A Long-lasting Winter Haze Episode in Xiangyang, Central China: Pollution Characteristics, Chemical Composition, and Health Risk Assessment

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ABSTRACT

This study investigated the characteristics and chemical composition of PM_{2.5} during a long-lasting winter haze episode (Jan. 13–24, 2018) in Xiangyang of central China. The average daily concentration of the PM_{2.5} equaled $169.29 \pm 56.98 \mu\text{g m}^{-3}$, with water-soluble inorganic ions (WSIIs), organic carbon (OC), elemental carbon (EC), and trace elements accounting for 111.45 ± 44.62 , 20.74 ± 6.79 , 6.48 ± 1.79 , and $10.53 \pm 3.84 \mu\text{g m}^{-3}$, respectively. The OC/EC ratios indicated mixed contributions from intensive traffic emission and secondary formation, and the estimated concentrations for the primary organic carbon (POC) and the secondary organic carbon (SOC) increased with the level of pollution. POC dominated the OC during mild and moderate pollution, whereas SOC dominated it during severe pollution. A strong positive correlation was found between the enrichment factor (EF) and geo-accumulation index (I_{Gco}) values, which were used to assess the contamination level of PM_{2.5}-bound metal(loid)s. A health risk assessment, which was conducted to examine the non-carcinogenic and carcinogenic risks of the PM_{2.5}-bound metal(loid)s, found that As, Cr, Pb, and Sb posed potential non-carcinogenic risks to both children and adults and that two of these elements, As and Pb, also posed potential carcinogenic risks. The total non-carcinogenic and carcinogenic risks from the PM_{2.5}-bound metal(loid)s were slightly higher for adults (3.07×10^3 and 3.78×10^{-3}) than children (2.71×10^3 and 2.99×10^{-3}) and depended on the concentrations of the metal(loid)s rather than the level of pollution. Thus, the public and the government should implement appropriate measures to mitigate the health risks posed by PM_{2.5}-bound metal(loid)s during winter haze episodes in Xiangyang.

Keywords: PM_{2.5}; Haze episode; Metal(loid)s; Winter; Health risk assessment.

INTRODUCTION

Fine particulate matter (PM_{2.5}) has attracted increased attention by the public and government over the past years, due to its significant impact on global climate change, atmospheric visibility degradation, cloud processes, and public health risk (Huang *et al.*, 2014). PM_{2.5} is directly emitted from emission sources, including industrial process, coal-fired power plant, vehicle exhaust, agricultural biomass burning, crustal dust. It is also indirectly formed through gas-to-particle conversions of volatile organic compounds (VOCs) and gaseous precursors (SO₂, NO_x and NH₃) (Liu *et al.*, 2016a).

As the world's second largest economy, China has been

facing air quality deterioration in recent years. A long-lasting severe haze event in 2013 significantly impacted the public; the event covered 17 provinces and autonomous regions and threatened the health of 600 million people due to exposure to PM_{2.5}-bound metal(loid)s or other potentially toxic compounds (Liu *et al.*, 2016a). Specifically, approximately 690 (490–890) premature deaths, 45,350 (21,640–57,860) acute bronchitis and 23,720 (17,090–29,710) asthma cases were caused by the PM_{2.5} concentrations during the severe haze event of January 2013 in Beijing area (Gao *et al.*, 2015). In 2015, deaths from PM_{2.5} pollution accounted for 31.14% (approximately 2.62 million people) of all deaths in China (Xie *et al.*, 2018). Studies have evaluated the pollution characteristics and chemical compositions of PM_{2.5} in Chengde (Qu *et al.*, 2019), Shijiazhuang (Shen *et al.*, 2019), Zhengzhou (Wang *et al.*, 2019), Hefei (Xue *et al.*, 2019a), Shanghai (Wei *et al.*, 2019), Beijing (Shen *et al.*, 2019), and Wuhan (Liu *et al.*, 2016b). However, there have been no investigations of PM_{2.5} during winter haze episodes, and at different pollution levels for Xiangyang.

Xiangyang (31°13'–32°38'N, 110°45'–113°47'E) occupies a 19,800 km² area and has more than 6 million people. It lies in the northwest of Hubei Province and in the middle reaches

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of the Han River, and is approximately 300 km from Wuhan (the capital of Hubei Province). It has a typical subtropical monsoon climate with four distinct seasons and is an industrial city producing iron and steel, rutile, coal, and cars. The east, middle, and west of Xiangyang is surrounded by hills (20%), humpy grounds (40%) and mountains (40%), respectively.

The *Xiangyang Statistics Yearbook* (http://tjj.xiangyang.gov.cn/tjsj/sjcx/tjnb/201912/t20191230_2001072.shtml) indicates the gross domestic product (GDP) of Xiangyang reached USD 62.59 billion in 2019, and was composed of agriculture (4.88%), industry (51.50%) and other industries (43.62%). This ranked second highest in Hubei Province. Xiangyang has more than 900,000 cars in 2018, and there were 7114 Gg of coal consumption for power plants and 551 Gg of coal consumption for residential biofuel. These are all potential emission sources of PM_{2.5}. Statistically, the percentage of average number of days with moderate or higher pollution in January from 2015 to 2018 was more than 60% in Xiangyang. This is a high PM_{2.5} level, with an average PM_{2.5} daily mass concentration of 140 $\mu\text{g m}^{-3}$ (Fig. S1). This makes it urgent to study the pollution characteristics, chemical composition, and health risks of PM_{2.5} during haze events in Xiangyang, with the goal of providing policy advice for the government to control haze pollution.

In this study, PM_{2.5} samples were collected during a long-lasting winter haze episode from Jan. 13–24, 2018, in Xiangyang. Study goals were as follows: (1) to analyze the pollution characteristics and chemical compositions of PM_{2.5}, including water-soluble inorganic ions (WSIIs), carbonaceous species (organic carbon [OC] and elemental carbon [EC]) and trace elements (TEs); (2) to estimate the formations of primary organic carbon (POC) and secondary organic carbon (SOC); (3) to simultaneously report the enrichment degree and contamination level of PM_{2.5}-bound metal(loid)s; and (4) to assess the potential human health risks, including non-carcinogenic and carcinogenic risk, caused by exposure to PM_{2.5}-bound metal(loid)s in ambient air at four different pollution levels.

MATERIALS AND METHODS

Field Sampling Campaign and Determination of PM_{2.5} Concentration

The sampling site (XY) was located at the Xiangyang Environmental Protection Monitoring Station (XYEPMS; 32°01'09"N, 112°09'18"E), which is surrounded by a residential area, school, supermarket, hospital and highways. The site is a state-controlled, typical urban air sampling site in Xiangyang, central China (Fig. 1). On the roof of the XYEPMS (15 m height), forty-eight pairs of PM_{2.5} samples and one pair of field blank samples were collected on quartz fiber filters (QFFs; Whatman, UK) and Teflon filters (TFs; Munktell, Sweden). The QFFs were prebaked at 500°C for 6 h in a muffle furnace to remove any contaminants on the filters and the TFs were prepared at a constant temperature and relative humidity ($25 \pm 1^\circ\text{C}$, $50 \pm 5\%$) for 48 h in advance, respectively.

The samples on QFFs were used to analyze WSIs and carbonaceous species. The samples on TFs were used to determine the concentration of PM_{2.5} and TEs. The particles were collected using a medium-volume sampler (100 L min⁻¹; TH-150F; Wuhan Tianhong Instrument Co., Ltd., China). To track the haze bloom-decay process, sample collection tried to increase the number of PM_{2.5} samples classified at different pollution levels as much as possible. This prevented the stoppage of sampling due to excessive filter resistance caused by a haze episode. Samples were collected four times a day from 06:00–11:00 (5 h), 11:30–16:30 (5 h), 17:00–22:00 (5 h), and 22:30–05:30 (7 h) the next day, from January 13–24, 2018. After sampling, all filters were folded, wrapped in aluminum foil, sealed in plastic bags, and stored in a refrigerator at -18°C to prevent any loss of volatiles prior to analysis.

To determine the PM_{2.5} mass concentrations, the filters were weighed before and after the samples were collected using an electronic microbalance (Secura 125-1S; Sartorius Lab Instruments GmbH & Co. KG, Göttingen, Germany). After being weighed, the filters were stored in the refrigerator at -18°C prior to chemical analysis. Since the pollution

Fig. 1. The location of the sampling site (XY).

characteristics, chemical compositions, formation reasons, and health risks of PM_{2.5} might be different at different pollution levels, sampling periods that experienced different PM_{2.5} mass concentrations were categorized at four pollution levels: mild pollution ($75 \mu\text{g m}^{-3} < \text{PM}_{2.5} \leq 115 \mu\text{g m}^{-3}$), moderate pollution ($115 \mu\text{g m}^{-3} < \text{PM}_{2.5} \leq 150 \mu\text{g m}^{-3}$), heavy pollution ($150 \mu\text{g m}^{-3} < \text{PM}_{2.5} \leq 250 \mu\text{g m}^{-3}$) and severe pollution ($\text{PM}_{2.5} > 250 \mu\text{g m}^{-3}$) according to the National Ambient Air Quality Standard (GB 3095-2012; http://www.mee.gov.cn/ywggz/fgbz/bz/bzwb/dqhjbh/dqhjzl/bz/201203/t20120302_224165.shtml) (Xie *et al.*, 2019).

Air-mass Back-trajectory Analysis

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (v.4.8; <https://www.arl.noaa.gov/hysplit/>), provided by the U.S. National Oceanic and Atmospheric Administration, was used to calculate physical travel trajectories. Trajectories reaching the sampling site were calculated for a period extending 72 h into the past at a frequency of four times a day (00:00, 06:00, 12:00, 18:00 UTC). Each trajectory was estimated at 100 m above ground level and was cross-checked at 500 m and 1000 m above ground level. To determine the pollutant sources, three typical types of trajectories were classified using geographic information system (GIS) software (ArcGIS v.10.2) using a hierarchical clustering method because the corresponding percentage change in total spatial variance (TSV; %) was the smallest one as three clusters were combined (Table S1).

Chemical Analysis

The analysis procedure of WSIs, carbonaceous species and TEs was discussed in our previous study (Zhang *et al.*, 2014; Lyu *et al.*, 2015; Zhang *et al.*, 2015). Briefly, a punch (3.14 cm²) of QFFs was extracted using 15 mL of Milli-Q water (18.25 MΩcm) and was sonicated for 45 min in an ultrasonic ice-water bath. The water extracts were filtered through a 0.22 mm hydrophilic filter and were then stored in a pre-cleaned centrifugal tube for samples analysis. Five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) and four anions (F⁻, Cl⁻, NO₃⁻ and SO₄²⁻) were analyzed using ion chromatography (883 Basic IC plus; Metrohm, Switzerland). Before a targeted sample analysis, standard solution (ANPEL Laboratory Technologies Inc., China) and blank test were performed, and the correlation coefficients of standard samples exceeded 0.999. The method detection limits of F⁻, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺ were 0.010, 0.012, 0.027, 0.030, 0.019, 0.020, 0.025, 0.037 and 0.020 μg m⁻³, respectively.

To assess the carbonaceous species, OC and EC were analyzed using a thermal/optical reflectance carbon analyzer (DRI 2001 A; Desert Research Institute, USA). Briefly, a punch (0.518 cm²) of QFFs were heated stepwise in the oven at 140°C (OC1), 280°C (OC2), 480°C (OC3) and 580°C (OC4) for 150 s at each stage in a pure He gas atmosphere for OC volatilization and 580°C (E1), 740°C (E2) and 840°C (E3) for 150 s at each stage in a 2% O₂/98% He atmosphere for EC oxidation. Pyrolyzed organic carbon (OPC) was produced in the inert atmosphere, decreasing the reflected light to correct for charred OC (Yu *et al.*, 2002). According to the Interagency Monitoring of Protected Visual Environments

(IMPROVE)_A protocol, OC = OC1 + OC2 + OC3 + OC4 + OPC and EC = EC1 + EC2 + EC3 – OPC. Replicate analyses were performed on 10% of the total samples, yielding differences within 3.95% for OC and 2.53% for EC. Standard concentrations of CH₄/CO₂ mixed gases were used to calibrate the analyzer in each day before and after the sample analysis.

To assess TEs, TFs were digested using an acid mixture (5 mL 68% HNO₃ + 2 mL 40% HF) in a microwave digestion system. Twenty-five elements (Li, Be, Al, Si, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Tl, Pb, Bi, Th and U) in solution were measured using inductively coupled plasma mass spectrometry (ICP-MS; NexION 350D; PerkinElmer, USA). The relative standard deviations between real values of soil national standard materials (Sigma-Aldrich, USA) were calculated, with results ranging from 0.10–18.00%. The detection limits ranged from 0.00001–0.0005 μg L⁻¹ for trace elements. All reported data of WSIs, carbonaceous species, and trace elements were corrected by the filter blank results.

Contamination Level Assessment

Enrichment Factor

To determine whether PM_{2.5}-bound metal(loid)s found in greater abundance in ambient air originated from the earth's crust, the enrichment factor (EF) was used to assess the degree of enrichment of metal(loid)s in PM_{2.5} samples using Eq. (1) (Zhang *et al.*, 2019).

$$EF = \frac{(C_i/C_{ref})_{Aerosol}}{(C_i/C_{ref})_{Crust}} \quad (1)$$

In this expression, $(C_i/C_{ref})_{Aerosol}$ and $(C_i/C_{ref})_{Crust}$ represent the ratio of the concentration of metal *i* to the concentration of a reference metal in the aerosol samples and earth crust, respectively. Fe, Al, and Si are generally used as reference metal(loid)s. Al was selected as the reference metal for this study, because it is stable in the earth crust and is not easily affected by human activities. In this study, the metal concentrations in the earth crust were adopted from “The Background Values of Elements in Chinese Soil” in Hubei Province. The EF values between 2–10 indicated the important mixed impacts of crustal sources and anthropogenic emissions. Values exceeding 10 indicated that the anthropogenic emissions were the main source of metal(loid)s in ambient air (Dehghani *et al.*, 2017).

Geo-accumulation Index

To compare the present concentration of metal(loid)s in PM_{2.5} samples with the concentration in the earth's crust, the geo-accumulation index (*I*_{Geo}) was used to evaluate the contamination levels for metal(loid)s. The *I*_{Geo} values were calculated using Eq. (2) (Zhang *et al.*, 2019).

$$I_{Geo} = \log_2 \frac{C_{iAerosol}}{(1.5 \times C_{iCrust})} \quad (2)$$

In this equation, $C_{iAerosol}$ and C_{iCrust} represent the

concentration of metal i in aerosol samples and the earth crust, respectively. The constant 1.5 allowed us to verify the natural fluctuations of a specific substance in the environment; very small anthropogenic influences were found. The I_{Geo} values for $PM_{2.5}$ -bound metal(loid)s have been typically classified as uncontaminated ($I_{Geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{Geo} \leq 1$), moderately contaminated ($1 < I_{Geo} \leq 2$), moderately to heavily contaminated ($2 < I_{Geo} \leq 3$), heavily contaminated ($3 < I_{Geo} \leq 4$), heavily to extremely contaminated ($4 < I_{Geo} \leq 5$) and extremely contaminated ($I_{Geo} > 5$) (Li et al., 2019). I_{Geo} values higher than 1 may indicate the influence of anthropogenic emissions.

Human Exposure and Health Risk Assessment

Human Exposure Dose

Potentially adverse human health risks, including non-carcinogenic and carcinogenic risks, can be caused by exposure to $PM_{2.5}$ -bound metal(loid)s in ambient air. Potential exposure can occur through three different pathways: ingestion, inhalation, and dermal contact. Human exposure was defined in terms of average daily exposure dose (ADED) of each metal and was then computed individually for each metal and each exposure pathways. ADED values were calculated through three exposure pathways, ingestion ($ADED_{Ing}$), inhalation ($ADED_{Inh}$), and dermal contact ($ADED_{Der}$), using Eqs. (3)–(5).

$$ADED_{Ing} = C_i \times \frac{R_{Ing} \times EF \times ED}{BW \times AT} \times CF \quad (3)$$

$$ADED_{Inh} = C_i \times \frac{R_{Inh} \times EF \times ED}{BW \times AT \times PEF} \quad (4)$$

$$ADED_{Der} = C_i \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (5)$$

In this expression, C_i was the concentration of metal(loid)s i in $PM_{2.5}$ ($mg\ kg^{-1}$). In particular, the Cr concentration was calculated as one-seventh of the total Cr because only Cr(VI) was carcinogenic, while Cr(III) was not (Massey et al., 2013). The variable R_{Ing} was the ingestion rate; R_{Inh} was the inhalation rate; ABS was the dermal absorption factor; EF was the exposure frequency; ED was the exposure duration; BW is the body weight; AT was the averaging time; PEF was the particle emission factor; SA was the skin surface area in contact with air; AF was the adherence factor for airborne particulates to skin; and CF was the conversion factor. Table S1 lists these variables (U.S. EPA, 2011; Ferreira-Baptista and De Miguel, 2005; Hu et al., 2012; Li et al., 2013).

Non-carcinogenic risk

The non-carcinogenic risks due to exposure to $PM_{2.5}$ -bound metal(loid)s (As, Cd, Cr(III), Co, Cu, Mn, Ni, Zn, Pb, Ag, Al, Ba, Mo, Sb, Sr, U and V) were evaluated using the hazard quotient (HQ) and hazard index (HI). The HQ values are calculated by dividing ADED into a specific reference

dose (RfD). The total HI (THI) values indicated the mixed non-carcinogenic risk due to exposure to an individual metal and multiple metal(loid)s of three pathways in ambient air, respectively. The total non-carcinogenic risks through ingestion, inhalation, and dermal contact were estimated using Eqs. (6) and (7).

$$HQ_i = \frac{ADED_i}{RfD_i} \quad (6)$$

$$THI = \sum HQ_i \quad (7)$$

If the HI values were less than 1, there was no significant non-carcinogenic risk; otherwise, there may be a non-carcinogenic risk with respect to human health.

Carcinogenic Risk

The carcinogenic risks (CRs) due to exposure to $PM_{2.5}$ -bound metal(loid)s (As, Cd, Co, Cr(VI), Ni and Pb) (U.S. EPA, 2011; Massey et al., 2013; IARC, 2020) were equals to ADED multiplied by a specific slope factor (SF). The CR and total carcinogenic risk (TCR) indicated the mixed carcinogenic risk due to exposure to an individual metal and multiple metal(loid)s of three pathways in ambient air, respectively. The CRs through ingestion, inhalation, and dermal contact, were estimated using Eqs. (8) and (9).

$$CR_i = ADED_i \times SF_i \quad (8)$$

$$TCR = \sum CR_i \quad (9)$$

Usually, a CR and TCR within the range of 1×10^{-6} to 1×10^{-4} is acceptable, meaning that the metal(loid)s in ambient air likely does not have a carcinogenic risk for human health. The carcinogenic risk is categorized as very low ($CR \leq 1 \times 10^{-6}$), low ($1 \times 10^{-6} \leq CR < 1 \times 10^{-4}$), moderate ($1 \times 10^{-4} \leq CR < 1 \times 10^{-3}$), high ($1 \times 10^{-3} \leq CR < 1 \times 10^{-1}$), and very high ($CR \geq 1 \times 10^{-1}$) for human life (Roy et al., 2019).

RESULTS AND DISCUSSION

General $PM_{2.5}$ Mass Concentration and Pollution Characteristic

Fig. 2 presents the mass concentrations of $PM_{2.5}$, WSIs, carbonaceous species, and trace elements in samples collected from Jan. 13–24, 2018. During this sampling period, Xiangyang had experienced a 12 d haze episode, with average daily $PM_{2.5}$, WSIs, OC, EC and TE concentrations of 169.29 ± 56.98 , 111.45 ± 44.62 , 20.74 ± 6.79 , 6.48 ± 1.79 and $10.53 \pm 3.84\ \mu g\ m^{-3}$, respectively. The average $PM_{2.5}$ concentrations were 2.26-fold higher compared to the secondary standard ($75\ \mu g\ m^{-3}$) of the National Ambient Air Quality Standard. There were 8 d with pollution at heavy levels or above, and the proportion of moderate or greater pollution was 85.42%, with a high pollution level in winter. The $PM_{2.5}$ concentration during severe pollution ($306.92 \pm 36.26\ \mu g\ m^{-3}$) was approximately 2–3 times the level when

Fig. 2. The mass concentrations of (a) PM_{2.5} and WSIs, (b) carbonaceous species, and (c) trace elements from Jan. 13–24, 2018. (The green, cyan, red, and violet dash line means mild pollution ($75 \mu\text{g m}^{-3} < \text{PM}_{2.5} \leq 115 \mu\text{g m}^{-3}$), moderate pollution ($115 \mu\text{g m}^{-3} < \text{PM}_{2.5} \leq 150 \mu\text{g m}^{-3}$), heavy pollution ($150 \mu\text{g m}^{-3} < \text{PM}_{2.5} \leq 250 \mu\text{g m}^{-3}$) and severe pollution ($\text{PM}_{2.5} > 250 \mu\text{g m}^{-3}$), respectively.)

there was mild pollution ($103.27 \pm 10.06 \mu\text{g m}^{-3}$), moderate pollution ($113.64 \pm 11.56 \mu\text{g m}^{-3}$), and heavy pollution ($182.31 \pm 25.59 \mu\text{g m}^{-3}$).

The PM_{2.5} concentration reached the highest level from Jan. 18–19 during severe pollution. This may have been caused by air masses from the NNW–NE (Cluster 3) direction, accounting for 14% of all trajectories. These air masses originated from Inner Mongolia, passed through Hebei and Shanxi Province, turned a corner in Shandong Province, and finally approached the sampling site through Henan Province with higher transport speeds (4.74 m s^{-1}) than the average wind speed (3.02 m s^{-1}) obtained from Hubei Meteorological Service during the whole winter haze episode (Fig. 3). The PM_{2.5} and its components had higher concentrations than other directions (Table S2). This may be influenced by Hebei, Shanxi, and Henan Province, due to significant amounts of polluted air carried down from these high-pollution areas. Shanxi Province has the largest explored coal reserves and abundant mineral resources in China, with many industries, including power plants and steel works. This is also the case for Hebei and Henan Province.

In contrast, the PM_{2.5} concentration reached the lowest level on Jan. 23–24 during mild pollution. This level may have

been affected by air masses from the NW–NE (Cluster 2) direction, accounting for 24% of all trajectories. This air mass initiated in Gansu Province, passed through Shaanxi and Hebei Province, turned a corner in Henan Province, and finally approached the sampling site through Henan Province with similar transport speeds (2.72 m s^{-1}) to the average wind speed. During this period, the wet deposition from weather, such as snow and rain, dominated Xiangyang, resulting in low pollutant concentrations at XY site.

A total of 62% of the air masses came from NW–SW (Cluster 1) direction; this pattern prevailed from Jan. 13–17 and Jan. 19–22, 2018, during moderate and heavy pollution. The pattern originated from Henan Province, turned a corner in Hubei Province, and then approached the sampling site with relatively lower transport speeds (2.45 m s^{-1}) than the average wind speed. The PM_{2.5} and associated species were present at high concentrations; this did not support pollutant dispersion due to unfavorable meteorological conditions and local emissions dominating Xiangyang during this period.

When compared to other cities around the world (Table S3), the PM_{2.5} concentration in Xiangyang was comparable to the concentration in Wuhan ($159.5 \mu\text{g m}^{-3}$) in 2013. The level was significantly higher compared to most cities in China,

Fig. 3. Three typical air-mass back trajectories estimated at 100 m, 500 m, and 1000 m above ground level at XY during Jan. 13–24, 2018.

including Beijing ($117.0 \mu\text{g m}^{-3}$) (Shen *et al.*, 2019), Tianjin ($124.0 \mu\text{g m}^{-3}$) (Shen *et al.*, 2019), Guilin ($144.0 \mu\text{g m}^{-3}$) (Zhong *et al.*, 2019), Xinxiang ($109.9 \mu\text{g m}^{-3}$) (Liu *et al.*, 2019), Chengdu ($113.2 \mu\text{g m}^{-3}$) (Qu *et al.*, 2019), Shanghai ($92.9 \mu\text{g m}^{-3}$) (Wei *et al.*, 2019), and Hefei ($81.0 \mu\text{g m}^{-3}$) (Xue *et al.*, 2019b). The level was also higher than cities in other countries, for example, Riyadh, Saudi Arabia ($71.9 \mu\text{g m}^{-3}$) (Modaihsh *et al.*, 2015); Zonguldak, Turkey ($37.3 \mu\text{g m}^{-3}$) (Akyüz and Çabuk, 2009); and Iasi, Romania ($23.4 \mu\text{g m}^{-3}$) (Galon-Negru *et al.*, 2018). The level was significantly lower than the levels in Zhengzhou ($188.2 \mu\text{g m}^{-3}$) (Wang *et al.*, 2019); Shijiazhuang ($215.0 \mu\text{g m}^{-3}$) (Shen *et al.*, 2019); and Delhi, India ($293.1 \mu\text{g m}^{-3}$) (Khanna *et al.*, 2018).

Chemical Composition

Water-soluble Inorganic Ions

Fig. 4(a) shows the mass concentration of WSIs and the ratios of secondary inorganic aerosol (SNA) to WSIs and WSIs to $\text{PM}_{2.5}$ at four pollution levels. The average ratios of WSIs to $\text{PM}_{2.5}$ ($\text{WSIs}/\text{PM}_{2.5}$) were $64.91 \pm 5.04\%$ (56.66–76.99%), explaining the most components of $\text{PM}_{2.5}$ (Fig. 4(a)). In addition, SO_4^{2-} , NO_3^- , and NH_4^+ dominated the WSIs, at a

proportion of $91.62 \pm 3.90\%$. The average NO_3^- concentration ($54.38 \pm 25.09 \mu\text{g m}^{-3}$) was approximately 2 times higher compared to SO_4^{2-} concentration ($25.85 \pm 10.86 \mu\text{g m}^{-3}$). The NO_2 concentration ($54.89 \mu\text{g m}^{-3}$) from emission sources was significantly higher compared to the SO_2 concentrations ($23.86 \mu\text{g m}^{-3}$). Moreover, a high temperature, high relative humidity, and high radiation were more favorable for the formation of SO_4^{2-} (Yang *et al.*, 2018). Hence, lower temperature and radiation levels may not support the formation of SO_4^{2-} during winter in this city.

Almost all the WSIs concentrations increased as the pollution level increased: mild pollution ($63.01 \pm 5.57 \mu\text{g m}^{-3}$) < moderate pollution ($83.60 \pm 9.38 \mu\text{g m}^{-3}$) < heavy pollution ($119.91 \pm 20.59 \mu\text{g m}^{-3}$) < severe pollution ($222.37 \pm 37.69 \mu\text{g m}^{-3}$). The SNA-to-WSIs ratio (SNA/WSIs) and WSIs-to- $\text{PM}_{2.5}$ ratio increased as the pollution levels increased. This indicated an intensification in the secondary formation of winter haze episodes in Xiangyang.

The average ratios of anions to cations at the four pollution levels of mild, moderate, heavy, and severe were 1.06 ± 0.02 , 1.13 ± 0.06 , 1.11 ± 0.06 and 1.09 ± 0.01 , respectively (Fig. 4(b)). The average ratios of anions to cations approached 1,

Fig. 4. (a) WSIs concentrations and (b) PM_{2.5} acidity at the four pollution levels.

with strong positive correlations ($r = 0.96, 0.89, 0.95$ and 0.99 , $p < 0.05$, respectively) between anions and cations. This indicated these ions were the important alkaline and acidic species in the PM_{2.5} (Wang *et al.*, 2005). The ratio of anions to cations is also an effective indicator to study aerosol acidity (Cheng *et al.*, 2014); that ratio exceeded 1 at the four pollution levels, indicating that the aerosols were acidic during the haze episodes.

The NO₃⁻/SO₄²⁻ ratio is generally considered a good indicator to assess the relative contribution of sulfur and nitrogen between stationary sources (e.g., power plant) and mobile sources (e.g., vehicle exhaust) in the atmospheric environment (Yin *et al.*, 2014). The average NO₃⁻/SO₄²⁻ values were 1.61 ± 0.16 , 2.48 ± 0.94 , 2.18 ± 0.70 and 2.39 ± 0.54 at mild, moderate, heavy, and severe pollution level, respectively. The NO₃⁻/SO₄²⁻ value at a mild pollution level was lower compared to the other three pollution levels. This indicated that the mobile sources contributed more to PM_{2.5} at the other three pollution levels compared to the stationary sources at a mild pollution level.

The sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) has also been considered to be indicators for evaluating the secondary transformation processes from gaseous precursors (Yang *et al.*, 2018). In general, SOR and NOR were below 0.10 in the primary pollutant and exceeded 0.10 when the photochemical oxidation of gaseous precursors, SO₂ and NO₂, would occur in atmosphere environment (Feng *et al.*, 2018). The SOR and NOR had similar values at the four pollution levels, with average values of 0.43 ± 0.14 and 0.43 ± 0.09 , respectively. This indicated that the secondary conversion of SO₂ to SO₄²⁻ and NO₂ to NO₃⁻ occurred during haze episodes. The higher SOR and NOR indicated that the oxidation of gaseous precursors may increase, and more secondary aerosols may be present in the ambient air.

Carbonaceous Species

The average concentrations of total carbon (TC; which is the sum of OC plus EC) during haze episodes were $27.22 \pm 8.22 \mu\text{g m}^{-3}$ ($9.68\text{--}47.24 \mu\text{g m}^{-3}$). The proportion of TC to PM_{2.5} was $16.31 \pm 2.20\%$. The concentrations of OC, EC and TC increased as the pollution levels increased (Fig. 5(a)). OC reached the highest and lowest concentrations on Jan. 18 during severe pollution and Jan. 24 during mild pollution, respectively. In contrast, the EC experienced an opposite trend when compared to OC. In addition, the average OC/EC ratio was 3.23 ± 0.67 ($1.59\text{--}4.60$) and reached maximum and minimum levels on Jan. 18 and Jan. 17, respectively.

The OC/EC ratios also increased slowly as the pollution levels increased from mild to moderate to heavy to severe levels of pollution (2.76 ± 0.71 , 3.18 ± 0.57 , 3.29 ± 0.69 , and 3.71 ± 0.69 , respectively). Moreover, the OC/EC ratios may indicate the formation of secondary aerosols when it was higher than 2. The average OC/EC ratios exceeded 2 at the four pollution levels, indicating that secondary aerosols were formed at all four pollution levels. OC was positively correlated with EC ($r = 0.76$, $p < 0.05$) (Fig. 5(b)), indicating they may have the same sources during the sampling period. In addition, low OC/EC ratios ($1.5 < \text{OC/EC} < 2.5$) may suggest the contribution of intensive traffic emissions. In contrast, high OC/EC ratios ($\text{OC/EC} > 2.5$) may imply the rapid transformation of SOC precursors, such as VOCs (Pachauri *et al.*, 2013), during the haze episodes (Fig. 5(c)). The average OC/EC ratio was higher at a severe pollution level than that at a heavy pollution level. This indicated that more secondary organic aerosols were produced during period of severe pollution compared to periods of heavy pollution, followed by periods of moderate and mild pollution. The average mass concentrations of organic matter (OM), primary organic carbon and secondary organic carbon were

Fig. 5. The variations of carbonaceous species at four pollution levels: (a) OC, EC, and TC; (b) estimated species; (c) OC vs. EC; and (d) OC/EC.

estimated using Eqs. (10)–(12) (Li *et al.*, 2019).

$$OM = 1.6 \times OC \quad (10)$$

$$SOC = OC - (OC/EC)_{\min} \times EC \quad (11)$$

$$POC = OC - SOC \quad (12)$$

In this expression, $(OC/EC)_{\min}$ was the minimum value of OC/EC, which was 1.59 in this study. This was consistent with a different study in the cold season (1.60), done by Cesari *et al.* (2018).

Fig. 5(d) shows the variations in the estimated OM, POC, and SOC at four pollution levels. The average OM concentration was $33.18 \pm 10.86 \mu\text{g m}^{-3}$, ranging from $11.57 \mu\text{g m}^{-3}$ to $60.01 \mu\text{g m}^{-3}$. The estimated average mass concentrations of OM, POC and SOC increased as pollution levels increased. This further verifies the aggravation of secondary transformation as discussed above. It was unexpected to have the POC dominate the OC during periods of mild and moderate pollution (62% and 52%, respectively). In contrast, SOC dominated the OC during periods of severe pollution (56%). The proportions of POC and SOC remained at the same level during periods of heavy pollution (50%) in Xiangyang.

Trace Elements

The TE concentrations were 11.24 ± 2.75 , 10.85 ± 4.48 ,

10.71 ± 2.43 and $9.60 \pm 3.54 \mu\text{g m}^{-3}$ at mild, moderate, heavy, and severe pollution levels, respectively. The proportion of TEs to $\text{PM}_{2.5}$ was $6.78 \pm 2.86\%$. Eleven trace elements, including As, Sb, Al, Zn, Si, Pb, Co, Mn, Ba, As, and Sn, dominated 96.80% of the mass concentrations of TEs. Fig. 6 shows the variation in the mass concentrations of trace elements at the four pollution levels. The mass concentrations of Li, Al, Mn, Cu, Zn, Se, Sr, Cd, Sn, Tl and Bi increased as pollution levels intensified, while the mass concentrations of Co, Sb and Th decreased as pollution levels increased. This may be due to variations in emissions from industrial sources or influences from meteorological conditions.

Pb/Cd ratios are commonly used to distinguish the sources of metals (Bressi *et al.*, 2014). The results showed that the average Pb/Cd ratios at moderate and severe pollution levels (46.42 ± 14.14 and 38.11 ± 4.79 , respectively) approached 46 (anthropogenic emissions). This indicated that Pb and Cd can likely be attributed to anthropogenic activities at these two pollution levels. In addition, Pb correlated well with Cd at times of heavy pollution ($r = 0.74$, $p < 0.05$), indicating they may come from the same sources. V/Ni ratios are generally used to characterize industrial emissions (0.7–1.9) and shipping emissions (2.1–3.1) (Mamane *et al.*, 2008; Bressi *et al.*, 2014). The average V/Ni ratio ranged from 0.7–1.9 at moderate and heavy pollution levels, except for mild and severe pollution levels. This indicated that V and Ni can be attributed to industrial processes at moderate and heavy pollution levels. Meanwhile, V was positively correlated well

Fig. 6. The concentrations of trace elements at the four pollution levels. (The pink arrow and black arrow represent an uptrend and downtrend, respectively.)

with Ni at mild and severe pollution levels ($r = 0.78, 0.97, p < 0.05$). This indicated that V and Ni may have the same sources at these two pollution levels.

Chemical Mass Closure

Chemical mass closure, including mineral dust (MD; i.e., soil, dust, or mineral), trace element oxides (TEOs), OM, EC, SNA, Cl⁻ and unidentified matter (UM), were calculated to better understand the PM_{2.5} chemical compositions, which were estimated by Eqs. (13)–(16) (Zhang *et al.*, 2013; Kong *et al.*, 2015; Zheng *et al.*, 2019).

$$MD = Si \times 2.14 + Ti \times 1.67 + Al \times 1.89 + Mn \times 1.59 + Mg \times 1.67 + Ca \times 1.95 + Na \times 1.35 + K \times 1.21 + Fe \times 1.43 \quad (13)$$

$$TEO = [(Sr + Ba + Mn + Co + Rb + Ni + V) \times 0.5 + (Cu + Zn + Mo + Cd + Sn + Tl + Pb + As + Cs) \times 1.0] \times 1.3 \quad (14)$$

$$SNA = [SO_4^{2-}] + [NO_3^-] + [NH_4^+] \quad (15)$$

$$UM = PM_{2.5} - MD - TEO - OM - EC - SNA - Cl^- \quad (16)$$

Figs. 7(a)–7(d) presents the percentage variation of species in PM_{2.5} at the four different pollution levels. The percentage of SNA in PM_{2.5} increased with the aggravation of pollution levels, while the percentage of EC and TEOs in PM_{2.5} decreased as the pollution levels increased. The other species (MD, OM and Cl⁻) fluctuated with an “up-down” trend at four pollution levels, which may imply changes in the contribution of pollution sources to species. Among

them, approximately 80% of PM_{2.5} could be explained by SNA and OM during the whole winter haze episode. On average, about 3.45% of the PM_{2.5} could not be identified in this study, which indicated that the chemical mass of PM_{2.5} at each pollution level was balanced within the limits of error.

Contamination Level

Figs. 8(a)–8(e) show the EF and I_{Geo} values of PM_{2.5}-bound metal(loid)s. The EF values for PM_{2.5}-bound metal(loid)s range widely, from 2 to 100,000 in this study. This indicated that most PM_{2.5}-bound metal(loid)s were impacted by both natural and anthropogenic activities. Most metal(loid)s, including Cr, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Tl, Pb, and Bi (EF > 10), showed significant anthropogenic emissions, most likely from industrial and vehicular activities. The EF values of Be, Th, U, Li, V, Mn, Sr and Ba ranged from 2–10. This indicated that these metal(loid)s were slightly enriched in ambient air and were most likely to be affected both by crustal sources and anthropogenic emissions.

The samples were uncontaminated with Li, Be, Al, V, Sr, Ba, Th, and U (I_{Geo} ≤ 0). The Mn concentration ranged from uncontaminated to moderately contaminated (0 < I_{Geo} ≤ 1), and there was moderate Cr and Ni contamination (1 < I_{Geo} ≤ 2). There was heavy contamination with Cu and Mo (3 < I_{Geo} ≤ 4). As, Ag, and Tl were present at heavy to extreme contamination levels (4 < I_{Geo} ≤ 5). Co, Zn, Se, Cd, Sn, Sb, Pb, and Bi levels signified extreme contamination (I_{Geo} > 5). It is likely that PM_{2.5}-bound metal(loid)s, including Cr, Ni, Cu, Mo, As, Ag, Co, Zn, Se, Cd, Sn, Sb, Pb and Bi concentrations, received significant contributions from anthropogenic emissions (I_{Geo} > 1). Moreover, the EF and

I_{Geo} values for $PM_{2.5}$ -bound metal(loid)s were strongly positively correlated with a consistent variation trend, confirmed by Izhar *et al.* (2016). Moreover, the EF and I_{Geo} values decreased as the pollution levels increased.

Human Exposure and Health Risk

Human Exposure Dose

Table 1 presents the ADEs of $PM_{2.5}$ -bound metal(loid)s during the sampling period for three different exposure

Fig. 7. The chemical mass balance of $PM_{2.5}$ for (a) mild pollution, (b) moderate pollution, (c) heavy pollution, and (d) severe pollution.

Fig. 8. The EF and I_{Geo} values of $PM_{2.5}$ -bound metal(loid)s for (a) mild pollution, (b) moderate pollution, (c) heavy pollution, (d) severe pollution, and (e) entire sampling.

pathways: ingestion, inhalation, and dermal contact. The ADEds of PM_{2.5}-bound metal(loid)s through three different exposure pathways for both children and adults showed the same variation trend ($ADED_{Ing} > ADED_{Der} > ADED_{Inh}$). This result was consistent with a study by Izhar *et al.* (2016). The levels through the ingestion exposure pathway were 1–2 and 3–4 orders of magnitude higher compared to the dermal contact and inhalation exposure pathways, respectively, at the four pollution levels (Table S4). Among all the PM_{2.5}-bound metal(loid)s, U and Sb had the minimum and maximum ADED values (1.56×10^{-3} and 3.97×10^{-1}) for both children and adults through all the three exposure pathways. Moreover, the ADEds for children through the three exposure pathways were approximately 6-fold higher than for adults. This indicated that children tended to be exposed to more PM_{2.5}-bound metal(loid)s than adults. However, the results were obtained only due to exposure to PM_{2.5}-bound metal(loid)s in this study.

Non-carcinogenic Risk

Fig. 9(a) provides the non-carcinogenic risks due to exposure to PM_{2.5}-bound metal(loid)s (As, Cd, Cr(III), Co, Cu, Mn, Ni, Zn, Pb, Ag, Al, Ba, Mo, Sb, Sr, U and V) for children and adults during the sampling period. The HI values ranged from 4.10×10^{-3} – 2.64×10^3 and 1.45×10^{-3} – 3.03×10^3 for children and adults, respectively, through the three exposure pathways. Among all the PM_{2.5}-bound metal(loid)s, Sr and Sb had the minimum and maximum non-carcinogenic risks, respectively, for both children and adults through the three different exposure pathways. The total non-carcinogenic risk was slightly higher for adults (3.07×10^3) compared to children (2.71×10^3). The total non-carcinogenic risks decreased as the pollution levels increased for both children and adults: mild pollution (4.22×10^3 and 4.84×10^3) > moderate pollution (2.49×10^3 and 2.81×10^3) > heavy pollution (1.65×10^3 and 1.86×10^3) > severe pollution (1.05

$\times 10^3$ and 1.19×10^3).

This outcome may be due to the fact that TE concentrations dropped as the pollution levels increased, consistent with the section “Trace elements,” in which As, Cr(III), and Pb had greater non-carcinogenic risks on human health among all the metal(loid)s. With the exception of Co for children and V for adults, the total non-carcinogenic risks of As, Cr(III), Pb and Sb were more significant both for children and adults among all the PM_{2.5}-bound metal(loid)s during the winter haze episodes.

Carcinogenic Risk

Fig. 9(b) presents the carcinogenic risks due to exposure to PM_{2.5}-bound metal(loid)s (As, Cd, Co, Cr(VI), Ni and Pb) for children and adults during the sampling period. The decreasing order of carcinogenic risks due to exposure to PM_{2.5}-bound metal(loid)s followed similar trends for both children and adults: As > Pb > Cr(VI) > Co > Cd > Ni. The CR values ranged from 7.28×10^{-9} – 1.87×10^{-3} and 1.64×10^{-8} – 3.30×10^{-3} for children and adults, respectively, through the three different exposure pathways. Among all the PM_{2.5}-bound metal(loid)s, Ni and As were found to pose the minimum and maximum carcinogenic risks for both children and adults, respectively, through the three different exposure pathways. The total carcinogenic risks were also slightly higher for adults (3.78×10^{-3}) compared to children (2.99×10^{-3}).

The total carcinogenic risk decreased as the pollution levels increased for both children and adults: mild pollution (1.64×10^{-1} and 2.21×10^{-1}) > moderate pollution (2.71×10^{-3} and 3.77×10^{-3}) > heavy pollution (2.27×10^{-3} and 2.30×10^{-3}) > severe pollution (1.48×10^{-3} and 1.65×10^{-3}). This may be due to fact that TE concentrations fell as pollution levels increased, as discussed above in the section “Trace elements.” The elements As, Cr(VI), and Pb resulted in greater carcinogenic risks to human health among all the

Table 1. The average daily exposure doses (mg kg⁻¹ day⁻¹) of PM_{2.5}-bound metal(loid)s for the three different exposure pathways during the sampling period.

Metal(loid)s	Children				Adults			
	$ADED_{Ing}$	$ADED_{Inh}$	$ADED_{Der}$	$ADED$	$ADED_{Ing}$	$ADED_{Inh}$	$ADED_{Der}$	$ADED$
As	1.26E-02	3.52E-07	1.32E-03	1.39E-02	1.67E-03	2.45E-07	2.85E-03	4.52E-03
Cd	7.61E-04	2.13E-08	2.66E-06	7.64E-04	1.01E-04	1.48E-08	5.75E-06	1.07E-04
Cr	5.48E-03	1.53E-07	1.92E-04	5.68E-03	6.12E-04	9.01E-08	3.49E-04	9.62E-04
Co	3.09E-02	8.64E-07	1.08E-03	3.20E-02	4.10E-03	6.03E-07	2.34E-03	6.44E-03
Cu	7.76E-03	2.17E-07	2.72E-04	8.04E-03	8.32E-04	1.22E-07	4.74E-04	1.31E-03
Mn	1.51E-02	4.22E-07	5.28E-04	1.56E-02	1.62E-03	2.38E-07	9.22E-04	2.54E-03
Ni	3.93E-03	1.10E-07	1.38E-04	4.07E-03	5.21E-04	7.66E-08	2.97E-04	8.18E-04
Zn	6.22E-02	1.74E-06	2.18E-03	6.44E-02	6.67E-03	9.81E-07	3.80E-03	1.05E-02
Pb	4.87E-02	1.36E-06	1.70E-03	5.04E-02	6.45E-03	9.49E-07	3.68E-03	1.01E-02
Ag	9.93E-05	2.77E-09	3.47E-06	1.03E-04	1.06E-05	1.56E-09	6.06E-06	1.67E-05
Al	2.61E-01	7.28E-06	9.12E-03	2.70E-01	2.79E-02	4.11E-06	1.59E-02	4.38E-02
Ba	1.12E-02	3.12E-07	3.91E-04	1.16E-02	1.20E-03	1.76E-07	6.83E-04	1.88E-03
Mo	6.09E-04	1.70E-08	2.13E-05	6.30E-04	6.52E-05	9.59E-09	3.72E-05	1.02E-04
Sb	3.84E-01	1.07E-05	1.34E-02	3.97E-01	4.11E-02	6.04E-06	2.34E-02	6.45E-02
Sr	2.09E-03	5.85E-08	7.33E-05	2.17E-03	2.24E-04	3.30E-08	1.28E-04	3.52E-04
U	3.26E-05	9.10E-10	1.14E-06	3.37E-05	3.49E-06	5.13E-10	1.99E-06	5.48E-06
V	1.50E-03	4.20E-08	5.27E-05	1.56E-03	1.61E-04	2.37E-08	9.19E-05	2.53E-04

Fig. 9. The human health risks due to exposure to PM_{2.5}-bound metal(loid)s for children and adults: (a) non-carcinogenic risk and (b) carcinogenic risk. (The green, violet, and cyan dash line means carcinogenic risk is very low ($CR \leq 1 \times 10^{-6}$), low ($1 \times 10^{-6} \leq CR < 1 \times 10^{-4}$), moderate ($1 \times 10^{-4} \leq CR < 1 \times 10^{-3}$), high ($1 \times 10^{-3} \leq CR < 1 \times 10^{-1}$) and very high ($CR \geq 1 \times 10^{-1}$)).

metal(loid)s. Therefore, the non-carcinogenic and carcinogenic risks due to exposure to PM_{2.5}-bound metal(loid)s mainly depended on the concentrations of PM_{2.5}-bound metal(loid)s, and may not have been dependent on the pollution levels.

Carbonaceous species, such as polycyclic aromatic hydrocarbons (PAHs), may impact human health and need to be more fully evaluated in the future. The total non-carcinogenic risks of As and Pb were at or above moderate levels for both children and adults. In contrast, the total non-carcinogenic risks of Cr(VI), Co, Cd, and Ni were below moderate levels for both children and adults among all the PM_{2.5}-bound metal(loid)s. The results indicate that the public and government should implement effective measures to mitigate health risks, including non-carcinogenic and carcinogenic risks due to exposure to these PM_{2.5}-bound metal(loid)s during the winter haze episode in Xiangyang.

CONCLUSIONS

In this study, we collected forty-eight samples of PM_{2.5} during a 12 d winter haze episode (Jan. 13–24, 2018) in Xiangyang of central China in order to determine their characteristics, chemical composition, and associated health risks. On average, the daily concentrations of the PM_{2.5}-bound WSIs, OC, EC, and TE equaled 111.45 ± 44.62 , 20.74 ± 6.79 , 6.48 ± 1.79 , and $10.53 \pm 3.84 \mu\text{g m}^{-3}$, respectively, and that of the total PM_{2.5} equaled $169.29 \pm 56.98 \mu\text{g m}^{-3}$, which exceeded the national secondary standard by 2.26 times. The

high PM_{2.5} concentrations during episodes of severe pollution may have been partially due to the arrival of air masses from the NNW–NE, whereas the lower concentrations during periods of less pollution may have been influenced by air masses from the NW–NE or NW–SW.

The OC/EC ratios indicated mixed contributions from intensive traffic emission and secondary formation; hence, the estimated OM, POC, and SOC concentrations predictably increased with the pollution level. However, the POC unexpectedly dominated the OC during mild and moderate pollution, whereas the SOC dominated it during severe pollution.

Additionally, the contamination levels for PM_{2.5}-bound metal(loid)s evaluated by the enrichment factor (EF) and geo-accumulation index (I_{Geo}) values exhibited a strong positive correlation, but significant anthropogenic emissions also played a role in enriching these PM_{2.5}-bound elements.

Of the PM_{2.5}-bound metal(loid)s, As, Cr, Pb, and Sb pose potential non-carcinogenic risks to both children and adults, and two of these elements, As and Pb, also pose potential carcinogenic risks. The average daily exposure doses via ingestion, dermal contact, and inhalation displayed the same trend for both children and adults, $ADED_{\text{Ing}} > ADED_{\text{Der}} > ADED_{\text{Inh}}$, but the total non-carcinogenic and carcinogenic risks were slightly higher for adults (3.07×10^3 and 3.78×10^{-3} , respectively) than children (2.71×10^3 and 2.99×10^{-3}) and primarily depended on the concentrations of the metal(loid)s, not the level of pollution. Thus, the public and

the government should implement efficient measures for mitigating the health risks posed by PM_{2.5}-bound metal(loid)s during winter haze episodes in Xiangyang. Furthermore, carbonaceous species, such as PAHs, may also harm human health and therefore should be more comprehensively investigated in the future.

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DISCLAIMER

The authors declare no competing financial interest.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2020.02.0068>

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