Response to the comments by the reviewers
Qingcai Chen, Haoyao Sun and Yanlin Zhang.

We appreciate the comments from editor and the reviewers. We have answered the supplementary comments and improved the sentence expression of the article. We look forward to the successful publication of this article.

Our responses to the comments from the reviewers and changes made in the paper are listed below.

The authors have done a good job responding to the referee's comments. There remain a few points where some clarification or correction is needed.

We appreciate the positive evaluation of this work.

Specific comments:
(1) In their response to Reviewer #1 concerning Section 2.2, the authors say "Cut the sample filter into thin strips". It would be much better if they said "The filters were cut into thin strips".

We appreciate this comment from the reviewer. We have modified this part as follows:

L105-107: The filters were cut into thin strips (5 mm × 28 mm), and put it into the sample tank of the quartz tissue cell (the size of the sample tank is 10 mm × 30 mm).

(2) In their response to Reviewer #1 concerning Section 2.3, It is not clear what is meant by "qualified ions".

We appreciate this comment from the reviewer. Qualified ions here refers to the typical ion fragments of each PAHs, which was used to determine the type of PAHs. We have provided another reference that describes the PAHs analysis in detail (Song et al., 2020). In addition, we also changed the expression about this point as follows:

L134-136: Sixteen target PAHs were identified based on retention time and typical ion fragments of each PAH standards, including 16 EPA parent PAHs (p-PAHs).

L141-142: Specific testing protocols have been described previously (Han et al., 2018; Song et al., 2020).

Song, W., Cao F., Lin Y., Haque, M. M., Wu, X., Zhang, Y., Zhang, C., Xie, F., Zhang Y., 2020. Extremely high abundance of polycyclic aromatic hydrocarbons in aerosols from a typical coal-combustion rural site in China: Size distribution, source identification and cancer risk assessment. Atmos. Res. 248, 105192.

(3) The response that explains the g-factor: Instead of "using EPR to detect the sample", it would be more correct to say "using EPR to analyze the sample". This phrase appears in several places, so should be corrected everywhere.

We appreciate this comment from the reviewer. We have modified this section as follows:

L221-222: The *g*-factor obtained by using EPR to analyze the sample is an important parameter to distinguish the type of EPFR.

(4) The response to the Reviewer's question on L204-206, the authors have still not specified if the percentages were by mass.

We appreciate this comment from the reviewer. It is not the contribution by PM mass but is the concentration of EPFRs. We have modified this section as follows:

L205-206: Figure 1b shows the concentration ratio of EPFRs in coarse and fine particles. The contribution of EPFRs in fine PM in summer is only 14.9%, while in winter is 58.5%.

(5) The authors response L220-242. The phrase "the variation in the g-factor with concentration in different season is different." Is a bit awkward, it would be better to simply say "the g-factor varied differently depending on season".

We appreciate this comment from the reviewer. We have modified this section as follows:

L235-236: As shown in Figure 2b, the g-factor varied differently depending on season.

(6) The response to Comment (7). What is "the catering process"?

We appreciate this comment from the reviewer. The catering process refers to the process of cooking, mainly including cooking fume and the process of burning biomass on stoves in rural areas.

(7) Line 24 , Instead of "other fuel combustions", just say "other fuels"

We appreciate this comment from the reviewer. We have modified this section as follows:

L24: …while other fuels are the major source in summer.

(8) Line 159. The phrase that was changed is better, but should be changed to the past tense. "A gradient-based multiplication algorithm was used to find a solution….. and then the first algorithm was used….. based on the least-squares effective-set algorithm."

We appreciate this comment from the reviewer. We have modified this section as follows:

L154-157: A gradient-based multiplication algorithm was used to find a solution from multiple random starting values, and then the first algorithm was used to find the final solution based on the least-squares effective-set algorithm.

Size-resolved exposure risk of persistent free radicals (PFRs) in atmospheric aerosols and their potential sources

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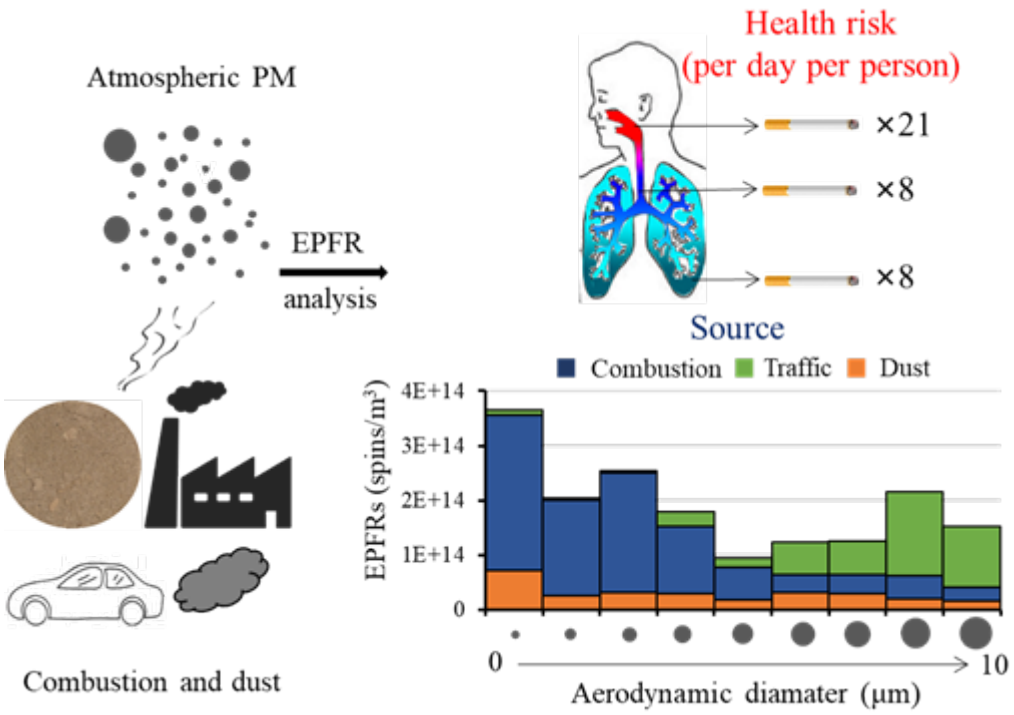
Abstract: Environmentally persistent free radicals (EPFRs) are a new type of substance with potential health risks. EPFRs are widely present in atmospheric particulates, but there is a limited understanding of the size-resolved health risks of these radicals. This study reports the exposure risks and source of EPFRs in atmospheric particulate matter (PM) of different particle sizes (<10 μm) in Linfen, a typical coal-burning city in China. The type of EPFRs in fine particles (< 2.1 μm) is different from that in coarse particles (2.1-10 μm) in both winter and summer. However, the EPFR concentration is higher in coarse particles than in fine particles in summer, and the opposite trend is found in winter. In both seasons, combustion sources are the main sources of EPFRs with coal combustion as the major contributor in winter, while other fuel ~~combustionss~~s are the major source in summer. Dust contributes part of the EPFRs and it is mainly present in coarse particles in winter and the opposite in summer. The upper respiratory tract was found to be the area with the highest risk of exposure to EPFRs of the studied aerosols, with an exposure equivalent to that of approximately 21 cigarettes per person per day. Alveolar exposure to EPFRs is equivalent to 8 cigarettes per person per day, with combustion sources contributing the most to EPFRs in the alveoli. This study helps us to better understand the potential health risks of atmospheric PM with different particle sizes.

Key words: EPFRs; particle size distribution; source; generation process

34 **TOC Art:**


Atmospheric PM
EPFR
analysis
Combustion and dust
Health risk
(per day per person)
×21
×8
×8
Source
Combustion
Traffic
Dust
EPFRs (spins/m³)
4E+14
3E+14
2E+14
1E+14
0
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10
Aerodynamic diamater (μm)

35

1. Introduction

Free radicals are atoms or groups containing unpaired electrons, such as hydroxyl radicals and superoxide radicals, and they usually have strong chemical reactivity and short lifetimes (Pryor et al., 1986; Finkelstein., 1982). Free radicals with long lifetimes (months or even years) in the environment are currently called environmentally persistent free radicals (EPFRs), which have received much attention in recent years as new environmentally hazardous substances (Vejerano et al., 2018; Gehling, 2013; Chen et al., 2019c). EPFRs can be used as an active intermediate to catalyze the production of reactive oxygen species (ROS) by oxygen molecules, thus endangering human health (D'Arienzo et al., 2017; Thevenot et al., 2013; Harmon et al., 2018; Blakley et al., 2001; Khachatryan et al., 2011). Studies have found that EPFRs are present in different environmental media, such as water and soil, and even in the atmosphere (Dellinger et al., 2001; Truong et al., 2010; Vejerano et al., 2012).

A number of studies have investigated the occurrences, sources and formation process of EPFRs in atmospheric particulates in different regions. For example, in the studies of Rostock in Germany, Taif in Saudi Arabia and Xuanwei in China, the average concentration of EPFRs in atmospheric particulate matter (PM) was reported to be in the range of ~ 10^{16} - 10^{18} spins/g (Wang et al., 2018; Arangio et al., 2016; Shaltout et al., 2015). Atmospheric EPFRs are mainly carbon-centered radicals with adjacent oxygen atoms (Gehling et al., 2013). EPFRs of different lifetimes are present in atmospheric PM, with only a few hours for short-lifetime EPFRs and several years for long-lifetime EPFRs that show no signs of decay (Gehling et al., 2013; Chen et al., 2019c). Most studies indicate that sources of transportation and combustion may be the primary EPFR sources in atmospheric PM (Wang et al., 2018; Yang et al., 2017; Chen et al., 2019b). Chen et al. (2018b and 2019b) found that strong atmospheric photochemical effects in summer and dust particles may also be important sources of EPFRs. The process of electron transfer and stabilization between the surface of metal oxides (such as iron, copper, zinc and nickel) and substituted aromatic molecules

under high temperatures is considered to be the main process for the formation of EPFRs in atmospheric particles (Truong., 2010; Vejerano et al., 2012a; Patterson et al., 2013; Vejerano., 2010; Vejerano et al., 2012b). However, the study by Chen et al. (2018a) suggests that EPFRs in atmospheric particulates are mainly derived from graphite oxide-like substances produced during combustion. In addition to primary sources such as combustion, secondary chemical processes in the atmosphere may also be an important source of EPFRs in atmospheric PM (Chen et al. 2019b and 2019d; Tong et al., 2018).

Different particle sizes of atmospheric PM pose different health risks to humans, depending on the deposition efficiency of the particles and the chemical composition and concentrations of hazardous substances they contain (Strak et al., 2012; Valavanidis et al., 2008). Among various hazardous substances, EPFRs may also be involved in the toxicity of atmospheric particulates. Yang et al. (2017) studied the the EPFRs that are extractable by dichloromethane in different particle sizes in Beijing in winter and found that the concentration of EPFRs was the highest in particles with sizes < 1 μm. Arangio et al. (2016) found that the concentration of EPFRs in 180 nm particles was the highest in the 56 nm - 1.8 μm particle size range. Although several studies have examined the particle size distribution of EPFRs, systematic studies have not been conducted on the formation process, source and exposure assessment of EPFRs in atmospheric particles with different particle sizes.

This study takes Linfen as an example. Linfen is one of the cities in China with the most serious air pollution and is a typical coal-burning city. The particle size distribution of EPFRs in atmospheric PM in this region was studied by EPR spectrometry. The effects of particle size and season on the source, formation process, and health risk of EPFRs were revealed. In particular, the comprehensive health risks of EPFRs were evaluated, and it was found that the upper respiratory tract is the area with the highest risk of EPFRs exposure, which is equivalent to twenty-one cigarettes per person per day. This study is of great significance for understanding the source and formation process of EPFRs in atmospheric particulates as well as for health risk

93 assessments.

94 2. Experimental section

95 *2.1 Sample collection*

96 The sampling site for this study is located in Hongdong (36°23', 111°40'E) in
97 Shanxi, China. To collect atmospheric particles of different sizes (0-10 μm), this study
98 used a Thermo-Anderson Mark II sampler to collect aerosol samples of 9 sizes. The
99 samples were collected on a prebaked quartz filter (450 °C, 4.5 hours), and the
100 sampling dates were as follows: in winter, January 26 to February 4, 2017, n = 10; and
101 in summer, July 31 to August 24, 2017, n = 12. The samples were placed in a -20 °C
102 refrigerator prior to analysis.

103 *2.2 EPFR analysis*

104 The EPR spectrometer (MS5000, Freiberg, Germany) is used to detect EPFRs in
105 atmospheric samples. The filters were cut into thin stripsCut the sample filter into thin
106 strips (5 mm × 28 mm), and put it into the sample tank of the quartz tissue cell (the
107 size of the sample tank is 10 mm × 30 mm).~~,~~ Then the quartz tissue cell with attached
108 filter sample was placed in a resonant cavity and analyzed by an EPR spectrometer.
109 The detection parameters were magnetic field strength, 335 - 342 mT; detection time,
110 60 s; modulation amplitude, 0.20 mT; number of detections, 1; and microwave
111 intensity, 8.0 mW. Specific testing protocols have been described previously (Chen et
112 al., 2018c).

113 *2.3 Carbon composition analysis*

114 The contents of organic carbon (OC) and elemental carbon (EC) in the filter
115 samples were analyzed using a semicontinuous OC/EC analyzer (Model 4, Sunset Lab.
116 Inc., Oregon, USA) with a NIOSH 5040 detection protocol (Lin et al., 2009).
117 The water-soluble organic carbon (WSOC) concentration was analyzed using an
118 automatic TOC-LCPH analyzer (Shimadzu, Japan). The WSOC extraction was

performed with ultrapure water under ultrasonication for 15 minutes, and all WSOC concentrations were blank corrected. The concentration of OC in the MSM (Methanol-soluble materials) was calculated as the difference between the OC and WSOC (Water-soluble organic carbon) concentrations. This calculation assumes that all water-insoluble organic carbon (WISOC) in the aerosol can be extracted with MeOH, and the rationality of this assumption has been verified elsewhere (Mihara et al., 2011; Liu et al., 2013; Cheng et al., 2016; Chen et al., 2019a).

2.4 PAH analysis

PAHs were detected using gas chromatography/mass spectrometry (GC/MS) on a GC7890B/MS5977A (Agilent Technologies, Clara, CA). Quartz-fiber filter samples (8 mm in diameter) were cut from each 25-mm quartz-fiber filter substrates used on the ELPI impactor stages using a stainless-steel round punch over a clean glass dish and loaded into the TD glass tube. Next, the TD glass tube was heated to 310 °C at a rate of 12 °C/min and thermally desorbed at 310 °C for 3 min. The desorbed organic compounds were trapped on the head of a GC-column (DB-5MS: 5% diphenyl-95% dimethyl siloxane copolymer stationary phase, 0.25-mm i.d., 30-m length, and 0.25-mm thickness). Sixteen target PAHs were identified based on retention time and typical ion fragments of each PAH standards~~qualified ions of the standards~~, including 16 EPA parent PAHs (p-PAHs). The method detection limits (MDLs) ranged from 0.2 pg/mm2 (Ace) to 0.6 pg/mm2 (Incdp). Naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene D12 were used for the analytical recovery check. All compounds were recovered with a desorption recovery percentage of > 90%. Specific testing protocols have been described previously (Han et al., 2018; Song et al., 2020).

2.5 Metal element analysis

The concentration of metal elements in the samples was determined by a Thermo X2 series inductively coupled plasma mass spectrometer (ICP-MS, Thermo, USA). The metal elements analyzed in summer were Na, Mg, K, Ca, Ti, V, Cr, Mn, Fe, Co,

Ni, Cu, Zn, As, Cd, Pb, and Al, and those in winter were Al, Zn, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Cd, Ba, and Pb. The specific measurement method is based on the study of Qi et al (2016).

2.6. Data statistics method

The source and formation process of EPFRs in PM with different particle sizes were analyzed by nonnegative matrix factorization (NMF). The method is based on the study of Chen et al (2016 and 2019e). Briefly, NMF analysis of EPFR data, metal element contents, OC/EC contents and PAH contents was performed in MATLAB. The version of the NMF toolbox is 1.4 (https://sites.google.com/site/nmftool/). A gradient-based multiplication algorithm was used to find a solution from multiple random starting values, and then the first algorithm was used to find the final solution based on the least-squares effective-set algorithm~~Use the gradient-based multiplication algorithm to find a solution from multiple random starting values, and then use the first algorithm to find the final solution based on the least squares effective set algorithm~~. To find a global solution, the model was run 100 times, each time with a different initial value. By comparing the 1-12 factor model (Figure S4) with the residual of the spectral load, the 6 factor (summer) and 10 factor (winter) NMF models were finally selected.

2.7. EPFR exposure evaluation

To assess the health risks of EPFRs, this study divided the respiratory system into three parts based on the human breathing model: extrathoracic (ET) areas, including the anterior nasal cavity, posterior nasal cavity, oral cavity, and throat; tracheobronchial (TB) areas, including the trachea, bronchi, bronchioles, and terminal bronchi; and pulmonary (P) areas, including the alveolar ducts and alveoli. Then, the sedimentation rates of different particle sizes in different areas of the respiratory system were determined to calculate the exposure risk of EPFRs. Here, the human respiratory system particulate deposition model of Salma et al. (2002) was used, and the specific data can be found in Table S3 and S4.

In addition, the daily inhaled concentration of EPFRs into the concentration of free radicals in cigarettes were converted. The specific conversion method is as follows:

$$N_{cig} = (C_{EPFRs} \cdot V)/(RC_{cig} \cdot C_{tar}) \quad (1)$$

where N_{cig} represents the number of cigarettes (/person/day), C_{EPFRs} (spins/m^3) represents the atmospheric concentration of EPFRs in PM, and V represents the amount of air inhaled by an adult per day (20 m^3/day) (Environmental Protection Agency, 1988). RC_{cig} (4.75×10^{16} spins/g) (Baum et al., 2003; Blakley et al., 2001; Pryor et al., 1983; Valavanidis and Haralambous, 2001) indicates the concentration of free radicals in cigarette tar, and C_{tar} (0.013 g/cig) indicates the amount of tar per cigarette (Gehling et al., 2013).

3. Results and discussion

3.1 Concentrations and types of EPFRs

Figure 1a shows the concentration distribution of EPFRs with different particle sizes in different seasons. EPFRs were detected in the particles of each tested size (the EPR spectrum is shown in Figure S1), but their EPFR concentration levels were different. In summer, the concentration of EPFRs in fine particles (particle size < 2.1 μm) is (3.2 - 8.1) × 10^{13} spins/m^3, while the concentration of EPFRs in coarse particles (particle size > 2.1 μm) is 1-2 orders of magnitude higher than that of fine particles, reaching values of (2.2 - 3.5) × 10^{14} spins/m^3. Winter samples show completely different characteristics from summer samples. The concentration of EPFRs in fine particles (particle size < 2.1 μm) is (1.8 - 3.6) × 10^{14} spins/m^3, while the concentration of EPFRs in coarse particles (particle size > 2.1 μm) is smaller than that of fine particles, with values of (1.0 - 2.1) × 10^{14} spins/m^3. In addition, the concentration of EPFRs in particulates <0.43 μm in winter is very high, but it is very low in summer. According to the results of factor analysis in part 3.2 of this study, this particulate matter is related to combustion, which indicates that coal combustion in winter may provide an important contribution to EPFRs. The EPFR concentration in

the fine PM of Linfen reported above is equivalent to that in the fine PM of Xi'an, but it is ten times smaller than that in the fine PM of Beijing (Yang et al., 2017; Chen et al., 2019b). Although the particle size distribution characteristics of EPFRs in winter and summer are different, their concentration levels are similar, which indicates that the EPFR concentration is not related to the PM concentration, but is determined by the source characteristics. The source characteristics will be discussed in detail in the factor analysis section.

Figure 1b shows the concentration ratio of EPFRs in coarse and fine particles~~Figure 1b shows the size-segregated contribution of EPFR concentration to the overall~~. The contribution of EPFRs in fine PM in summer is only 14.9%, while in winter is 58.5%. The differences in EPFR concentrations with particle size may be related to the source of EPFRs. For example, coarse particles are often associated with dust sources and biogenic aerosols. In another study, the results have shown that dust particles contain large amounts of metallic EPFRs and that they can be transported over long distances (Chen et al., 2018b). EPFRs in fine particles may be mainly derived from the combustion process, such as traffic sources, which are considered to be an important source of EPFRs in atmospheric PM (Secrest et al., 2016; Chen et al., 2019b). Due to winter heating in the Linfen area, the amount of coal burning increases sharply in this season. In 2017, the nonclean heating (Coal-fired heating) rate of urban heating energy structures in Linfen was 40% (data source: http://www.linfen.gov.cn/). With the burning of coal, large amounts of EPFRs are produced, and in the summer, EPFRs emitted by burning coal should be much less than those emitted in winter. This can explain to a certain extent that the contribution of fine particles to summer EPFRs is small, and the contribution of winter EPFRs is very large.

The *g*-factor obtained by using EPR to analyze the sample is an important parameter to distinguish the type of EPFR. It is the ratio of the electronic magnetic moment to its angular momentum (Shaltout et al., 2015; Arangio et al., 2016). The *g*-factor of carbon-centered persistent free radicals is generally less than 2.003, the *g*-factor of oxygen-centered persistent radicals is generally greater than 2.004, and the

g factor of carbon-centered radicals with adjacent oxygen atoms is between 2.003 and 2.004 (Cruz et al., 2012). Figure 2a shows the *g*-factor distribution characteristics of EPFRs in different particle sizes in summer and winter. The *g*-factor of fine particles and coarse particles shows different characteristics. The *g*-factor of EPFRs in fine particles (particle size < 2.1 μm) ranges from 2.0034 to 2.0037, which may be from carbon-centered radicals with adjacent oxygen atoms. However, the *g*-factor of EPFRs in coarse particles (particle size > 2.1 μm) is significantly less than that of fine particles. The *g*-factor ranges from 2.0031 to 2.0033, indicating that EPFRs in coarse particles are more carbon-centered than those in fine particles and are free of heteroatoms. As shown in Figure 2b, the g-factor varied differently depending on season. The *g*-factor of summer PM showed a significant decreasing trend with increasing concentration, while the *g*-factor of winter PM showed a significant increasing trend with increasing EPFR concentration. Oyana et al. (2017) studied EPFRs in the surface dust of leaves in the Memphis region of the United States and found that the concentration of EPFRs was positively correlated with the *g*-factor, and they believed that this was related to the source of EPFRs. This phenomenon indicates that the sources and toxicity of EPFRs in winter and summer are different.

3.2 Factor Analysis of EPFRs

To explore the possible sources and formation process of EPFRs in atmospheric particles with different particle sizes, the NMF model was used to statistically analyze EPFRs, carbon components, PAHs and metal elements in samples. The factors obtained by the NMF model should reflect the different sources and generation process of EPFRs. As shown in Figure 3a1 and b1, the three main contributing factors to EPFRs in summer and winter are shown (see Figure S5, S6 for spectra of other factors), which explain 94.5% and 83.8% of the EPFR concentrations in summer and winter, respectively.

As shown in Figure 3a1, the typical spectral characteristic of summer factor 1 is that it contains a small fraction of EC components and a large amount of OC components, which indicates that combustion may be the source associated with this

factor. This factor has the highest loading of OC, especially WISOC; this fraction mainly contains macromolecular organic substances, which are considered to contribute to the main atmospheric particulate EPFRs and to be graphite oxide-like substances (Chen et al., 2017; Chen et al., 2018a). Factor 2 is different from factor 1; factor 2 is more likely the combustion of fossil fuels, while factor 1 should be other combustion sources instead of burning coal, such as biomass combustion. The generation process is similar to a hybrid process, which includes the graphite oxide-like substances produced by incomplete combustion and the EPFRs formed by some metal oxides. The typical characteristic of factor 3 is that the contribution of metal elements is relatively high, while the contributions of EC and OC are very low. Metal elements such as Al, Ti, Mn, and Co are typical crust elements, so this factor may represent dust sources (Pan et al., 2013; Srivastava et al., 2007; Trapp et al., 2010). The generation process of EPFRs. The others are likely derived from the electroplating metallurgy industry (detailed in S1). As shown in Figure 3a2, the contribution ratios of different factors show that the contribution ratios of factor 1 and factor 2 are the highest, and factor 3 has only a small contribution, which indicates that combustion sources, especially incomplete combustion, are the main sources of EPFRs. The particle size distribution characteristics show that factor 1 is mainly distributed in particles larger than 2.1 μm, while factor 2 is mainly distributed in particles smaller than 0.43 μm.

The results of the factor analysis in winter are different from those in summer. As shown in Figure 3b1, the typical spectral characteristic of factor 1 is that it contains a large amount of OC components and As and Se. As and Se are trace elements of coal combustion, as shown in many studies (Pan et al., 2013; Tian et al., 2010), so coal combustion may be the source represented by this factor. From the generation process viewpoint, the factor does not contain EC, but the content of OC is very high. In the particles with a particle size of less than 3.3, which is mainly present in factor 1, the concentration of OC is 16 times that of EC. So it may be mainly a graphite oxide-like substance formed by the agglomeration of gaseous volatile organic compounds

(VOCs) generated during combustion. The typical spectral characteristics of factor 2 are due to a large amount of V and some Al, EC and OC. OC and EC are also typical combustion products. V is rich in fossil fuels, especially fuel oil (Karnae et al., 2011). Therefore, traffic is the source represented by this factor. The factor contains crust elements such as Al and Mn, so it is speculated that this factor may also include traffic-related dust. The typical spectral characteristics of factor 3 are similar to those of factor 1, and both contain relatively large amounts of As and Se, with the exception that factor 3 contains a large amount of EC, indicating that it is also mainly derived from incomplete combustion sources. The generation process of factor 3 should be different from factor 1, which may include both the graphite oxide-like material generated by fuel coking and the EPFRs generated by the metal oxide. The other factors are mainly atmospheric dust and electroplating or metallurgy (see text S1). As shown in Figure 3b2, factor 1 and factor 2 have the highest proportions, and factor 3 also has a small contribution, which indicates that winter is the same as summer, and combustion sources are the main source of EPFRs. The particle size distribution characteristics show that factor 1 is mainly distributed in particles with a size of 0.43 - 3.3 μm, while factor 2 is mainly distributed in particles lager than 3.3 μm.

Based on the above analysis, it can be found that combustion sources are the main sources of EPFRs, and EPFRs from these sources are mainly graphite oxide-like substances generated by the polymerization of organic matter or fuel coking. Studies have shown that graphene oxide can cause cell damage by generating ROS (Seabra et al., 2014). The surface of these compounds contains not only carbon atoms but also some heteroatoms, which leads to disorder and the presence of defects in the carbon-based structure (Lyu et al., 2018; Chen et al., 2017a; Mukome et al., 2013; Keiluweit et al., 2010). The dust source is also a source of important EPFRs identified in this study (with a contribution of approximately 10%). It was shown in the above analysis that the concentration of EPFRs in coarse particles has a significant correlation with the concentration of metallic elements, particularly crustal elements. Some crustal elements, such as Al, and Fe, not only have their own paramagnetism

318 (Li et al., 2017; Yu et al., 2013; Nikitenko et al., 1992), but also interact with aromatic
319 compounds attached to the surface of the particles to produce a stable single-electron
320 structure.

321 3.3 *Health risk of EPFRs*

322 To evaluate the health risks of EPFRs in PM with different particle sizes, this study
323 evaluated the comprehensive exposure of EPFRs based on the deposition efficiency of
324 PM with different particle sizes in different parts of the human body. The results are
325 shown in Figure 4a. The ET region is the region with the highest EPFR exposure,
326 while the TB and P regions have relatively close EPFRs. This result shows that
327 atmospheric EPFRs are the most harmful to the health of the human upper respiratory
328 tract. Comparing the EPFR exposure in different seasons indicates that the exposure
329 risk in the ET area in summer is significantly higher than that in winter. This
330 difference occurs because the concentration of EPFRs in coarse particles is much
331 higher than that of fine particles in summer and the deposition efficiency of large
332 particles in the ET area is generally higher. Fine particles are more efficiently
333 deposited in the P region, leading to a higher risk of EPFR exposure in the P region in
334 winter.

335 EPFRs were found early in cigarette tar and are considered one of the health risk
336 factors in cigarette smoke (Lyons et al., 1960); thus, in this study, the exposure risks
337 of EPFRs in particles deposited in the human body were converted to the equivalent
338 number of cigarettes inhaled per adult per day. As shown in Figure 4b, the ET area is
339 the most contaminated area, with an average equivalence of twenty-one cigarettes
340 (twenty-five in summer and sixteen in winter). The average values for the TB area
341 (nine in summer and seven in winter) and P area (seven in summer and ten in winter)
342 are eight. The results indicate that EPFRs pose significant health risks to human lungs
343 in both winter and summer. Other similar studies, such as a study of the average
344 amount of EPFRs in $PM_{2.5}$ inhaled per person per day in Xi'an in 2017, found values
345 equivalent to approximately 5 cigarettes (Chen et al., 2018a). Gehring and Dellinger
346 (2013) found that EPFR exposure in $PM_{2.5}$ is equivalent to approximately 0.3

cigarettes per person per day in St. Joaquin County, the location with the worst air pollution in the United States. The average exposure risk of EPFRs in fine particles in the Linfen area (approximately 13 cigarettes) was higher than those in these two studies. However, these previous studies only studied the exposure risk of EPFRs in fine particles. The results of this study indicate that the health risks of EPFRs are significantly increased when the particle size distribution of EPFRs is taken into account. Therefore, it is important to study the source characteristics and generation process of EPFRs with different particle sizes, which will be discussed in detail in the following sections.

This study calculated the proportion of EPFRs with different particle sizes in different parts of the respiratory system based on the deposition efficiency of particles with different particle sizes. As shown in Figure 4c, in the ET region and the TB region, coarse particles are the dominant component in summer and winter. In particular, in summer, the proportion of EPFRs in coarse particles in these two regions exceeds 95%. In the P region, there are significant differences between summer and winter. The P region in summer is still dominated by coarse particles, but its proportion is significantly lower than those in the ET and TB regions. In the P region in winter, fine particles are the dominant component (approximately 70%). These distribution characteristics indicate different sources of EPFRs in different regions. As shown in Figure 4d, in summer, combustion sources are the main source of EPFRs in the respiratory system. In winter, combustion and transportation sources contribute equally in the EP and ET regions, while in the alveoli, combustion sources are the main contributor. The ET region is the area with the highest risk of exposure to EPFRs (21 cigarettes). The generation process of these EPFRs is mainly attributable to graphene oxide-like substances. Studies have shown that graphene oxide is cytotoxic (Harmon et al., 2018). In the alveoli, the contribution of combustion sources is significantly increased (especially in winter). These EPFRs are mainly generated by the action of metal oxides and organic substances. Studies have shown that such EPFRs can generate ROS in the lung fluid environment (Khachatryan et al., 2011).

4. **Conclusions and environmental implications**

This study systematically reported the particle size distribution of EPFRs in atmospheric PM in Linfen, which is one of the most polluted cities in China and is located in a typical coal-burning area. In addition, this study evaluated the comprehensive health risks of EPFRs, and reported possible sources and formation process of atmospheric EPFRs with respect to different particle sizes. The following main conclusions were obtained.

(1) This study found that EPFRs are widely present in atmospheric particles of different particle sizes and exhibit significant particle size distribution characteristics. The results of this study demonstrate that the concentrations and types of EPFRs are dependent on particle size and season. This seasonal characteristic of EPFRs is mainly affected by the PM sources, this result also indicates that the potential toxicity caused by EPFRs may also vary with particle size and season.

(2) This study reported the possible source and formation process of atmospheric EPFRs in different particle sizes. The results show that combustion is the most important source of EPFRs (>70%) in both winter and summer PM samples in Linfen. The graphite oxide-like process has the highest contribution (~70%) and is mainly distributed in particles with a size of > 0.43 μm. These findings deepen our understanding of the pollution characteristics of atmospheric EPFRs and are useful for controlling EPFR generation in heavily polluted areas.

(3) This study assessed the exposure risk of EPFRs in different areas of the respiratory system. The results show that the upper respiratory tract is the area with the highest EPFR exposure. The trachea and alveoli are also exposed to EPFRs, and the risk of exposure is equivalent to that of 8 cigarettes per person per day. Coarse particles are the main source of EPFRs in the upper respiratory tract, while fine particles are mainly involved in the alveoli.

Through this study, the results have shown that there are significant differences in the concentrations and types of EPFRs in particles of different sizes and these differences are due to the influence of the source and generation process. In the future,

assessments of the particle size distribution and the seasonality of EPFRs in atmospheric PM should be considered. Health risks are another focus of this study. It is found that the upper respiratory tract is the key exposure area of EPFRs, and the traffic source is the main source of EPFRs in this area. This finding is significant for a systematic assessment of the health risks of EPFRs. In view of the complexity and diversity of the formation process of EPFRs in actual atmospheric particulates, the relative contributions of EPFRs generated by different process and their associated health risks should be more comprehensively studied in the future.

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Appendix A. Supplementary data

Appendix A contains additional details, including the EPR spectra of samples of different particle sizes, correlations between EPFRs and carbon in particles of different particle sizes, the results and errors of factor analysis, correlation analysis of EPFRs with metallic elements, and EPFR exposure in different areas of the human respiratory tract.

Code/Data availability: All data that support the findings of this study are available in this article and its Supplement or from the corresponding author on request.

Author contribution: Qingcai Chen: Research design, Methodology, Writing - Original Draft, Writing - Review & Editing, Project administration, Funding acquisition; Haoyao Sun: Investigation, Sample analysis, Writing - Original Draft, Writing - Review & Editing, Methodology, Formal analysis; Wenhuai Song: Investigation, Sample collection, Chemical analysis; Fang Cao: Investigation, Sample

collection; Chongguo Tian: Investigation, Chemical analysis; Yan-Lin Zhang: Conceptualization, Writing - Review & Editing, Formal analysis, Validation, Funding acquisition.

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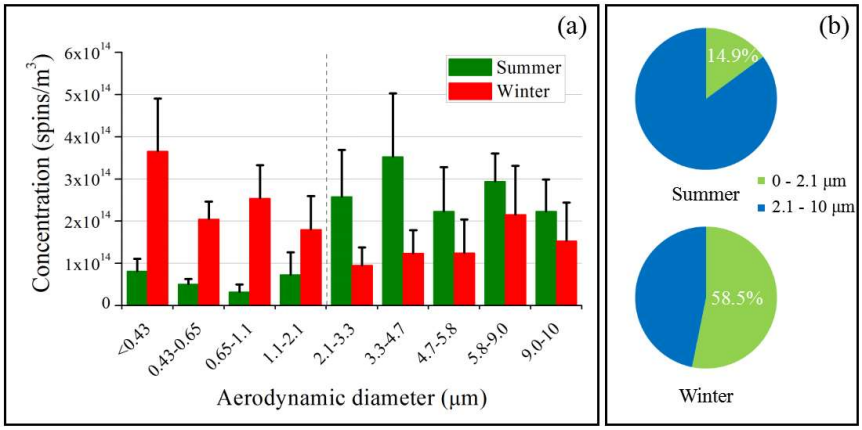


631

632 Figure 1. The concentration of EPFRs in PM with different particle sizes. (a) Atmospheric
633 concentrations of EPFRs in different particle sizes in summer and winter. (b) The relative
634 contribution of fine particles and coarse particles to the total EPFR concentration.

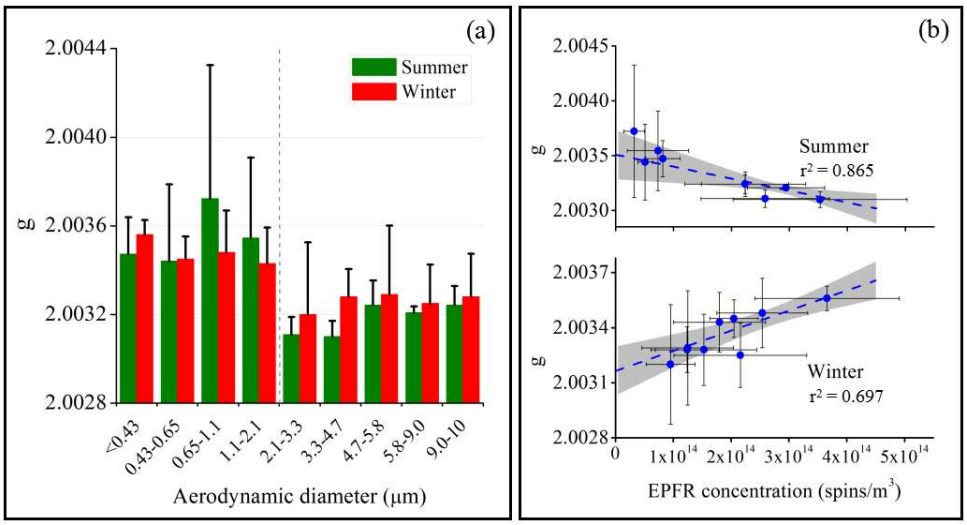
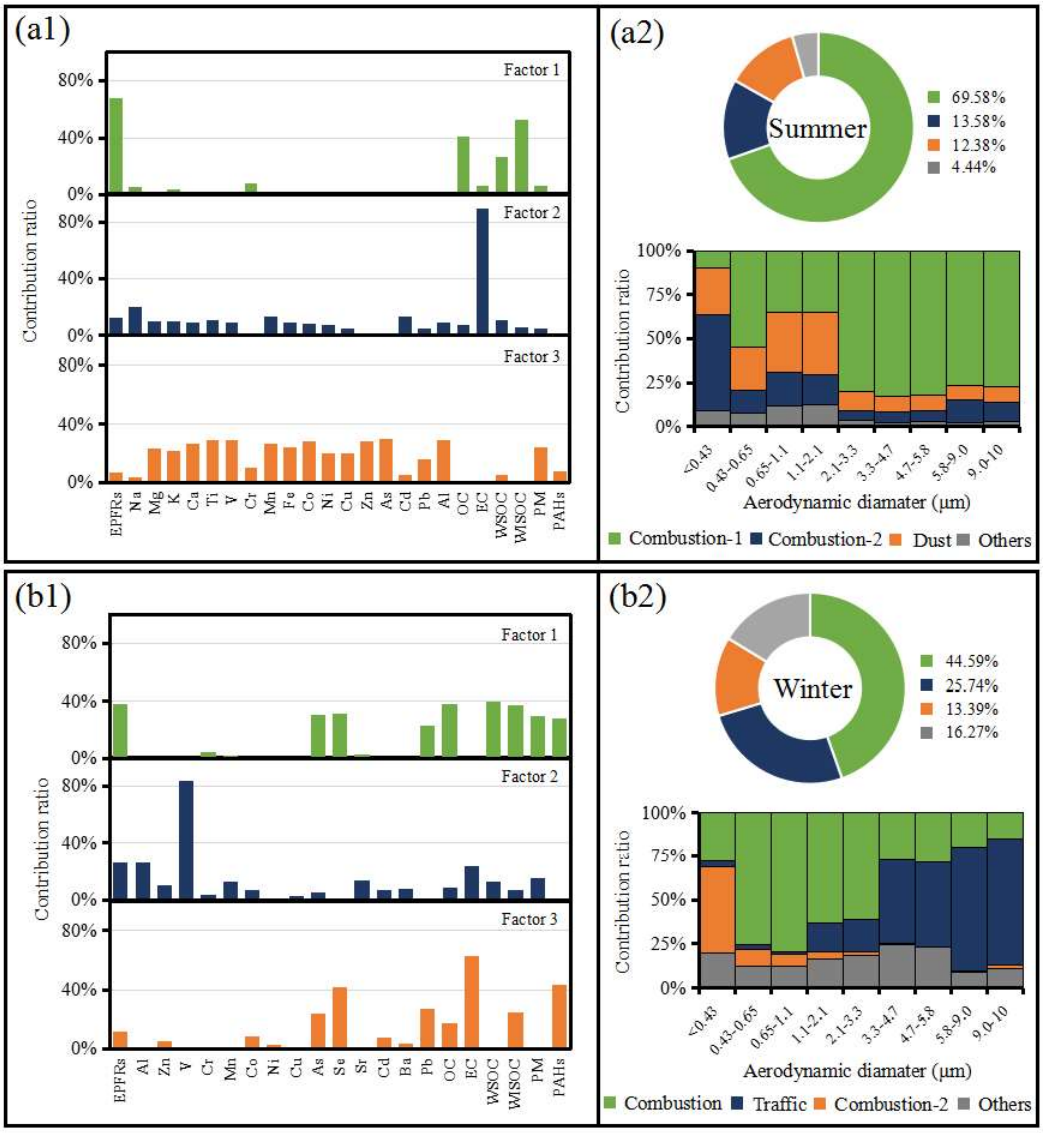
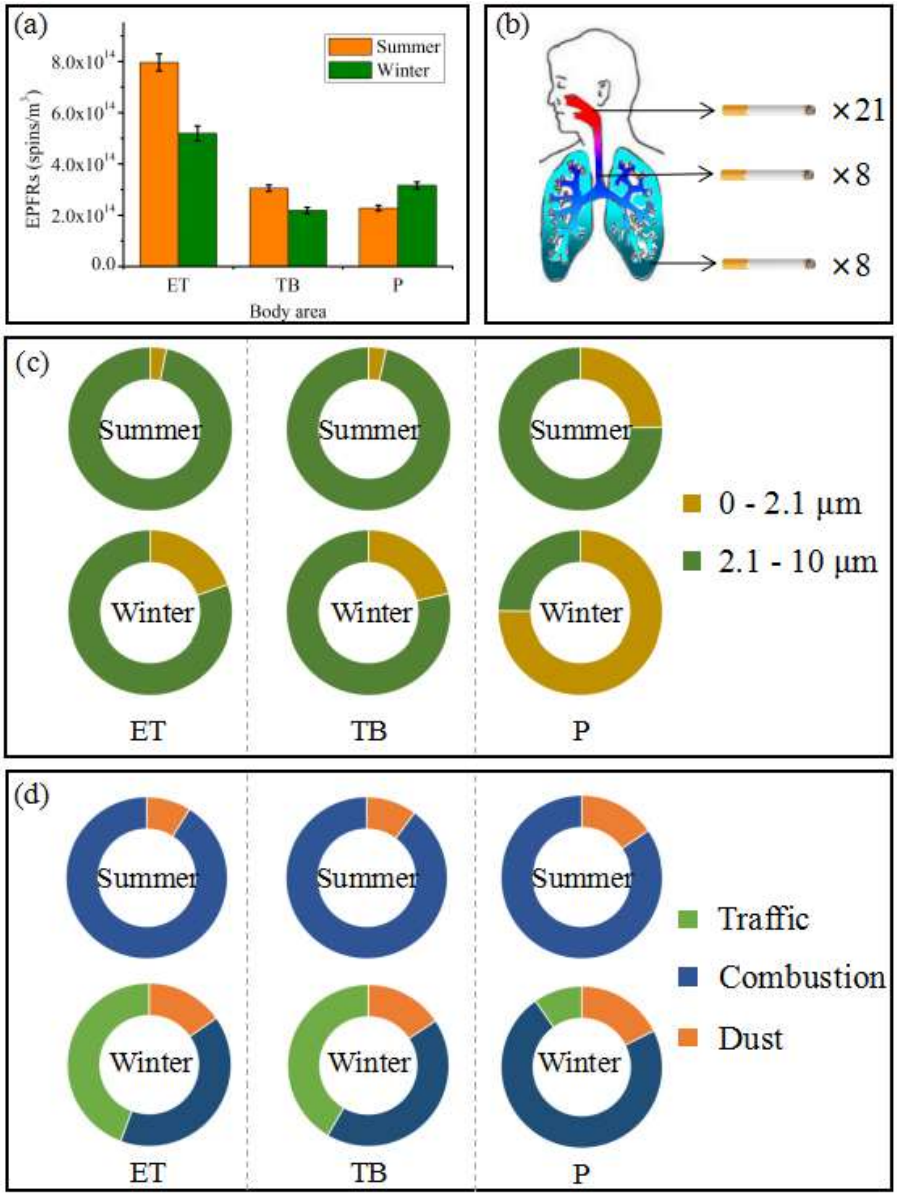


Figure 2. A *g*-factor comparison. (a) Comparison of *g*-factors of EPFRs in different particle sizes in different seasons. (b) Correlation analysis of *g*-factors and concentrations of EPFRs in summer and winter PM. The gray areas in the figure represent 95% confidence intervals.



639

640 Figure 3. Factor analysis of EPFRs in different particle sizes in different seasons. (a1) and (b1)
641 represent the results of factor analysis for summer and winter, respectively. (a2) and (b2) represent
642 the contribution of various factors in summer and winter, respectively, to EPFRs and the relative
643 contributions of each factor for different particle sizes.



644

645 Figure 4. Exposure risks to EPFRs. (a) EPFR exposure in the ET, TB, and P regions. (b) Cigarette
646 exposure to EPFRs in the human respiratory system. (c) Exposure ratio of EPFRs with different
647 particle sizes in different areas of the respiratory system. (d) Contribution of EPFRs from different
648 sources to different areas of the respiratory system.