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Potential health risks of inhaled toxic elements and risk sources during different COVID-19 lockdown stages in Linfen, China

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Abstract

Levels of toxic elements in ambient PM$_{2.5}$ were measured from 29 October 2019 to 30 March 2020 in Linfen, China, to assess the health risks they posed and to identify critical risk sources during different periods of the COVID-19 lockdown and haze episodes using positive matrix factorization (PMF) and a health-risk assessment model. The mean PM$_{2.5}$ concentration during the study period was 145 μg/m$^3$, and the 10 investigated toxic elements accounted for 0.31% of the PM$_{2.5}$ mass. The total non-cancer risk (HI) and total cancer risk (TCR) of the selected toxic elements exceeded the US EPA limits for children and adults. The HI for children was 2.3 times that for adults for all periods, which is likely due to the high inhalation rate per unit body weight for children. While the TCR for adults was 1.7 times that of children, which is mainly attributed to potential longer exposure duration for adults. The HI and TCR of the toxic elements during full lockdown were reduced by 66% and 58%, respectively, compared to their pre-lockdown levels. The HI and TCR were primarily attributable to Mn and As, respectively. Health risks during haze episodes were significantly higher than the average levels during COVID-19 lockdowns, though the HI and TCR of the selected toxic elements during full-lockdown haze episodes were 68% and 17% lower, respectively, than were the levels during pre-lockdown haze episodes. During the study period, fugitive dust and steel-related smelting were the highest contributors to HI and TCR, respectively, and decreased in these emission sources contributed the most to the lower health risks observed during the full lockdown. There, the control of these sources is critical to effectively reduce public health risks.

1. Introduction

Ambient fine particulate matter (PM$_{2.5}$, particles with an aerodynamic diameter ≤ 2.5 μm) is an environmental health risk factor. Toxic elements, such as As, Mn, Cr, Zn, etc., in ambient PM$_{2.5}$ are able to induce adverse health effects owing to their bioavailability and bioaccumulation (Chen and Lippmann, 2009; Gerlofs-Nijland et al., 2009; Zheng et al., 2016). Epidemiological studies found that the most toxic elements can play important roles in nerve damage (Shen et al., 1996; Utsunomiya et al., 2004; Wang and Zhang, 2006), cardiopulmonary inflammation (Joseph et al., 2015; Mukhtar and Limbeck, 2013), and respiratory infections (Bollati et al., 2010; Ghio et al., 1999), and the health risks of toxic elements in ambient PM$_{2.5}$ (Betha et al., 2014; Feng et al., 2016; Li et al., 2016; Lin et al., 2016) and critical risk sources (Huang et al., 2018; Lin et al., 2020; Sun et al., 2021) have been widely studied.

The health risks posed by toxic elements in ambient PM$_{2.5}$ can increase remarkably during haze episodes compared to the risks on non-haze days (Li et al., 2017; Liang et al., 2019; Singh and Gupta, 2016). Previous research has shown that the non-cancer risks of toxic elements are higher for children than adults during haze episodes, while cancer risks are in the opposite case (Cao et al., 2018; Lyu et al., 2017; Sulong et al., 2017). Quantifying the health risks of toxic elements emitted at particular sources and identifying critical risk sources can support
effective controls to promote public health (Liu et al., 2021), especially for haze episodes. Huang et al. (2018), Lin et al. (2020), and Xie et al. (2020) conducted the source-specific health risk analysis during haze episodes by combining the quantification of element-specific health risks and source apportionment and found that coal combustion and traffic-related emissions were the pivotal health risk sources. However, relatively few studies have adopted this approach.

In early 2020, China experienced a mass outbreak of a novel coronavirus disease (COVID-19) (Huang et al., 2020; Kang et al., 2020; Zhou et al., 2020). To curb the spread of the epidemic, the Chinese government implemented strict lockdown measures including quarantines, transportation shutdowns, and businesses suspension across the whole country (Tu et al., 2020), leading to a sharp decline in pollutant emissions nationwide (Wang et al., 2021; Zheng et al., 2020). It was reported that source emissions changed dramatically during the lockdown periods (Dai et al., 2020). However, it remains unclear whether the health risk of ambient toxic elements during the lockdown period declined and the source-specific health risks induced by toxic elements changed as well. Control measures aim at reducing health risk rather than the total PM masses are therefore crucial to formulate instructive measures to further protect the public health.

Linfen is located in Shanxi Province and represents one of the most polluted cities in China (Bai et al., 2021; Li et al., 2020a). A prior study in Linfen suggested that coal combustion and traffic emissions were the dominant sources of non-cancer risk and cancer risk, respectively, during haze episodes (Lin et al., 2020). After the outbreak of COVID-19, the Linfen government launched its highest level of lockdown measures since 26 January 2020 (http://www.shanxi.gov.cn/yw/sxyw/202001/20200125_762173.shtml) until 10 February 2020 when the economy and production resumed (http://nyj.linfen.gov.cn/contents/2019/496547.html), which resulted in substantial changes in emission activities. The ambient toxic element concentrations and their health risks varied with the changes in emission activities. This provided an opportunity to investigate the critical control sources that can effectively reduce the health risks of ambient toxic elements. Therefore, this study placed specific focus on the critical toxic elements for health risks and main risk sources in this highly polluted city during different lockdown stages, and further identified the critical sources to target with control measures from the perspective of effectively reducing health risks from ambient toxic elements. The results are expected to help in the development of effective strategies to mitigate toxic emissions and reduce public health risks.

2. Materials and methods

2.1. Study site

Linfen sits within the basin of Shanxi Province in northern China (Fig. S1a), an area that is not conducive to atmospheric diffusion. The region has a semi-humid monsoon climate, and southerly winds prevailed during the study period (Fig. 1c). Linfen’s urban area spans 20302 km² with a population of approximately 4.5 million and 665 thousand vehicles in 2018. Linfen contains several steel and coking enterprises, and industrial coal consumption reached more than 38.1 million tons in 2018. In this study, ambient PM$_{2.5}$ were sampled simultaneously at four sites (Fig. S1b), including the Linfen City Committee building, Lingang Hospital, the Hongtong Branch of Linfen Ecological Environment Bureau, and the Xiangfen Branch of Linfen Ecological Environment Bureau. Table S1 lists additional details of the areas around the sampling sites. All sampling sites were within 10 m of the China National Air Quality Monitoring Stations where the meteorological parameters were collected. The time series of meteorological parameters measured during the study are shown in Fig. 1c and d.
2.2. Sampling and chemical analysis

2.2.1. Sampling

Ambient PM$_{2.5}$ was sampled synchronously from 29 October 2019 to 30 March 2020 using two medium volume samplers (100 L/min, LY-2030, Qingdao Laoying Co., China) with separately loaded quartz (90 mm-diameter; Pall, USA) filter and polypropylene filter (90 mm-diameter; Tianjin Xinyao Trading Co., LTD, China). Samples were collected for 23 h from 10:00 to 09:00 on the next day. All sampling sites were on building rooftops approximately 10–15 m above the ground level. Field blanks and parallel samples were simultaneously collected at each site for quality assurance and quality control (QA/QC). Prior to sampling, quartz filters were baked in a muffle furnace at 500 °C, and polypropylene filters were baked in a stove at 60 °C. All filters were stored in a refrigerator at 4 °C for subsequent analyses after sampling.

2.2.2. Gravimetric and chemical analysis

Before the gravimetric analysis, filter equilibration was conducted for 48 h under a constant temperature (20 ± 1 °C) and humidity (45–55%). A microbalance with a 10 µg resolution (XPE105, Mettler Toledo, Switzerland) was employed for the gravimetric analysis. To ensure accuracy, static was eliminated before measurement, and all filters were weighed at least twice until the differences were less than 50 µg.

For the chemical analysis, polypropylene filters were used for element determination, and quartz filters were used to analyze the water-soluble inorganic ions and carbon species. The elements (Fe, Al, Si, Ti, K, Ca, Mg, Na, Co, As, Cd, Cr, Ni, Pb, Zn, Mn, Cu, and V) were identified via inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo ICAP 7000, Thermo Fisher Scientific, USA). Water-soluble inorganic ions (NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, and Cl$^-$) were analyzed using ion chromatography (Thermo ICS900, Thermo Fisher Scientific, USA). Organic carbon (OC) and elemental carbon (EC) were measured using a thermal/optical carbon analyzer (DRI Model 2001A, Desert Research Institute, USA) according to the IMPROVE_A thermal/optical reflectance (TOR) protocol. Further analysis procedures and QA/QC measures are described in the Supplementary Materials.

2.3. Analysis methods

2.3.1. Health risk (HR) model

The HR model was applied to assess the health risks associated with selected toxic elements in ambient PM$_{2.5}$ based on US EPA standards. People are exposed to health risks from toxic elements via three pathways: ingestion, inhalation, and dermal contact. Building on previous reports (Agarwal et al., 2017; Huang et al., 2018; Li et al., 2017; Lin et al., 2020; Sulong et al., 2017), this study mainly considered the health risks of the selected toxic elements through inhalation exposure. Children and adults were considered separately owing to their different sensitivities to toxicity. Ten elements (Co, As, Cd, Cr, Ni, Pb, Zn, Mn, Cu, and V) were investigated as toxic elements in this study in terms of Integrated Risk Information System (IRIS) of US EPA (USEPA, 2019). The concentration of Cr(VI) considered within the assessment was calculated as one-seventh of the total chromium concentration (Heu and Lee, 2010; Park et al., 2008). Co, As, Cd, Cr(VI), and Ni are ranked as carcinogens or possible carcinogens by the International Agency for Research on Cancer (IARC) (IARC, 2021).

The exposure dose was calculated as follows:

\[ \text{ADD}_j (\text{LADD}_j) = C_j \cdot \frac{\text{InhR} \cdot \text{EF} \cdot \text{ED}}{\text{BW} \cdot \text{AT}} \]

where $C_j$ represents the average daily dose for the $j$th non-carcinogen and LADD$\_j$ represents the average daily dose for the $j$th carcinogen (mg/(kg-day)); InhR represents the concentration of the $j$th toxic element in PM$_{2.5}$ (mg/m$^3$); EF represents the exposure frequency (day/y); ED is the exposure duration (y); BW is body weight (kg); and AT is the average time (day). The values of InhR, EF, ED, BW, and AT for children and adults are listed in Table S2.

Health risks were calculated as follows. The non-cancer risk was defined as:

\[ \text{HI} = \sum \text{HQ}_j \quad \text{with} \quad \text{CR}_j = \frac{\text{LADD}_j}{S_f} \]

where HQ$\_j$ is the hazard quotients of the $j$th element (unitless); RfD$\_j$ is the reference dose of the $j$th element (mg/(kg-day)); HI is the hazard index (unitless); CR$\_j$ refers to the cancer risk of the $j$th element (unitless); S$\_f$ represents the slope factor of the $j$th element (kg-day/mg); and TCR is the total cancer risk (unitless). The values of RfD$\_j$ and S$\_f$ are listed in Table S3.

For non-cancer risk, an HQ value of 1 is regarded as the criterion limit according to the US EPA (2009), i.e., HQ < 1 is acceptable, and HQ > 1 is unacceptable. For cancer risk, a CR value of 10$^{-6}$ serves as the threshold criterion (Betha et al., 2014), i.e., CR < 10$^{-6}$ is acceptable, and CR > 10$^{-6}$ is unacceptable. The larger the values of HQ and CR, the higher the respective non-cancer and cancer risks.

2.3.2. PMF model

The positive matrix factorization (PMF) is an effective approach to identify source categories and estimate their contributions. Its principle is the decomposition of sample composition dataset (X) into two matrices: source profiles (F) and source contributions (G) (Paatero and Tapper, 1994). It can be described as:

\[ x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \]

where $x_{ij}$ is the concentration of the $j$th species in the $i$th sample (µg/m$^3$); $g_{ik}$ represents the contribution of the $k$th source to the $i$th sample (µg/m$^3$); $f_{kj}$ is the source profile of the $j$th species from the $k$th source (µg/µg); $e_{ij}$ is the residual of the $j$th species in the $i$th sample; and $p$ is the number of sources.

The objective function $Q$ was estimated during the PMF analysis, which can be allowed to review the distribution of each species to evaluate the stability of solution. It can be expressed as follows.

\[ Q = \frac{\sum_{i=1}^{n} \sum_{j=1}^{m} \left[ x_{ij} - \frac{\sum_{k=1}^{p} g_{ik} f_{kj}}{\mu_k} \right]^2}{\mu_k} \]

where $\mu_k$ represents the uncertainty of the $j$th species in the $i$th sample. The optimal result of PMF is to minimize the value of $Q$. In our work, the missing values were replaced by median concentration of a given species with an uncertainty of four times of the median. Data below minimum detection limit (MDL) was replaced by half of the MDL with uncertainty set by 5/6 MDL. While for data above MDL, its corresponding uncertainty was calculated by equation (8). The MDLs of resolved species are shown in Table S4. More details about PMF analysis and the data treatment are described in Supplementary Materials.

2.3.3. PMF-HR model

In this study, according to the studies from Diao et al. (2021), Huang et al. (2018), Lin et al. (2020), Sun et al. (2021), and Tian et al. (2021),...
the PMF and HR models were combined to assess the health risks associated with different emission sources through the following three steps:

**Step one:** The source contributions to selected toxic elements levels are determined based on the PMF results as follows:

\[ C_j^k = g_j^i f_i^k \]  

(9)

where \( C_j^k \) is the concentration of the jth element from the kth source in the ith sample (μg/m³); \( g_j^i \) denotes the contribution of the kth source to the jth element in the ith sample (μg/m³); and \( f_i^k \) represents the mass fraction of the jth element for the kth source.

**Step two:** The exposure doses of the selected toxic elements attributable to each source are calculated as follows:

\[ ADD_j^k (LADD_j^k) = C_j^k \frac{InhR \cdot EF \cdot ED}{BW \cdot AT} \]  

(10)

where \( ADD_j^k \) is the average daily dose of the jth non-carcinogen from the kth source in the ith sample (mg/(kg·day)); \( LADD_j^k \) is the average daily dose of the jth carcinogen from the kth source in the ith sample (mg/(kg·day)); and \( C_j^k \) is the concentration of the jth toxic element from the kth source in the ith sample (mg/m³). The definitions and values of \( InhR, EF, ED, BW, \) and \( AT \) are the same as those in Eq. (1).

**Step three:** The health risks associated with each source are assessed as follows:

\[ HQ_j^k = \frac{ADD_j^k}{RfD_j} \]  

(11)

\[ HI_j^k = \sum HQ_j^k \]  

(12)

\[ CR_j^k = LADD_j^k \cdot SF_j \]  

(13)

\[ TCR_j^k = \sum CR_j^k \]  

(14)

where \( HQ_j^k \) is the hazard quotient of the jth element from the kth source in the ith sample (unitless); \( RfD_j \) represents the reference dose of the jth element (mg/(kg·day)); \( HI_j^k \) is the hazard index from the kth source in the ith sample (unitless); \( CR_j^k \) is the cancer risk of the jth element from the kth source in the ith sample (unitless); \( SF_j \) represents the slope factor of the jth element (kg·day/mg); and \( TCR_j^k \) is the total cancer risk from the kth source in the ith sample (unitless).

3. Results and discussion

3.1. Health risks during different periods of the COVID-19 lockdown

The time series of concentrations and proportions of the selected toxic elements in PM$_{2.5}$ during the study period are shown in Fig. 1a and b. The mean concentration of ambient PM$_{2.5}$ during the study period was 145 μg/m³, and the 10 selected toxic elements accounted for 0.31% of the PM$_{2.5}$ mass. The concentration and proportion of Zn (0.19 μg/m³, 0.13%) were significantly higher than those of other toxic elements during the study period (Mann-Whitney test, \( p < 0.05 \)), while those of Cd and Co were the lowest (Table S5). Zhang et al. (2016) and Cao et al. (2018) reported that Zn was the most abundant toxic element in PM$_{2.5}$. Further, compared with other toxic elements, the concentrations of Cr and As were clearly higher than the levels set by the national ambient air quality standard of China (0.025 ng/m³ for Cr(VI) and 6 ng/m³ for As). The correlation between Pb and Cd was significant (\( r^2 = 0.59 \)) during the study period, likely suggesting their high homology since they were good tracers for non-ferrous smelting (Fischer et al., 2003). In addition, a high correlation between Mn and Cu was also observed (\( r^2 = 0.56 \)), which implied that they probably originated from similar source like iron and steel smelting and refining (Tsai et al., 2020; Zong et al., 2016). There was significant correlation between Mn and V (\( r^2 = 0.56 \)), probably indicating that their sources such as fugitive dust and transport mechanisms were related (Lin et al., 2020). However, the correlations between other toxic elements were relatively poor during the study period (Table S6). Based on a report by Rahman et al. (2021) and the control measures implemented in Linfen, the COVID-19 lockdown period was divided into three sections: pre-lockdown (from 29 October 2019 to 25 January 2020), full lockdown (from 26 January to 9 February 2020), and partial lockdown (i.e. the resumption of work) (from 10 February to 30 March 2020) (Table S7). The concentrations of most of selected toxic elements were lowest during the full lockdown period. Compared with their pre-lockdown levels, the concentrations of Cu, V, Cr, and Mn decreased by 97%, 75%, 72%, and 71%, respectively. After partial lockdown, the concentrations of Cu, As, and V increased by 13.5, 12.5, and 8.1 times, respectively.

The exposure doses and health risks of the selected toxic elements during different periods of the lockdown are shown in Tables S8-S11 and Fig. 2. The total non-cancer risks (HIs) of the selected toxic elements for children and adults were 3.17 and 1.36, respectively, which exceeded the US EPA limit of 1.00. The HIs were here higher than those in Nanjing (Li et al., 2017; Wu et al., 2019), Xinxing (Feng et al., 2016), Huzhou (Peng et al., 2017), Mumbai (Botle et al., 2020), Abuja (Subaymon et al., 2020), and Warsaw (Juda-Rezler et al., 2021). The HI for children was 2.3 times that for adults during the study period, indicating that children were a high non-cancer risk group, which is in accordance with other reports (Botle et al., 2020; Chen et al., 2015; Yang et al., 2013). The high non-cancer risk for children was associated with high inhalation rate per unit body weight (USEPA, 2009). The HI for children exceeded the US EPA limit during the different periods, while that for adults exceeded the limit pre-lockdown and during the partial lockdown. The HQ of Mn was the highest among all selected toxic elements during the different periods, exceeding the US EPA limit of 1.00 pre-lockdown and during the partial lockdown. These findings suggest Mn is a key element constituting non-cancer risk, which was also concluded by Agarwal et al. (2017). Compared with their levels pre-lockdown, the total non-cancer risks (HIs) of the toxic elements for both children and adults were reduced by 66% during the full lockdown. The HQs of Cu, V, and Cr(VI) decreased the most, achieving reductions of 97%, 75%, and 72%, respectively, while that of Co increased by 42%. During the partial lockdown, the total non-cancer risks (HIs) of the selected toxic elements for both children and adults increased by 2.5 times, with the greatest HQ increases for Cu, As, and V, which increased by 13.5, 12.5, and 8.1 times, respectively. Moreover, the HQs of As, V, Mn, and Ni during the partial lockdown exceeded those pre-lockdown.

The total cancer risks (TCRs) of the selected toxic elements during the study period for children and adults were 4.94 × 10$^{-5}$ and 8.47 × 10$^{-5}$, respectively. These levels significantly exceeded the US EPA limit of 1.00 × 10$^{-5}$, which conforms to the results of previous risk evaluations of major cities in China (Li et al., 2020b), Iasi in Romania (Galan-Negru et al., 2019), Chennai in India (Peter et al., 2018), and Nicosia in Cyprus (Jakovides et al., 2021). The TCR for adults was 1.7 times that for children during the different periods, suggesting that adults were a high cancer-risk group. This was related to the fact that the potential exposure duration for adults was much longer than that of children (USEPA, 1991). The TCRs for both children and adults were beyond the criterion limit during all periods. The cancer risk (CR) of As was the highest among the selected toxic elements during the different periods, indicating that As was the key element constituting cancer risks, and similar results were reported by Sun et al. (2014) and Tsai et al. (2020). Compared with their pre-lockdown levels, the TCRs for both children and adults during full lockdown were reduced by 58%; the CRs of Cr (VI) and As markedly decreased by 72% and 62% (Mann-Whitney test, \( p < 0.05 \)), and similar results were reported by Sun et al. (2014) and Tsai et al. (2020).
Fig. 2. The non-cancer risk (HQ), total non-cancer risk (HI), cancer risk (CR), and total cancer risk (TCR) of the selected toxic elements during the study period and different lockdown periods. (a) non-cancer risks for children; (b) non-cancer risks for adults; (c) cancer risks for children; and (d) cancer risks for adults.

Fig. 3. Inhaled health risks of the selected toxic elements during the whole haze episodes (HEs) and the HEs occurred during different lockdown periods. (a) non-cancer risks for children; (b) non-cancer risks for adults; (c) cancer risks for children; and (d) cancer risks for adults.
partial lockdown, the TCRs of the selected toxic elements for both children and adults increased by 10.1 times, and the CR of As increased the most, reaching 13.5 times its earlier levels, while that of Cd decreased. Compared with their levels pre-lockdown, the TCRs of the selected toxic elements for both children and adults increased by 3.7 times during the partial lockdown, and the CRs of Co, As, and Ni also clearly increased (Mann-Whitney test, p < 0.05). Overall, the non-cancer and cancer risks of the selected toxic elements for both children and adults were at their lowest levels during the full lockdown.

3.2. Health risks during different haze episodes

Four typical haze episodes were chosen during different periods, including two before lockdown, one during the full lockdown, and one during the partial lockdown (Table S7). The exposure doses and health risks of the selected toxic elements during these episodes are shown in Tables S12–S15 and Fig. 3. The non-cancer and cancer risks of the selected toxic elements during the haze episodes were significantly higher than their overall levels throughout the study period. During haze episodes, the total non-cancer risks (HIs) of the toxic elements for children and adults were 4.37 and 1.87, respectively, both of which exceeded the US EPA limit of 1.00. The HIs calculated in this study were relatively higher than those reported during haze episodes in other cities in China (Li et al., 2016; Lin et al., 2020), Malaysia (Sulong et al., 2017), India (Mahilang et al., 2020), and Singapore (Betha et al., 2014; Huang et al., 2016). The HI for children was 2.3 times that for adults during the haze episodes, indicating that children were a high non-cancer risk group. Among the selected toxic elements, Mn had the highest HI during the haze episodes, indicating that Mn was the critical element driving non-cancer risks (Li et al., 2016); Mn played a similar role throughout the study period. The HI of the selected toxic elements for children exceeded the US EPA limit of 1.00 during all haze episodes in the study period, while the adults HI was less than the US EPA limit during the haze episodes during the full lockdown. The HI of the investigated toxic elements during the full-lockdown haze episodes was the lowest (68% lower than that during the pre-lockdown haze episodes), and the HQ declines of Cu and Cr(VI) were the greatest, reaching 97% and 88%, respectively. During the partial lockdown, the HI of the toxic elements during haze episodes increased by 4.9 times; and the HQ increases of Cu, Cr(VI), As, V, Ni, and Mn were the highest, reaching 31.0, 22.5, 15.4, 10.4, 7.6, and 6.0 times their previous levels, respectively.

The total cancer risk (TCR) of the selected toxic elements for adults during the haze episodes was $1.30 \times 10^{-4}$, which was 1.7 times that of children. Elevated cancer risks in adults were also noted by Li et al. (2016) and Sulong et al. (2017). However, the TCRs of the toxic elements during the haze episodes calculated in this study were lower than those of a prior study in Linfen (Lin et al., 2020). The TCR of the toxic elements for both children and adults during the investigated haze episodes exceeded the US EPA limit of 1.00. The CR of As significantly exceeded the US EPA limit, and As was a critical element driving cancer risk. This result was also observed by Behera et al. (2015) and Lin et al. (2016). Compared with the pre-lockdown levels, the TCR of the toxic elements for both children and adults decreased by 17% during full-lockdown haze episodes, and the decreases in CR for As, Cd, Cr(VI), and Ni ranged from 14% to 88%. During the partial lockdown, the TCR of the selected toxic elements increased by 13.7 times during the haze episodes, and the CR of Cr(VI), As, and Ni increased by 22.5, 15.4, and 7.6 times, respectively.

3.3. PMF source apportionment

3.3.1. Solution selection and interpretation

PMF solutions ranging from two to nine factors were explored utilizing data from throughout the study period. The solution that offered narrow distribution of scaled residuals, proper interpretability of factors, and acceptable displacement (DISP) results was selected as the best (Brown et al., 2015; Dai et al., 2020). In this study, a seven-factor solution was identified as optimal fit. The correlation coefficient ($r^2$) between the predicted PM$_{2.5}$ mass concentration and the measured value was 0.94 (Fig. S2), and no factors exhibited DISP swaps.

The factor profile is shown in Fig. 4. The first factor was characterized by high explained variations of Fe, Al, Si, Ca, Mg, Ti, Mn, and V with narrow DISP bounds. This factor was interpreted as secondary nitrate because of high explained variations of NO$_3^-$ and NH$_4^+$ associated with small DISP ranges and were present in relatively high concentrations (Hasheminassab et al., 2014; Tian et al., 2017).

The third factor had relatively high concentrations of Cl$^-$, OC, and EC, and low concentrations of Al, K, Mg, and Na, which were accompanied by narrow DISP intervals. These elements are distinctive tracers of coal combustion (Deng et al., 2014; Khan et al., 2021; Li et al., 2019; Liu et al., 2020). The fourth factor was interpreted as vehicle emissions, because it featured high explained variations of EC and Zn with narrow DISP intervals, and high concentration and explained variation of OC with wider DISP interval. OC and EC are notable indicators of vehicle emissions (Chen et al., 2014; Sulaymon et al., 2020; Zikova et al., 2017). Zn originates from vehicular tailpipe exhaust (Huang et al., 1994), debris from worn tires as well as brake linings (Bozlaker et al., 2014; Jiang et al., 2019; Lin et al., 2015).

The fifth factor was dominated by SO$_2^-$ and NH$_4^-$, which is commonly identified as secondary sulphate and mainly derives from the photochemical convention of SO$_2$ precursors (Garaga et al., 2020). The sixth factor was characterized as biomass burning, because it was mostly composed of K, Cl$^-$, and OC with tight DISP intervals (Dall’Osto et al., 2013; Hao et al., 2020). The final factor was characterized by high explained variations of Fe, As, Pb, Zn, Mn, and Cu with narrow DISP bounds. Previous studies have shown that steel sintering can emit large amounts of As, Pb, Zn, and Cu (Duan and Tan, 2013; Zong et al., 2016; Zong et al., 2018), and steel oxidation refining can release appreciable Fe and Mn (Tsai et al., 2020). Thus, this factor was classified as steel-related smelting.

3.3.2. Source contributions to PM$_{2.5}$ and selected toxic elements

The time series of source contributions to ambient PM$_{2.5}$ and the mean source contributions to ambient PM$_{2.5}$ during different COVID-19 periods are shown in Figs. S3–S4, respectively. On average, coal combustion (24.1%) and fugitive dust (23.9%) were the largest sources contributed to ambient PM$_{2.5}$ during the study period, as is often can be seen in northern China (Duan et al., 2020; Luo et al., 2018; Liu et al., 2019; Zhao et al., 2020). The predominant source was coal combustion before the lockdown and during full lockdown, though fugitive dust was the predominant source during the partial lockdown. Compared with their pre-lockdown contributions, the contributions of all primary sources decreased significantly during full lockdown, and fugitive dust and steel-related smelting decreased the most (82% and 92%, respectively) in direct response to the strict lockdown measures (Zheng et al., 2020). During the partial lockdown, the contributions of fugitive dust and steel-related smelting sharply rebounded, reaching 14.0 and 5.5 times their full-lockdown levels, respectively.

The contribution concentrations of emission sources to the selected toxic elements are shown in Fig. S5. Steel-related smelting was the predominant source of the selected toxic elements during the study period and pre-lockdown mainly due to Zn and Cu emissions. Many studies have demonstrated that emissions from industry section have gradually become the exclusive source of toxic elements (Duan et al., 2020; Wang et al., 2019), and the steel-related smelting is one of the pillar industries in Linfen (Kuai et al., 2015). After the full lockdown, the contributions of all sources, except for secondary sulphate, to the total toxic elements had obviously decreased, and steel-related smelting and...
fugitive dust decreased the most. Biomass burning and vehicle emissions were the chief contributors to the toxic elements during full lockdown. During partial lockdown, the contribution of fugitive dust to the toxic elements increased rapidly, reaching 14.0 times its level during full lockdown, and fugitive dust turned out to be the predominant source. The contribution of steel-related smelting remarkably increased by 4.5 times during partial lockdown.

3.4. Source-specific health risks

3.4.1. Different periods of the COVID-19 lockdown

The exposure doses of the selected toxic elements emitted from various sources during the study period are shown in Tables S16–S19. The contributions of total non-cancer risks (HIs) and total cancer risks (TCRs) of the selected toxic elements emitted from different sources to the HIs and TCRs from all emission sources during different periods of the COVID-19 lockdown are shown in Fig. 5 and Fig. S6. The HIs of the selected toxic elements emitted from fugitive dust for children and adults were 1.35 and 0.58, respectively, which was the greatest contributor to the HIs (2.88 for children and 1.23 for adults) of the toxic elements emitted from all sources during the study period. The HI value of fugitive dust for children clearly exceeded the US EPA limit of 1.00. The high HI of fugitive dust was primarily due to Mn, which was also reported by Tian et al. (2021). The HI of steel-related smelting emissions for both children and adults was highest pre-lockdown, and exceeded the US EPA limit for children. During the lockdown, the HIs of all the sources except for secondary sulphate obviously decreased, and steel-related smelting and fugitive dust contributed the most to the reduction in HI during full lockdown, accounting for 52% and 39% of the overall reduction, respectively. Therefore, the control of these sources is critical to effectively reduce non-cancer risks. While the HIs from coal combustion for both children and adults were the highest during full lockdown, they did not exceed the US EPA limit. During partial lockdown, the HI from fugitive dust increased the most rapidly, reaching 14.0 times its level during the full lockdown and even exceeding pre-lockdown levels. The HI from steel-related smelting
increased by 4.5 times compared with the full-lockdown level. Thus, fugitive dust contributed the most to the increase in non-cancer risk during partial lockdown, accounting for 85% of the total. However, the HI from coal combustion, biomass burning, and secondary sulphate significantly decreased during the partial lockdown, accounting for 54%, 26%, and 20% of the HI reduction, respectively.

The TCRs of the toxic elements emitted via steel-related smelting for both children and adults ($5.60 \times 10^{-6}$ and $9.59 \times 10^{-6}$, respectively) were higher than those of other sources during the study period and significantly exceeded the US EPA limit of $1.00 \times 10^{-6}$. Steel-related smelting was the largest contributor to the TCRs ($1.05 \times 10^{-5}$ for children and $1.79 \times 10^{-5}$ for adults) of the selected toxic elements emitted from all sources during the study period. Duan et al. (2020) also found that industry (iron and steel plants, power plants, etc.) was the most significant contributor to cancer risk. However, Fan et al. (2021) believed that local traffic emissions and long transported heavy-oil combustion were important sources of cancer risk. In our study, steel-related smelting contributed the most to the pre-lockdown TCR; however, during the full lockdown, the TCRs of all the sources, except for secondary sulphate, significantly decreased, and steel-related smelting contributed the most (79%) to the reduction of TCR during full lockdown. Thus, the control measures targeting this industry were critical to effectively reduce cancer risks. The TCRs from coal combustion for both children and adults were highest during full lockdown. During the partial lockdown, the TCRs from fugitive dust, steel-related smelting, secondary nitrate, and vehicle emissions increased significantly. Steel-related smelting and fugitive dust contributed the most to the increase in TCR during full lockdown, accounting for 58% and 41%, respectively. Nevertheless, the TCRs from coal combustion, biomass burning, and secondary sulphate remarkably decreased during partial lockdown, and coal combustion was the main contributor to the reduction in TCR, accounting for 81%.

3.4.2. Haze episodes in different periods

The exposure doses of the selected toxic elements emitted from sources during the haze episodes are shown in Tables S20–S23. The contributions of HIs and TCRs of the selected toxic elements emitted from different sources to the HIs and TCRs from all emission sources during haze episodes in different lockdown stages are shown in Fig. 6 and Fig. S7. Fugitive dust was the dominant contributor to non-cancer risks of the toxic elements emitted from all sources during haze episodes. The HIs from fugitive dust and steel-related smelting for both children and adults were highest in the pre-lockdown haze episodes, and the HIs from these sources for children exceeded the US EPA limit. During the full lockdown, the HIs from all the sources during the haze episodes significantly decreased compared to those during pre-lockdown haze episodes, and steel-related smelting and fugitive dust contributed the most to the decrease in HI, accounting for 47% and 46%, respectively. The HI of coal combustion for both children and adults was
the highest during full-lockdown haze episodes. During the partial lockdown, the HIs from fugitive dust and steel-related smelting during haze episodes significantly increased by 27.5 and 7.7 times, respectively, and fugitive dust contributed 80% of the increase in HI. Fugitive dust had the largest HI for both children and adults during partial-lockdown haze episodes and surpassed the US EPA limit. However, the HIs of coal combustion, secondary sulphate, and biomass burning obviously decreased during the partial-lockdown haze episodes, and coal combustion contributed the most (68%) to the decrease in HI.

Compared with other sources, steel-related smelting contributed the most to the toxic element levels during haze episodes. These results were similar to the findings of Sun et al. (2021), which indicated that industrial emissions had a significant impact on cancer risks associated with different heavy pollution, however, Lin et al. (2020) found that traffic emissions were the dominant source of cancer risks. In the present study, the TCR of steel-related smelting for both children and adults was the highest during the pre-lockdown haze episodes and exceeded the US EPA limit. During the full lockdown, the TCRs of all the sources clearly decreased during haze episodes compared to their levels during pre-lockdown haze episodes, and steel-related smelting contributed the most (77%) to the decrease in TCR. However, the TCRs of coal combustion, secondary nitrate, and steel-related smelting during full-lockdown haze episodes still exceeded the US EPA limit for adults. During the partial lockdown, the haze-episode TCRs from fugitive dust, steel-related smelting, and secondary nitrate significantly increased, and steel-related smelting contributed the most (63%) to the increase in TCR. Meanwhile, the TCRs of steel-related smelting and fugitive dust for both children and adults were the highest in the partial-lockdown haze episodes and exceeded the US EPA limit.

4. Conclusions

This study assessed the health risks associated with toxic elements and identified critical risk sources during different periods of the COVID-19 lockdown and haze episodes using PMF and a health risk assessment model. The mean PM$_{2.5}$ concentration during the study period was 145 $\mu$g/m$^3$, and the 10 selected toxic elements accounted for 0.31% of the PM$_{2.5}$ mass. The HI and TCR of the selected toxic elements for both children and adults exceeded the US EPA limits throughout the study period. The HI for children was 2.3 times that for adults during the different periods, while the TCR for adults was 1.7 times that for children. The HI and TCR of the selected toxic elements were at their lowest during the full lockdown. The HI and TCR were primarily attributable to Mn and As, respectively, and the health risks recorded during haze episodes were significantly higher than those calculated for the study period overall. The HI and TCR of the toxic elements during the full-lockdown haze episodes were considerably lower, however, than those during pre-lockdown haze episodes, decreasing by 68% and 17%, respectively. Coal combustion and fugitive dust were the highest contributors to PM$_{2.5}$ mass, accounting for 24.1% and 23.9%, respectively. Steel-related smelting was the primary source of the toxic elements (mainly attributable to Zn and Cu). The high HI and TCR during the study period were attributed to fugitive dust and steel-related smelting, respectively, suggesting that measures targeting these activities are critical to effectively reduce the health risks.

Credit author statement

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Liqin Duan, Lili Guo, and Jing Zhao: Data collection and Investigation.

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.

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Appendix A. Supplementary data

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