JOURNAL OF ENVIRONMENTAL SCIENCES 135 (2024) 424–432

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JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Research Article

Environmentally persistent free radicals in $PM_{2.5}$ from a typical Chinese industrial city during COVID-19 lockdown: The unexpected contamination level variation

Lingyun Wang[1,2,**], *Wuduo Zhao*[1,2,**], *Peiru Luo*[1,2], *Qingyun He*[1,2], *Wenfen Zhang*[1,2], *Chuan Dong*[4], *Yanhao Zhang*[3,*]

[1] *College of Chemistry, Zhengzhou University, Zhengzhou 450001, China*
[2] *Center of Advanced Analysis and Gene Sequencing, Key Laboratory of Molecular Sensing and Harmful Substances Detection Technology, Zhengzhou University, Zhengzhou 450001, China*
[3] *State Key Laboratory of Environmental and Biological Analysis, Department of Chemistry, Hong Kong Baptist University, Hong Kong 999077, China*
[4] *Institute of Environmental Science, Shanxi University, Taiyuan 030006, China*

ARTICLE INFO

Article history:
Received 6 March 2022
Revised 11 August 2022
Accepted 17 August 2022
Available online 27 August 2022

Keywords:
$PM_{2.5}$
EPFRs
COVID-19
City lockdown
Health risks

ABSTRACT

The outbreak of COVID-19 has caused concerns globally. To reduce the rapid transmission of the virus, strict city lockdown measures were conducted in different regions. China is the country that takes the earliest home-based quarantine for people. Although normal industrial and social activities were suspended, the spread of virus was efficiently controlled. Simultaneously, another merit of the city lockdown measure was noticed, which is the improvement of the air quality. Contamination levels of multiple atmospheric pollutants were decreased. However, in this work, 24 and 14 air fine particulate matter ($PM_{2.5}$) samples were continuously collected before and during COVID-19 city lockdown in Linfen (a typical heavy industrial city in China), and intriguingly, the unreduced concentration was found for environmentally persistent free radicals (EPFRs) in $PM_{2.5}$ after normal life suspension. The primary non-stopped coal combustion source and secondary Cu-related atmospheric reaction may have impacts on this phenomenon. The cigarette-based assessment model also indicated possible exposure risks of $PM_{2.5}$-bound EPFRs during lockdown of Linfen. This study revealed not all the contaminants in the atmosphere had an apparent concentration decrease during city lockdown, suggesting the pollutants with complicated sources and formation mechanisms, like EPFRs in $PM_{2.5}$, still should not be ignored.

* Corresponding author.
E-mail: yhzhang_skl@hkbu.edu.hk (Y. Zhang).
** These authors contributed equally to this work.

https://doi.org/10.1016/j.jes.2022.08.024
1001-0742/

Introduction

In December 2019, the unknown pneumonia cases were reported in Wuhan, China (Li et al., 2020b). World Health Organization (WHO) named this new pneumonia as the Corona Virus Disease 2019 (COVID-19). In January 2020, COVID-19 has been confirmed that could be transmitted between human through multiple ways such as respiratory droplets and close contact (Liu et al., 2020). The high infectivity of COVID-19 made it become a worldwide pandemic. To control the rapid spread of the COVID-19, multiple countries issued strict nationwide quarantine measures, such as closing public areas and reducing transportations (Chen et al., 2020; Mahato et al., 2020; Piccinini et al., 2020). China is the country that takes the earliest actions (Chen et al., 2020). Wuhan is the first city in lockdown on 23 January 2020 (Lian et al., 2020). After that, almost all people in China began to take home-based quarantine in order to efficiently avoid the spread of COVID-19 (Wells et al., 2020). Fortunately, the strict lockdown measures have been proven could effectively alleviate the COVID-19 transmission (Lau et al., 2020). Simultaneously, different studies reported another benefit of the lockdown measures, which was the increase of the air quality (Chen et al., 2020; Lian et al., 2020; Wen et al., 2022). This phenomenon may be due to the suspension of the normal social, economic and industrial activities during city lockdown. The anthropogenic emissions were greatly suppressed. In Wuhan and Shanghai, compared with the pollution status before COVID-19 lockdown, the concentrations of multiple air pollutants, such as carbon oxide (CO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), had significant reductions (Chen et al., 2020; Lian et al., 2020). The decreases of contamination levels for CO and NO_2 were also found in Hangzhou and other Chinese regions during nationwide full lockdown (Wang et al., 2020a; Wang et al., 2021a). Therefore, most current research believed that the city lockdown could effectively reduce the contamination levels of the great majority of ambient pollutants (Briz-Redón et al., 2021; Chu et al et al., 2021). In fact, reduction of traffic and industrial emissions has been the routine control strategy of air pollution in China for a long time. The COVID-19 city lockdown provided an unexpected opportunity for checking the efficiency of national air pollution control policy.

However, due to the complicated meteorological conditions and various emission sources, such pollution reduction strategies did not always seem to be effective. The raised concentration of secondary atmospheric pollutant, like ozone (O_3), was found in different regions during COVID-19 lockdown (Wang et al., 2020a). In particular, the strict lockdown measures did not prevent the occurrence of severe haze fog induced by air fine particulate matter ($PM_{2.5}$) in multiple countries like China and USA. There were no significant changes, or even increases of $PM_{2.5}$ mass concentrations in megacities in North China Plain (e.g., Beijing, Tianjin, Shijiazhuang and Taiyuan) and Midwestern/Southern regions of USA (Wang et al., 2020b; Chen et al., 2021). Although people reported the concentrations of multiple conventional pollutants in $PM_{2.5}$, like water-soluble ions, metallic elements and polyaromatic hydrocarbons (PAHs), had declines during quarantine measures (Chen et al., 2020; Lian et al., 2020), rare works have focused on whether the emerging pollutants had similar concentration variations in atmosphere. Environmentally persistent free radicals (EPFRs) are a good example of the novel contaminants in $PM_{2.5}$ (Yang et al., 2017a). Unlike the conventional transient free radicals, EPFRs are stable in the atmosphere (Yang et al., 2017a; Liu et al., 2021b) and mainly generated through the primary emissions (e.g., coal combustion and waste incineration) (Pan et al., 2019) and reaction of different organic precursors (e.g., phenol and PAHs) and transition metals (e.g., Zn, Ni and Cu) (Pan et al., 2019). Semi-quinone radicals, cyclopentadiene radicals and phenoxy radicals are common types of EPFRs (Liu et al., 2021b). Inhalation and ingestion of $PM_{2.5}$-bound EPFRs are believed to induce significant cytotoxicity and DNA damage and subsequently cause possible human health concerns (Saravia et al., 2013). Consequently, it is of great significance to investigate the contamination variations of $PM_{2.5}$-bound EPFRs during strict COVID-19 city lockdown, thereby assessing the impacts of the Chinese routine air pollution control strategies on atmospheric contaminants with complicated formation mechanisms.

In this work, a continuous collection of the $PM_{2.5}$ samples was conducted before (21 November 2019 – 22 January 2020) and during (23 January 2020 – 12 February 2020) COVID-19 lockdown in Linfen, a representative heavy industrial city with about 4 million people in North China (Liu et al., 2021a). Coal-driven factory is the most important type of the local industries (Liu et al., 2021a; Li et al., 2020a). Linfen is always one of the cities with the most serious $PM_{2.5}$ pollution in China. The contamination levels and types of $PM_{2.5}$-bound EPFRs were investigated and compared before and during home-based quarantine measures in this city. With the decrease of pollution levels of most conventional components (e.g., PAHs and metallic elements), unreduced EPFRs' concentrations in $PM_{2.5}$ were observed during city lockdown. The primary unsuspended home heating-related coal burning, and secondary Cu-related atmospheric reaction may have effects on this phenomenon. It was also found that the contamination levels of EPFRs in $PM_{2.5}$ during city lockdown possibly posed health concerns if inhaled by local adults. This study revealed that the suspension of most social and industrial activities was not always effective for pollution level reduction of $PM_{2.5}$-bound contaminants. The urban air pollutants should not be ignored even though the city was locked.

1. Materials and methods

1.1. *Sampling of $PM_{2.5}$*

The sampling site is located in Linfen (36°25′N; 111°68′E), a typical coal-driven city in Shanxi Province, China. The continuous collection of $PM_{2.5}$ was conducted between 21 November 2019 and 12 February 2020. During the sampling period, Linfen prepared to take lockdown measures on 23 January 2020 in order to control the spread of COVID-19 virus. 24 and 14 $PM_{2.5}$ samples were collected before and during city lockdown for further analysis, respectively. Corresponding sampling dates could be seen in Appendix A Table S1. Whatman quartz fiber filters (90 mm diameter) and medium-volume air sampler

(ADS-2062E, AMAE Co., Ltd, China) were used for $PM_{2.5}$ sampling. The daily particle collection lasted for 23.5 hr with the sampler flowrate of 0.1 m^3/min. All the filters were wrapped with aluminum foil and stored at -80 °C immediately for further use.

1.2. Chemicals and materials

PAH standards, including 1-methylnaphthalene, 2-methylnaphthalene, anthracene, fluorene, phenanthrene, fluoranthene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene and indeo(1,2,3-cd)pyrene, were purchased from AccuStandard Inc. (USA). Phenanthrene-d_{10} (1000 mg/L in dichloromethane) was purchased from ANPEL Laboratory Technologies Inc. (Shanghai) as internal standard for PAHs' determination. Internal standard was added for quantification before instrumental analysis. Standard solutions of 14 PAHs with different concentrations (10, 25, 50, 100, 200, 500 and 1000 ng/mL) were prepared with dichloromethane to construct calibration curves. Stock standard solutions of Al, Fe, Cu, Zn, Ni at concentrations of 1000 mg/L were purchased from Guobiao (Beijing) Testing & Certification Co., Ltd. Standard solutions of five metallic elements with different concentrations (0.1, 0.5, 1, 2, 5 and 10 mg/L) were prepared with 2% nitric acid to construct calibration curves.

1.3. Chemical analysis

The EPFRs in $PM_{2.5}$ were immediately analyzed using electron paramagnetic resonance spectrometer (EPR) (EMXplus-9.5/12/P/L, BRUKER, Germany) after sample collection. Direct detection method was used to quantify EPFRs in $PM_{2.5}$. Briefly, 1/8 of the $PM_{2.5}$ sample filter was put into a quartz tube. Then, the quartz tube containing the sample filter was inserted into the highly sensitive resonant cavity for direct measurement of EPFRs in $PM_{2.5}$. The detailed EPR parameters were listed in Appendix A Table S2.

The same $PM_{2.5}$ filters were also applied to determine metallic elements and PAHs. Considering the possible formation mechanism of EPFRs (Pan et al., 2019), five elements (Al, Fe, Ni, Cu and Zn) were analyzed. To detect metallic elements, 1/4 of the $PM_{2.5}$ filter was put into the Teflon bomb with highly purified water (5 mL), nitric acid (2 mL) and hydrogen peroxide (2 mL). Then, they were microwave-digested. After that, Zn, Fe, Cu and Ni were quantified by atomic absorption spectrometer (AAS, EWAI, AA-7020), and Al was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9820, SHIMADZU, Japan). Ultrasonication extraction was used for determination of $PM_{2.5}$-bound PAHs (Zhang et al., 2020). 1/8 of the $PM_{2.5}$ sample filter was cut into strips and put into 150 mL beaker. Dichloromethane/acetone (1:1, v/v) was added for three-cycle extraction (30 mL/30 min, 20 mL/30 min and 20 mL/30 min). The extract was concentrated to 1 mL and spiked with internal standard (phenanthrene-d_{10}). The final solution was directly analyzed by gas chromatography-tandem mass spectrometry (GC-MS/MS) (GCMS-TQ8050 NX, SHIMADZU, Japan). The instrumental parameters of AAS, ICP-AES and GC-MS/MS could be seen in Appendix A Table S3–S5.

1.4. Health risk assessment model

To evaluate the potential health risks of EPFRs in $PM_{2.5}$ collected from Linfen, an equivalent amount of cigarettes was used to represent the daily EPFR exposure per person. The conversion from the inhaled $PM_{2.5}$-bound EPFRs by adults to the number of cigarettes per day (N_{cig}) was performed based on the following Eq. (1) (Chen et al., 2019):

$$N_{\mathrm{cig}} = (C_{\mathrm{EPFRs}} \cdot V)/\left(RC_{\mathrm{cig}} \cdot C_{\mathrm{tar}}\right) \tag{1}$$

where, C_{EPFRs} (spins/m^3) represents the atmospheric concentration of EPFRs in $PM_{2.5}$, V represents the amount of air an adult male breathes per day (20 m^3/day) (US EPA National Center for Environmental Assessment 1988), RC_{cig} (4.75×10^{16} spins/g) is the concentration of free radicals in cigarette tar (Baum et al., 2003; Blakley et al., 2001; Pryor et al., 1983a; Valavanidis and Haralambous, 2001), and C_{tar} (0.013 g/cig) represents the amount of tar per cigarette (Gehling and Dellinger, 2013). Additionally, a Monte Carlo analysis was used to assess the uncertainty for the estimation of exposure risks for adults (Feng et al., 2022). The detailed parameters were listed in Appendix A Table S6.

1.5. Statistical analysis

Spearman correlation analysis and Mann–Whitney test (U-test) were performed using IBM SPSS. The Spearman correlations between EPFRs and conventional atmospheric pollutants ($PM_{2.5}$, SO_2, NO_2, CO and O_3)/meteorological factors (temperature and humidity)/metals/PAHs were investigated. The U-test was applied to analysis of significant difference of various contaminants before and during COVID-19 city lockdown. The concentrations of conventional air pollutants were obtained from China National Environmental Monitoring Centre (CNEMC). To conduct Monte Carlo analysis, the non-parametric Kolmogorov–Smirnov (K–S) test ($P > 0.05$), which was performed by IBM SPSS, was needed to verify the statistical distributions of the data (Appendix A Table S6). The Monte Carlo analysis was conducted using the add-in of Oracle Crystal Ball 11.1.2.4.400 (Oracle, USA) in Microsoft Excel 2010 (Microsoft, USA).

2. Results and discussion

2.1. Unexpected variation tendency of contamination levels of $PM_{2.5}$-bound EPFRs during COVID-19 lockdown in Linfen, China

The COVID-19 pneumonia was firstly reported in December 2019 and became a global pandemic in 2020 (Li et al., 2020b). To control the rapid spread of the virus, strict lockdown measures were conducted at regional and national levels in multiple countries (Ethan et al., 2021). Fortunately, the suspension of the social and industrial activities did not only efficiently control the virus' transmission, but also increased the air quality in Chinese cities. In Linfen, during city lockdown, the concentrations of most primary pollutants in $PM_{2.5}$, including PAHs and some metals, had possible reductions (Appendix A

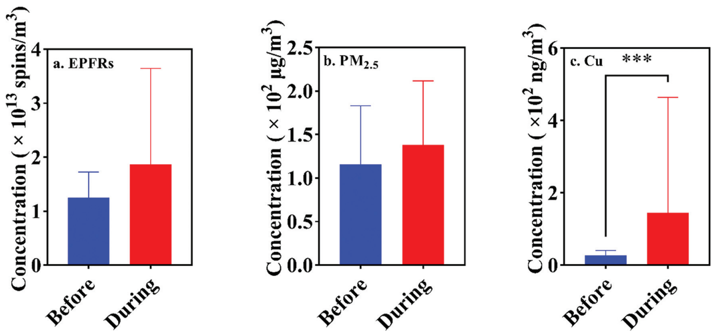

Fig. 1 – Average concentration variations of (a) EPFRs, (b) $PM_{2.5}$ and (c) particle-bound Cu before and during city lockdown in Linfen (U-test p-value: *** $p < 0.001$).

Fig. S1), which may be due to the significant decreases of coal combustion and traffic emissions (Wang et al., 2021b). However, surprisingly, the contamination levels of EPFRs in $PM_{2.5}$ did not have reductions during city lockdown (Fig. 1a). As shown in Appendix A Table S1 and Fig. 2, g-factor and the signal width (ΔHp-p), which revealed the types of EPFRs in $PM_{2.5}$ (Pan et al., 2019), were obtained. The g-factor of carbon-centered persistent free radicals was generally less than 2.003; oxygen-centered persistent radicals had corresponding value greater than 2.004; the g factor between 2.003 and 2.004 represented the carbon-centered radicals with adjacent oxygen atoms (Cruz et al., 2012). In this work, the relatively stable values of g-factor (before lockdown: 2.0042 – 2.0045; during lockdown: 2.0044 – 2.0046) and ΔHp-p (before lockdown: 4.0 G – 6.4 G; during lockdown: 4.7 G – 5.9 G) indicated the major class of EPFRs in $PM_{2.5}$ was oxygen-centered persistent radical during sampling period (Chen et al., 2019). The same type of persistent radicals was also detected in $PM_{2.5}$ in Xi'an and Nanjing (Chen et al., 2019; Guo et al., 2020). There was no obvious change of $PM_{2.5}$-bound EPFRs' type before and during city lockdown in Linfen. Yet, the contamination tendency of EPFRs in $PM_{2.5}$ was different from conventional pollutants that had possibly reduced concentrations (Fig. 1 and S1). The atmospheric concentrations of EPFRs in $PM_{2.5}$ before (21 November 2019 – 22 January 2020) and during (23 January 2020 – 12 February 2020) COVID-19 lockdown varied in the range of 6.5×10^{12} spin/m^3 – 2.7×10^{13} spin/m^3 (mean of 1.3×10^{13} spin/m^3) and of 6.2×10^{12} spin/m^3 – 5.2×10^{13} spin/m^3 (mean of 1.4×10^{13} spin/m^3), respectively (Table 1). The decrease of their concentrations was not observed. But the $PM_{2.5}$-bound EPFRs' average contamination level during city quarantine measures was greater than the corresponding mean value before lockdown (Fig. 1a). Compared to EPFRs, the concentrations of most detected pollutants in $PM_{2.5}$ became lower (Appendix A Fig. S1 and Appendix A Table S7). Although most changes were not significant, it was consistent with previous studies (Saadat et al., 2020; Lian et al., 2020). Hence, this unexpected phenomenon for $PM_{2.5}$-bound EPFRs attracted our attention and would be elaborated in the following section.

2.2. *Factors influencing the concentration of EPFRs in $PM_{2.5}$ during city lockdown*

As shown in Fig. 1a, the unexpected contamination variation revealed that the pollution levels of EPFRs in $PM_{2.5}$ did not decrease during the COVID-19 lockdown in Linfen. Previous study (Chen et al., 2020) and this work have shown that the contamination levels of $PM_{2.5}$-bound pollutants were generally reduced during the strict home-based quarantine measures. Therefore, it is necessary to investigate what led to this abnormal phenomenon. The sources and generation

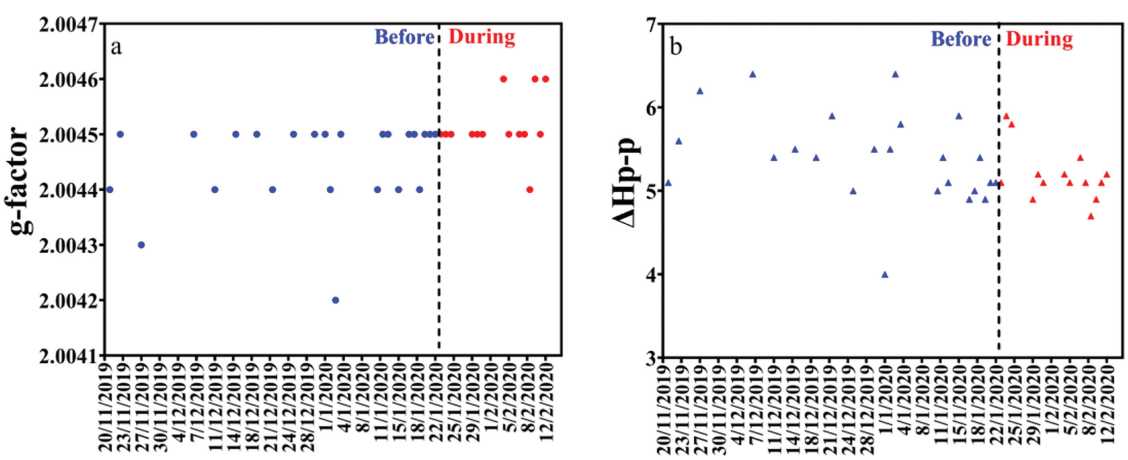

Fig. 2 – Variations of (a) g-factor and (b) ΔHp-p of $PM_{2.5}$-bound EPFRs before and during city lockdown in Linfen.

Table 1 – Pollution characteristics of EPFRs in $PM_{2.5}$ before and during city lockdown in Linfen.

	Before ($n = 24$)				During ($n = 14$)			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Concentration ($\times 10^{13}$ spins/m^3)	0.65	2.7	1.3	0.5	0.62	5.2	1.4	1.2
g-factor	2.0042	2.0045	2.0044	0.00008	2.0044	2.0046	2.0045	0.00005
$\Delta Hp\text{-}p$ (G)	4.0	6.4	5.4	0.54	4.7	5.9	5.2	0.32

mechanisms of EPFRs in different environmental matrices are complicated. According to previous works, the formation of atmospheric EPFRs is believed to be related to primary emissions (e.g., coal combustion and garbage incineration) (Pan et al., 2019) and secondary reactions between transition metals (e.g., Cu, Fe and Zn) and organic precursors containing benzene rings (e.g., PAHs) (Feld-Cook et al., 2017; Yang et al., 2017b). EPFRs formed by phenol on alumina were also found (Patterson et al., 2013). Intriguingly, the concentration levels of these reactants in urban $PM_{2.5}$ are all possibly affected by the industrial and social activities because most of them come from primary emissions (Bi et al., 2020; Zhang et al., 2019), thereby influencing the generation of the particle-bound EPFRs. Hence, investigating the contamination variations of the organic pollution markers and precursors is a possible efficient means to explain the effects of different sources on concentration tendency of EPFRs in $PM_{2.5}$ from Linfen (Zhang et al., 2021).

In this work, based on possible formation ways of EPFRs (Feld-Cook et al., 2017; Yang et al., 2017b), the atmospheric concentrations of 14 PAHs and 5 metallic elements (Cu, Al, Fe, Zn and Ni) in $PM_{2.5}$ from Linfen were determined (Appendix A Table S7). Different meteorological conditions (temperature and humidity) and the contamination levels of common pollutants in atmosphere ($PM_{2.5}$, SO_2, NO_2, CO and O_3) were also obtained from CNEMC (Appendix A Table S7). Spearman correlation analysis was conducted to discover the relationships between above contaminants and EPFRs in $PM_{2.5}$. It could be found that, before the city lockdown, except $PM_{2.5}$, the correlations were all insignificant (Table 2). Such phenomenon was possibly because the influences of general pollution sources were not obvious for contamination of EPFRs in $PM_{2.5}$ before the lockdown of Linfen. Moreover, since COVID-19 pandemic was a public health emergency in China, the sample size and collection time were limited, resulting in possible insignificant correlations. However, during city lockdown, with the stop of social and industrial activities, the effects of some sources, like primary coal combustion for home heating and secondary atmospheric formation, possibly became more critical for pollution of EPFRs in $PM_{2.5}$. Therefore, the significant correlations between EPFRs in $PM_{2.5}$ and multiple pollution markers (Cu, $PM_{2.5}$, SO_2 and NO_2) were observed (Table 2).

As shown in Table 2, no significant correlations were observed between PAHs and EPFRs in $PM_{2.5}$ during the whole sampling period. Meanwhile, concentrations of almost all PAHs were decreased during city lockdown in Linfen (Appendix A Fig. S1). As PAHs are possible organic precursors (Feld-Cook et al., 2017; Yang et al., 2017b), their concentration reduction is not beneficial for the generation of EPFRs in $PM_{2.5}$. Therefore, PAHs-related secondary formation may not significantly affect the contamination level of $PM_{2.5}$-bound EPFRs during COVID-19 lockdown of Linfen. The contamination variations of two determined metals (Fe and Zn) were similar to the PAHs (Appendix A Table S7 and Appendix A Fig. S1). However, the concentration of Cu in $PM_{2.5}$ became significantly ($p < 0.001$) higher during the city lockdown. Before the suspension of normal life, steel-related smelting, vehicle exhaust and coal burning were possible sources of Cu in $PM_{2.5}$ (Hieu and Lee, 2010; Duan et al., 2014; Liu et al., 2017; Wang et al., 2021c). During city lockdown, although the industrial and traffic emission were greatly reduced, coal combustion was still needed for home heating in Linfen (Li et al., 2020a, 2020b, 2020c).

Table 2 – Spearman correlation coefficients between EPFRs and relevant compositions in $PM_{2.5}$, common atmospheric pollutants and meteorological conditions before and during COVID-19 lockdown in Linfen.

	EPFRs (Before lockdown)	EPFRs (During lockdown)
Metallic elements		
Al	0.087	0.1
Cu	0.36	**0.56***
Fe	0.1	0.25
Zn	-0.2	0.43
Ni	-0.12	-0.2
PAHs		
2-Methylnaphthalene	-0.061	0.40
1-Methylnaphthalene	-0.086	0.49
Fluorene	-0.22	0.46
Phenanthrene	-0.11	0.21
Anthracene	-0.011	0.21
Fluoranthene	-0.090	0.40
Benz(a)anthracene	0.052	0.51
Chrysene	-0.004	0.49
Benzo(b)fluoranthene	-0.015	0.49
Benzo(k)fluoranthene	0.015	0.48
Benz(a)pyrene	0.044	0.46
Indeno(1,2,3-cd)pyrene	-0.030	0.57
Dibenz(a,h)anthracene	-0.023	0.49
Benzo(g,h,i)perylene	0.016	0.50
Atmospheric pollutants		
$PM_{2.5}$	-0.43*	**0.56***
SO_2	-0.18	**0.78****
NO_2	-0.16	**0.6***
CO	-0.23	0.44
O_3	-0.06	-0.11
Meteorological conditions		
Temperature	0.19	-0.29
Humidity	-0.33	0.19

* $p < 0.05$;
** $p < 0.01$.

Consequently, the ambient contamination of $PM_{2.5}$-bound Cu may become more serious. Furthermore, during home-based quarantine measures in Linfen, positive correlation (coefficient = 0.56, $p < 0.05$) was observed between EPFRs and Cu in $PM_{2.5}$ (Table 2). Previous work has illustrated that Cu possibly participates in the formation of EPFRs in $PM_{2.5}$ (Feld-Cook et al., 2017). The existence of oxide of Cu was proven to be beneficial for the EPFR generation (Yang et al., 2017b). Intriguingly, the results of computational simulation elucidated Cu could mediate the formation of oxygen-centered EPFRs (Ahmed et al., 2020), which may explain the occurrence of the same type of EPFRs in this work. Hence, the higher concentration of Cu might promote the Cu-mediated secondary formation of EPFRs in $PM_{2.5}$, resulting in their unreduced contamination level during city lockdown in Linfen.

In addition to PAHs and metallic elements, the relationships between common atmospheric pollutants/meteorological factors and $PM_{2.5}$-bound EPFRs were also investigated. Significant positive correlations were obtained for $PM_{2.5}$ (coefficient = 0.56, $p < 0.05$), SO_2 (coefficient = 0.78, $p < 0.01$) and NO_2 (coefficient = 0.6, $p < 0.05$) during city lockdown (Table 2). Relevant studies suggested that positive correlations between EPFRs and SO_2/NO_2 indicated the primary fossil fuel combustion had contributions to the atmospheric EPFRs (Chen et al., 2019; Guo et al., 2020). Meanwhile, as shown in Fig. 1 and Table 2, besides the significant correlation, the average mass concentration $PM_{2.5}$ was higher during suspension of normal life in Linfen. This phenomenon was also observed in China and USA (Yang et al., 2022; Chen et al., 2021), and theoretically, higher concentrations of $PM_{2.5}$ are favorable for the generation and adsorption of EPFRs. Considering the specific winter human activities in Linfen and stop of traffic and industries, the significant relationships between $PM_{2.5}/SO_2/NO_2$ and EPFRs in $PM_{2.5}$ were possibly due to the non-stopped coal combustion related home heating (Li et al., 2020c). Hence, primary coal burning for home heating might affect the concentration change of $PM_{2.5}$-bound EPFRs during lockdown of Linfen. Moreover, there was no significant correlations between $PM_{2.5}$-bound EPFRs and different meteorological conditions including temperatures and humidities (Table 2 and Appendix A Fig. S2). Although previous work suggested meteorological factors may influence EPFR evolution (Xu et al., 2020; Yang et al., 2020), our results indicated their impacts were not obvious during the sampling period.

2.3. *Exposure risk of $PM_{2.5}$-bound EPFRs during COVID-19 lockdown in Linfen*

The toxicity of EPFRs has been comprehensively studied for long time. It has been proven that EPFRs is cytotoxic to human bronchial epithelial cells (Balakrishna et al., 2009) and can cause heart and lung diseases in newborn rats (Balakrishna et al., 2011). Particles containing EPFRs have adverse effects on infants' respiratory health (Saravia et al., 2013). In addition, EPFRs in biochar are also toxic to plants, such as inhibiting germination, delaying root cap growth and plasma membrane damage (Liao et al., 2014). To compare the potential health risks of the EPFRs in $PM_{2.5}$ before and during the lockdown of the city, the amount of cigarettes was used to represent the daily EPFR exposure for people (Chen et al., 2019; Pryor et al., 1983a; Pryor et al., 1983b). As listed in Section 1.4, the intuitional assessment method was established. The results showed that the daily EPFRs' exposure amount before and during the city lockdown were 0.2–0.9 cigarettes and 0.2–1.7 cigarettes, respectively, for adults. The daily average number of cigarettes before and during the lockdown of the city was 1.25 and 1.44. To further quantify the uncertainties of exposure risks assessment, a Monte Carlo simulation was performed as described in Section 1.4. The cumulative probability distributions of the number of equivalent cigarettes before and during city lockdown *via* inhaling $PM_{2.5}$-bound EPFRs were shown in Appendix A Fig. S3. For adults, the probability of the N_{cig} to exceed the 1 cigarette per day was 62.22% before city lockdown, and 56.29% during city lockdown. Consequently, the COVID-19 lockdown measures in Linfen did not cause an obvious reduction of the exposure risks of EPFRs in $PM_{2.5}$. As shown in Table 3, the pollution levels and relevant exposure risks of EPFRs in $PM_{2.5}$ from Linfen were also compared to the corresponding values in other regions and country. The concentrations and exposure risks (N_{cig}) of $PM_{2.5}$-bound EPFRs in Nanjing, Wanzhou and Linfen (before and during city lockdown) in China were similar, and higher than corresponding values in Baton Rouge, Louisiana in USA (Table 3). However, they were lower than the contamination levels of EPFRs in $PM_{2.5}$ from Xi'an (N_{cig} = 1.4 – 22.5) and Beijing (2016: N_{cig} = 32 – 453; 2019: N_{cig} = 0.05 – 73) (Table 3). Since in past years severe haze fog often occurred in the Northern Chinese cities (Wang et al., 2020b), frequent $PM_{2.5}$ exposure may lead to the higher inhalation risks of particle-bound EPFRs in Xi'an and Beijing than in Linfen. Furthermore, recently, great ef-

Table 3 – Atmospheric concentrations (spins/m^3) and N_{cig}-based health risks of EPFRs in different regions.

Site	Min	Max	Mean	N_{cig}	Reference
Linfen, China (before lockdown)	6.5×10^{12}	2.7×10^{13}	1.3×10^{13}	0.2 – 0.9	This work
Linfen, China (during lockdown)	6.2×10^{12}	5.2×10^{13}	1.4×10^{13}	0.2 – 1.7	This work
Xi'an, China (2017)	4.44×10^{13}	6.95×10^{14}	1.35×10^{14}	1.4 – 22.5	Chen et al., 2019
Beijing, China (2016)	1.0×10^{15}	1.4×10^{16}	-	32 – 453	Yang et al., 2017a
Beijing, China (2019)	4.79×10^{14}	7.42×10^{17}	-	0.05 – 73	Xu et al., 2020
Nanjing, China (2019)	2.78×10^{12}	1.72×10^{13}	7.61×10^{12}	0.1 – 0.6	Guo et al., 2020
Wanzhou, China (2017)	5.3×10^{13}	8.7×10^{13}	7.0×10^{13}	1.7 – 2.8	Qian et al., 2020
Baton Rouge, Louisiana, USA, (2008)	2.46×10^{16} (spins/g)	2.79×10^{17} (spins/g)	-	0.3 – 0.9	Gehling and Dellinger, 2013

forts were conducted to control the serious $PM_{2.5}$ pollution in China (Liu et al., 2021a; Li et al., 2020a). Multiple policies of industrial transformation and prevention regulations of the coal-burning pollution were instituted in the cities that regards coal-related industries as their economical backbone, like Linfen (Liu et al., 2021a; Li et al., 2020a). Consequently, the contamination levels of $PM_{2.5}$ and particle-bound EPFRs may have some reductions in Linfen. However, as shown in Table 3, the concentrations of $PM_{2.5}$-bound EPFRs in Linfen during city lockdown were still higher than in some other city. With the unreduced atmospheric concentrations during suspension of normal industrial and social activities, the accumulative health effects of long-term exposure of EPFRs in $PM_{2.5}$ also should not be ignored in Linfen.

3. Conclusions

In the present study, the contamination status of $PM_{2.5}$–bound EPFRs was investigated in Linfen, a typical coal-driven industrial city in China, before and during COVID-19 lockdown. During city lockdown, compared to the common particle-bound pollutants with reduced concentrations, like PAHs, the contamination levels of EPFRs in $PM_{2.5}$ did not decrease. Based on the reported generation ways of EPFRs, the primary non-stopped coal combustion source and secondary Cu-related atmospheric generation might be associated with the unusual phenomenon. Additionally, the consumed cigarettes-based exposure risks revealed the possible health concerns of EPFRs in $PM_{2.5}$ from Linfen during COVID-19 lockdown. Compared to other relevant literatures, this work proved that not all contaminants in $PM_{2.5}$ had obviously decreased pollution levels during city lockdown induced by COVID-19 pandemic in China. Even though the normal social and industrial activities were suspended and the air quality generally became better, the pollutants, like EPFRs, with complex emission and formation mechanisms in the atmospheric particles still should not be ignored.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Nos. 22106129, 22076174 and 91843301).

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.08.024.

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