0 was used for EPFRs source appointment. Time series of PAH congeners and conventional pollutants and EPFRs were used as input file of this model. Generally, 3 to 6 factors were compared to optimize the result, and the 5 factors and 20 of runs were chosen. PAHs concentrations below the method detection limit (MDL) were half of the detection limit and their overall uncertainties
(Unc) were set with the formula $\text{Unc} = k \times C$, where $k$ are analytical uncertainty and $C$ is the measured chemical concentrations. $K$ of six conventional pollutants is 5%, and $k$ of PAHs and EPFRs is 10%. Missing values and uncertainty were input by the median concentration of the component and four times the median values to decrease their influence on the results (Chen et al., 2020; Qian et al., 2020; Wang et al., 2019b).

### 3 Results And Discussion

#### 3.1 Temporal variation of EPFRs

To probe the potential difference of PM$_{2.5}$-bound EPFRs between the non-heating period and heating period, samples were collected every month and monitored by EPR at room temperature, the $g$ factor, concentration and $\Delta H_{p-p}$ of EPFRs associated with PM$_{2.5}$ were displayed in Table S3. The EPFRs associated with PM$_{2.5}$ with a $g$ factor of 2.00312 ± 0.00034 (range: 2.00222–2.00393). The single, unstructured peak (shown in Fig. S1) and the $g$ factor indicated both carbon-centered radicals and carbon-centered radicals with adjacent oxygen atoms were exist in PM$_{2.5}$ in Dalian. The $\Delta H_{p-p}$ of PM$_{2.5}$-bound EPFRs in present study was from 4.3 to 9.1 G (average value: 6.7 G). The temporal variation of concentration of EPFRs was shown in Fig. 1 and Table S3. The concentration of EPFRs in PM$_{2.5}$ ranged from $1.22 \times 10^{13}$ to $8.97 \times 10^{15}$, with an average value of $1.14 \times 10^{15}$. During the heating period, the EPFRs concentrations in Dalian ranged from $2.99 \times 10^{14}$ to $8.97 \times 10^{15}$ spins/m$^3$ (average value, $1.96 \times 10^{15}$ spins/m$^3$). The EPFRs concentrations ranged from $1.22 \times 10^{13}$ to $2.97 \times 10^{14}$ spins/m$^3$ (mean value: $4.45 \times 10^{13}$ spins/m$^3$) in non-heating period. The comparisons of atmospheric concentrations of EPFRs in heating and non-heating periods showed that the EPFRs concentrations in heating period were one or two orders of magnitude higher than those in non-heating period, which may be caused by coal combustion during central heating. Yang et al. (2017b) and Chen et al. (2019a) have studied the levels of EPFRs bounded to PM$_{2.5}$ during heating period in Beijing and Xi’an, and found that the concentrations with a variation from $1.0 \times 10^{15}$ to $1.4 \times 10^{16}$ spins/m$^3$, from $4.4 \times 10^{13}$ to $6.95 \times 10^{14}$ spins/m$^3$, respectively. The level of PM$_{2.5}$-bound EPFRs in Nanjing, China in 2011 were found to be $2.78 \times 10^{12}$ to $1.72 \times 10^{13}$ spins/m$^3$ (average value: $7.61 \times 10^{13}$ spins/m$^3$) (Guo et al., 2020). Therefore, the concentrations of EPFRs in Dalian are one or two orders of magnitude lower than those in Beijing, and one or two orders of magnitude higher than those in Nanjing.

#### 3.2 Temporal variation of PAHs

Figure 2 showed the temporal variation of the total quantified PAH concentrations ($\Sigma_{15}$PAHs) in PM$_{2.5}$ different periods (non-heating and heating period). The $\Sigma_{15}$PAHs ranged between 1.88 and 76.24 ng/m$^3$ (mean value: 16.3 ng/m$^3$) for all samples (Table S2). The level of $\Sigma_{15}$PAHs in PM$_{2.5}$ during the heating and non-heating period in Dalian ranged from 7.46 to 76.24 ng/m$^3$ (mean value: 28.23 ng/m$^3$) and 1.88 to 9.16 ng/m$^3$ (mean value: 4.03 ng/m$^3$), respectively. The concentrations of $\Sigma_{15}$PAHs during heating
periods was higher than those during non-heating period and the average concentration was 7 times higher than that in non-heating period. The lowest $\Sigma_{15}$PAHs was detected during May 17th -19th, 2019, while the highest was the sample collected during January 23th -25th, 2019. The concentration of $\Sigma_{15}$PAHs in PM$_{2.5}$ of Xi’an China (northwest of China) were from 28.45 to 167.98 ng/m$^3$, with an mean value of 75.29 ng/m$^3$, which was 4.6 times higher than that in Dalian (Niu et al., 2019).

Figure 3 showed the abundance profiles of individual PAHs during different periods. The 4-ring PHAs (FLA, PYR, BaA, CHR) had the highest abundance profile (49%), followed by 5-ring PAHs (BkF, BaP, BbF, DahA) (30%), while 3-ring (FLU, ANT, ACY, ACE, PHE,) and 6-ring (IcdP, BghiP) PAHs showed a relatively low profiles in heating period. In non-heating period, 5-ring and 4-ring PAHs also had high profiles. Compared with the heating period, there was a significant increase in the profiles of 3-ring (from 9–18%), while the proportions of 4-ring and 5-ring PAHs decreased to 45% and 29%, respectively in non-heating period. The various profiles of PAH congeners in different periods were mainly caused by the different emission sources. The PAHs were divided into two groups: high-molecular-weight (HMW, four or more aromatic rings) and low-molecular-weight (LMW, with two or three aromatic rings) congeners (Delgado-Saborit et al., 2014; Janssen et al., 2014). HMW PAHs were dominant PAH congeners associated with PM$_{2.5}$ during the whole sampling period in Dalian. For PAH congeners, BbF was the dominant congener (16.02%), followed by FLA (14.08%), CHR (12.37%) and BaA (11.9%) for all samples during the entire sampling period, and ACE had the lowest proportion (0.2%). In addition, it was found the most abundant components were BbF (16%), FLA (14%), CHR (13%), PYR (12%) in heating period, and BbF (20%), FLA (14%), PHE (13%), and PYR (12%) were the most abundant compounds in non-heating period.

### 3.3 Temporal Variation of conventional air pollutants

Criteria and common ambient air contaminants are fine particulate matter (PM$_{10}$ and PM$_{2.5}$), ozone (O$_3$), nitrogen dioxide (NO$_2$), carbon monoxide (CO) and sulfur dioxide (SO$_2$), which acted as an essential symbol of air pollution and took part in the chemical reaction in atmospheric environment. According to the report from the Bureau of Ecology and Environment of Dalian, the concentrations of variations of typical air pollutants were shown in Fig. 4. The concentrations of PM$_{2.5}$ were from 12 to 75 µg/m$^3$, with the mean value of 30.1 ± 17.2 µg/m$^3$. The level of PM$_{10}$ were from 31 to 103 µg/m$^3$, with an average of 57.5 ± 21.7 µg/m$^3$. The level of CO, O$_3$, SO$_2$ and NO$_2$, were in the range of 0.26–1.2 mg/m$^3$, 34–142 µg/m$^3$, 5–25 µg/m$^3$ and 11–46 µg/m$^3$, with a mean value of 0.82 mg/m$^3$, 86.5 µg/m$^3$, 12.2 µg/m$^3$ and 26.8 µg/m$^3$ respectively. The concentration of CO, PM$_{10}$ and PM$_{2.5}$ increased significantly in January, 2019, in which haze happened frequently for coal combustion and meteorological condition. The concentration of SO$_2$ had no significant change during sampling period and was kept at a low level, which indicated that tail gas desulfurization was effective. O$_3$, a typical secondary pollutant of photo-oxidation, has a high oxidative ability. The concentrations of O$_3$ in heating period were lower than those in non-heating period as a result of the photochemical pollutant that occurred frequently in summer, which is consistent with previous studies (Guo et al., 2019). SO$_2$ is mainly discharged during coal
combustion, while NO₂ was formed during the combustion of petroleum, as a result, the criteria pollutants could play as indicators of air pollution.

### 3.4 Statistical correlation between criteria air pollutants, EPFRs and PAHs

The above results showed that PM\(_{2.5}\)-bound EPFRs and PAHs had different levels and characteristics in non-heating and heating periods, showing the temporal trends of different kinds of pollutants. To better understand the possible sources of EPFRs during different period in actual atmospheric environment in Dalian, this paper performed the statistical correlations between the concentrations of PM\(_{2.5}\)-bound EPFRs, PAHs and criteria pollutants, i.e. PM\(_{2.5}\), SO\(_2\), O\(_3\), NO\(_2\), PM\(_{10}\), and CO by Person’s correlation.

The statistical correlation results between the concentrations of criteria pollutants and EPFRs in PM\(_{2.5}\) were shown in Fig. 5 and Table S4. The concentrations of EPFRs had a significant positive correlation with those of SO\(_2\) (\(r = 0.602, p < 0.01, n = 46\)), NO\(_2\) (\(r = 0.453, p < 0.01, n = 46\)) and CO (\(r = 0.405, p < 0.01, n = 46\)) for all samples, reflecting that coal and petroleum combustion were the predominant sources of PM\(_{2.5}\)-bound EPFRs in Dalian. The correlation between EFPRs and SO\(_2\) is higher than those with NO\(_2\) indicating that coal combustion had a more significant influence on the EPFRs. The metal oxide and the organic molecules formed from the fuel combustion process, would generate abundant EPFRs in post flame zone and cool zone. And then the EPFRs were discharged into environment with particulate matters (Vejerano et al., 2018). Previous studies also showed that under irradiation of light, PAHs can turn into EPFRs in the presence of O\(_3\) (Borrowman et al., 2016). Nonetheless, there was a negative association between O\(_3\) and EPFR during the whole sampling period (\(r = -0.558, p < 0.01, n = 46\)). As shown in Fig. 1 and Fig. 4, the concentrations of O\(_3\) were higher in non-heating period than those in heating period, whereas the concentrations of EPFRs were higher in heating period than those in non-heating period, causing the negative association between the concentrations of O\(_3\) and EPFRs during the whole sampling period. Other study found there was few EPR signals of EPFRs in PM\(_{2.5}\) with a high concentration of O\(_3\), either(Xu et al., 2020). With a high level of O\(_3\), a high oxidative pollutant, the EPFRs may be oxidized quickly, causing the negative correlation between the EPFRs and O\(_3\), which indicates the O\(_3\) can both accelerate the formation and decay the EPFRs(Xu et al., 2020). Unpredictably, the concentrations of EPFRs has no significant correlations with those of PM\(_{2.5}\), indicating that fine particulate matters were only the carrier of EPFRs and have no significant effect on the formation of EPFRs, which is consistent with previous results (Chen et al., 2019a; Schendorf et al., 2019).

Many reports showed that the PAHs were important precursors of EPFRs (Zhao et al., 2019; Zhu et al., 2019). Thus, this statistical correlation was also performed between the concentrations of 15 kinds of PAH congeners and EPFRs in PM\(_{2.5}\) to better illustrate the potential sources of PM\(_{2.5}\)-bound EPFRs in Dalian. The result was presented in Table S1. The concentrations of PM\(_{2.5}\)-bound EPFRs had a significant positive correlation (\(r = 0.560, p < 0.01, n = 46\)) with the concentrations of \(\sum_{15}\)PAHs, which implied that PAHs and EPFRs might have similar sources. As for PAH congeners, a significant correlation was found
between EPFR concentrations and those of 12 kinds of PAH congeners \((0.422 < r < 0.606, \ p < 0.01, \ n = 46)\)
except for ACE, FLU and ANT in the whole sampling period. These PAH congeners are the maker for coal
and biomass combustion and vehicle emission\(\text{(Wang et al., 2019b)}\), indicating the combustion process
of fuel and biomass source may contribute to EPFRs in PM\(_{2.5}\).

### 3.5 Source apportionment

To investigate the potential sources and formation process of EPFRs in PM\(_{2.5}\), the PMF model was used
to statistically analyze EPFRs, PAH congeners and six conventional pollutants in samples. The factors
obtained by PMF model would reflect the different sources and formation processes of EPFRs. Five main
contributing factors to EPFRs in PM\(_{2.5}\) were shown in Fig. 6 and Fig. 7. The typical characteristic of factor
1, dominated by PM\(_{10}\) and PM\(_{2.5}\), was identified as the dust source. There was no contribution to EPFRs
in PM\(_{2.5}\), which is consistent with previous study\(\text{(Qian et al., 2020)}\). Factor 2 indicates coal combustion
source, which has high proportions of BghiP, InD and DiB, associated with coal combustion emission\(\text{(Qin
et al., 2013; Wang et al., 2019b)}\). Coal combustion source contributed about 58.7\% to EPFRs. The central
heating in winter in Dalian consume lots of coal, leading the high level of EPFRs in PM\(_{2.5}\) during heating
period. Factor 3 indicates secondary source, which is dominated by O\(_3\) \(\text{(Lengyel et al., 2004; Wang et al.,}
2019b)}\). This factor contributed about 0.6\% to EPFRs, indicating secondary sources barely contributed to
the EPFRs in PM\(_{2.5}\). Wang et al. \(\text{(2019a)}\) also reported that secondary reaction only contributed 3.42\% to
the PM\(_{2.5}\)-bound EPFRs in Xi’an, a northwest city of China, which was in line with our result. Factor 4
indicates vehicle emission due to the presence of high levels of NO\(_2\), FLA, PYR, BaA, CHR, BbF and BkF
\(\text{(Wang et al., 2019b)}\), which contributed 11.7\% to PM\(_{2.5}\)-bound EPFRs. Factor 5 indicates biomass
combustion due to the presence of high level of ACY, ACE and CO \(\text{(Wang et al., 2019b)}\), which contributed
28.7\% to EPFRs in PM\(_{2.5}\). Overall, the sources of EPFRs in PM\(_{2.5}\) in Dalian were mainly coal and biomass
combustion, followed by the vehicle emission, which mean that the primary source made a dominate
contribution to PM\(_{2.5}\)-bound EPFRs in Dalian. Even though PAHs can be oxidized by O\(_3\) and form EPFRs
under laboratory conditions, the EPFRs derived from PAHs had a shorter lifetime in aerobic environment
than in anoxic environment \(\text{(Borrowman et al., 2016; Jia et al., 2019a)}\). Our study also showed that the
extraction solution of PM\(_{2.5}\) could generate an extensive signal under the irradiation of light and then
decayed quickly after removing the light source, as shown in Fig. S3. which indicated the photo-formation
of EPFRs in PM\(_{2.5}\) has a short lifetime. Thus, the secondary sources to PM\(_{2.5}\)-bound EPFRs, which are
involved in the photoreaction of O\(_3\), are negligible. Further studies are necessary to illustrate the formation
mechanism of EPFRs in the actual atmosphere.

### 4 Conclusion And Environmental Implications

The concentration levels, species characteristics of EPFRs and PAHs were investigated in PM\(_{2.5}\) in Dalian
during heating and non-heating period. The concentration of PAHs and EPFRs in PM\(_{2.5}\) samples in Dalian
ranged from 1.88 to 76.24 ng/m\(^3\) and 1.22×10\(^{13}\) to 8.97×10\(^{15}\) spins/m\(^3\), respectively. The g factors of
PM\(_{2.5}\) bounded EPFRs in Dalian ranged from 2.00222–2.00393, which are the major representative of
organic carbon-centered free radicals and carbon-centered radicals with adjacent oxygen atoms. The source appointment result indicated that the primary sources, i.e. fuel and biomass combustion, vehicle emission, are the dominate sources of PM$_{2.5}$-bound EPFRs in Dalian. As for actual atmospheric environment, the portion of secondary EFPRs associated O$_3$ is negligible. Over all, this study provides a better insight the sources of PM$_{2.5}$-bound EPFRs in Dalian. The study warrants further attention on the formation mechanism of PM$_{2.5}$-bound EPFRs in atmospheric environment.

**Declarations**

**Ethics approval and consent to participate**

Not applicable

**Consent for publication**

Not applicable

**Availability of data and materials**

Not applicable

**Competing interests**

The authors declare that they have no competing interests

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**Authors' contributions**

ZL: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing-original draft,

HZ: Funding acquisition, Project administration, Resources, Supervision, Writing-reviewing and editing

XL: Methodology, Writing-reviewing and editing, Resources
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Figures

Figure 1

Temporal variation of concentrations of environmentally persistent free radicals (EPFR) bounded to PM2.5 measured in Dalian, China, during heating and non-heating period.
Figure 2

Temporal evolution of concentrations of PAHs contained in atmospheric PM2.5 measured in Dalian, China
Figure 3

Compositions of PAHs in the PM2.5 of Dalian.
Figure 4

Temporal evolution of concentrations of conventional air pollutants during the sampling period. (The right axis is for CO and the left for PM2.5, PM10, SO₂, O₃, NO₂)
Figure 5

Pearson correlation coefficients of criteria pollutant and PAHs with EPFRs during the whole sampling period.
Figure 6

Percentages of different source contributions to PM2.5-bound EPFRs
Figure 7

Factor identification of pollution sources during the whole sampling period

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