

The Characteristics of Exposure and Health Risk to PM_{2.5} for Urban Cyclists

Wang Bao Qing*, Liu Bo Wei, Niu Hong Hong, Liu Jian Feng, Ren Zi Hui, Chen Rong Hui, Wang Ze Bei and Zhao Jia Jia

College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

Abstract

To study the characteristic of inorganic elements, carbon species, PAHs of exposure and elements health risk to PM_{2.5} for urban cyclists in Tianjin. Exposure to PM_{2.5} samples in cycling were collected during Summer in Tianjin. The non-carcinogenic risk and carcinogenic risk of personal exposure heavy metal in PM_{2.5} were discussed. The average personal exposure mass concentration of PM_{2.5} is 340.63 µg/m³ in the weekday, 281.25 µg/m³ at the weekend for cyclists. Enrichment factor analysis showed that Pb, Zn, Ni, and Cu exhibited heavy or extreme contamination, indicating the influence of anthropogenic sources, but K, Ca, Mg, Mn and Fe were minimally enriched and were mainly influenced by crustal sources or lesser anthropogenic sources. The average SOC is 23.33 µg/m³. The proportion of SOC is 34.78% in OC. PAHs in PM_{2.5}, 2-ring and 3-ring compounds were predominant with NAP, PHE and ACY accounting for 25%, 48% and 9% of PAHs for the personal exposure for cyclist, respectively. For non-carcinogenic effects, Hazard index values for all studied metals were lower than the safe level of 1 for cyclists. The carcinogenic risk for Cr and Ni were all below the acceptable level (10⁻⁴~10⁻⁶). The present study demonstrated the elements health risk in Urban Cyclists. The study may provide a scientific basis for protecting cyclists's health and safety.

Keywords: PM_{2.5}; Cyclists; Inorganic elements; Carbon specials; PAHs; Health risk

Introduction

Bicycle sharing schemes have become increasingly popular in countries throughout Europe, Asia, and America to encourage cycling as an alternative means of transport in urban areas [1]. The World Health Organization report on the health effects of traffic-related air pollution points out that people spend 1-1.5 h/d commuting in many countries [2]. Health effects such as myocardial infarction have been specifically linked with presence in the transport environment [3].

In China, a combination of rapid industrialization and high population density has inevitably made the air quality deteriorating, of which PM (particulate matter) has been frequently observed as the principal pollutant in most urban area [4]. Tianjin is also faced with serious problems of particulate matter pollution and poor visibility. The problem is compounded by the fact that traffic congestion has caused many vehicles to stay on the road and in traffic microenvironments for extended stretches, exposing the commuters of these vehicles to air pollutants over prolonged periods of time [5]. Tianjin is a major city of a production of bicycle and also is a city of cycling as a mode of transport. So, it is vital investigate cyclists' exposure to traffic-related air pollutants.

Recent studies investigated the exposure of commuters in different commuting modes. Rank et al. [6] measured higher total dust concentrations when driving in cars than when riding on bicycles in the city of Copenhagen. Adams et al. [7-9] detected highest exposures to PM_{2.5} in buses, followed by cars, and lowest on bicycles in London. They found that elemental carbon (EC) exposure was highest when riding in cars, followed by buses, and lowest when riding on bicycles. Kaur et al. [10] found that exposure to particulate matter was higher in buses and cars than were exposures encountered during walking or cycling in central London. In another study, McNabola et al. [11] found that PM_{2.5} exposures were highest in buses, followed by cars and bicycles, and lowest when walking in Dublin. Simon et al. [12] found that car and bus occupants were exposed to higher average levels of UFP than cyclists in Christchurch, New Zealand. Karanasiou et al. [13], reviewed personal exposure to particulate air pollution during commuting in European cities for different modes. Above studies located in the clean Europe and Oceania, and showed exposure to particulate matter was

higher in buses or cars than were exposures encountered during walking or cycling. However, Huang et al. [5] found that taxi commuters were exposed to lower concentrations of PM_{2.5} compared with bus commuters and cyclists in Beijing. That is, PM_{2.5} exposures were highest when walking in Beijing. It is possibly related this situation to high PM_{2.5} concentration in China. However, there are few studies exploring personal exposure to PM_{2.5} for cyclists in China.

Research into cyclist's exposure to PM_{2.5} has focused on measuring actual exposure levels of samples of cyclists on pre-selected routes using personal samplers. In this paper we present the results of measurements of concentrations of fine particulate matter on a bicycle.

Materials and Methods

Study design

The study was performed in the summer of Tianjin on August 15-24. No measurements were taken during days with rain. A selected route of approximately 6 km that linked Sheng-an Street bus station and Sports Hotel bus station along three main roads (Nanmenwai Street, Weijin Road and Weijin south Road). This route is one of the "8 ring roads" in Tianjin that commuters frequently use and this road was selected because there are two universities and two spots in this section of the road and heavy congestion can reflect the traffic situation of most of the main roads in Tianjin. We selected 4 non-smoking volunteers and simultaneously collected commuters exposure data to PM_{2.5} on the same route. The volunteers carried real-time PM_{2.5} monitors during both traffic heavy times (07:00-09:00 in the morning and 17:00-19:00 in

*Corresponding author: Wang Bao Qing, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China, Tel: +13702057415; E-mail: wbcchina@163.com

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PM _{2.5} exposure	Equipment	Number of samples	Mean, µg/m ³	Min-max	References
London, UK	High flow personal sampler	56	23.5	6.8-76.2	[7]
London, UK	High flow personal sampler	48	33.5	9.7-77.5	[10]
Dublin, Ireland	High flow personal sampler (HFPS)	56 (route 1) 48 (route 2)	88.1 (route 1) 71.6 (route 2)		[11]
Amnhem, Netherlands	Personal aerosol monitor, DataRAM	16 (days)	72.3 (high traffic) 71.7 (low traffic)		[23]
Beijing, China	4L/min flow personal sampler	43	49.10	18.9-112.5	[5]

Table 1: Related Studies about Exposure Levels When Commuting by Bicycle.

the afternoon). During the sampling periods, volunteers departed from the start point of the route and returned from the end point through the same route.

PM_{2.5} measurement

When commuting by bicycle, volunteers wore a small bag with two PM samplers on their back. Tubes attached to air intakes of each instrument were run to collect measurements as close as possible to participants' breathing zones.

There are eight Libra LP-5 sampling pumps (BUCK, USA) and fine particle separate devices (PEM-2000-25AA, SKC, USA) fitted with 37 mm 2.5 µm pore size polytetrafluoroethylene (PTFE) filters that connected to collect PM_{2.5} at a flow rate of 4.000 L/min. Before sampling, PTFE filters were heated for one hour in the 60°C oven, then conditioned in a room with constant temperature and relative humidity for at least 72 h and weighed using a microbalance (XS105, Mettler Toledo, USA) with 0.01 mg precision. After sampling, PTFE filters were also conditioned in a same room for 48 h, then weighed using same microbalance to analysis PM_{2.5}. The climate controlled weighing room had a temperature of 20°C ± 2°C, and relative humidity of 37% ± 2%. The mini-BUCK soap film flow calibrator (M-30, BUCK, USA) is used for correction of sampling pump flow to make sampling flow stabilized in 4.000 ± 0.100 L/min.

Chemical analysis

Inorganic elements: The PTEE filters were used to analyze the inorganic elements. Some elements in PM_{2.5} are measured by ICP-OES (Vista-MPX, Varian Co, USA), such as Al, Fe, Ca, Ba, Si, Mg, Sr and Ti. Ten metals, including V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd and Pb, were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) (Agilent 7500a, Agilent Co. USA). Each polypropylene filter was cut into pieces and placed to a 100 mL polyfluortetraethylene beaker with 5 mL HNO₃ (pH=5.6) and a drop of HF (pH=5.3) was added. After being covered, the solution was heated on a hot plate at 220°C for 2.5 h. Then the hot plate was shut off and 5 mL hydrochloric acid was added to the solution which was then transferred into a 10 mL plastic bottle. Finally, the digested samples were diluted to 10 mL with deionized water.

Carbon species: OC and EC were analyzed by Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer [14-17]. In the analysis, a 0.188 cm² punch from the quartz fiber filter sample was analyzed and the four OC fractions (OC1, OC2, OC3, and OC4) were respectively obtained at 120, 250, 450, and 550°C in a helium atmosphere; the pyrolyzed carbon fraction (OP) was determined when a reflected laser light attained its original intensity after O₂ was added to the analysis atmosphere; and three EC fractions (EC1, EC2, and EC3) were respectively obtained at 550, 700, and 800°C in a 2% O₂/98% helium atmosphere. Each day the analyzer was calibrated with known quantities of CH₄. One sample per group of 10 samples was repeated. In all the procedure, the blanks filters were also analyzed to get the blank

OC and EC concentrations. The average blank concentrations were used to correct the sample results.

PAHs analysis: For PAHs analysis, the filters were extracted ultrasonically with dichloromethane, concentrated using a rotary evaporator, purified with a silica gel cleanup technique, re-concentrated by rotary evaporation, and finally condensed to exactly 1 ml under a gentle nitrogen stream in 60°C water bath. The extracts were transferred into two ampoule bottles and stored in refrigerator until GC/MS analysis. The PAHs determined in the process were: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(ah)anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP) and benzo(g,h,i)perylene (BghiP).

PAHs in the final extracts were analyzed with a trace 2000 GC/MS (Thermo Finnigan, USA) apparatus with selected ion monitoring (SIM). Each standard and sample was measured in duplicate, and the sample was re-analyzed if the relative standard deviation of the two measurements was higher than 5%. For every set of 10 samples, a reference sample was run to check the interference and cross-contamination, and minimize any errors due to losses during the extraction, cleaning, and concentration procedures.

Results and Discussion

PM_{2.5} concentrations

Bicycle commuting is being encouraged in many cities around the world to improve public health, air quality, and traffic congestion. However PM_{2.5} which emits from motor vehicles can result in bicycle commuting health risk. The mass concentration of PM_{2.5} ranged from 234.38 to 427.08 µg/m³, with an arithmetic average of 340.63 µg/m³ in the weekday for cyclist, but the arithmetic average concentration is 281.25 µg/m³ at the weekend. It resulted from the different traffic volume in weekday and weekend. The traffic volume is 5122 and 4507 vehicle/h in weekday and weekend, respectively. So, the traffic volume is also important factor to the exposure to PM_{2.5}. Ni [18] carried out a field investigation measuring elderly personal exposure to PM_{2.5} in Tianjin family community and showed that personal exposure concentrations of PM_{2.5} were 124.2 ± 75.2 µg/m³ in June and 170.8 ± 126.6 µg/m³ in December of 2011, which is lower than the results of our experiment. The major reason is related to the higher concentration of PM_{2.5} nearby the road for cyclist. Kaur et al. [19] thought that the mass concentration of PM_{2.5} ranged from 9.7 to 77.5 µg/m³, with an arithmetic average of 33.8 µg/m³ for cyclist. The possible reason is that there are lower concentration of PM_{2.5} in the ambient environment around a street canyon intersection in Central London, UK. Weichenthal et al. [20] concluded that an interquartile range increase in UFP levels (18,200/cm³) was associated with a significant decrease in high-frequency power 4 h after the start of cycling. So we easily know it is significant that the concentrations of PM_{2.5} personal exposure are connected with the

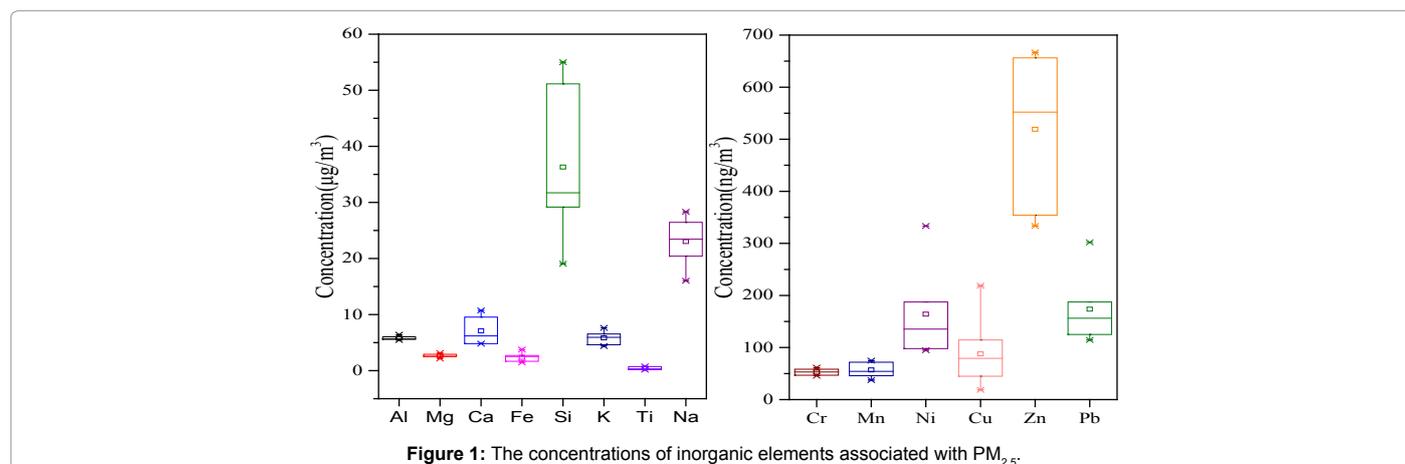


Figure 1: The concentrations of inorganic elements associated with PM_{2.5}.

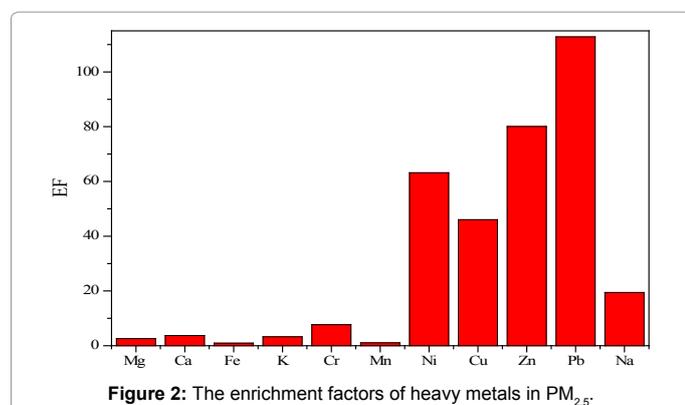


Figure 2: The enrichment factors of heavy metals in PM_{2.5}.

respiratory rate and the concentration of PM_{2.5} in ambient environment while cycling. Table 1 is other related studies about exposure levels when commuting by bicycle. Exposure to air pollution while cycling in urban areas is generally considered high if taking into account that the minute ventilation (volume of air per minute) of cyclists is 1-5 times the minute ventilation of car and bus passengers [13,21,22].

Inorganic elements

The inorganic elements attached to PM_{2.5} were usually more concern because of heavily polluting in recent years [23-25]. The concentrations of inorganic elements associated PM_{2.5} were showed in Figure 1.

Enrichment factor (EF) is a good tool to differentiate the metal source between anthropogenic and naturally occurring [26,27]. According to this way, metal concentrations were normalized to metal concentrations of certain elements [28,29].

The metal enrichment factor (EF) is defined as follows:

$$EF = \frac{C_{sample} / C_{refsample}}{C_{background} / C_{refbackground}} \quad (1)$$

Where, EF refers to the Enrichment factor of element; C_{sample} refers to concentration of the examined metal in PM_{2.5}; C_{refsample} refers to concentration of the reference metal in PM_{2.5}; C_{background} refers to concentration of the examined metal in the topsoil of Tianjin; C_{refbackground} refers to concentration of the reference metal in the top soil of Tianjin.

In our study, Al was selected as a reference element to differentiate

and quantify the degree of inorganic elements pollution. In general, the enrichment level can be divided into 5 degrees including deficiency to minimal enrichment (EF<2), moderate enrichment (2 ≤ EF<5), significant enrichment (5 ≤ EF<20), very highly enrichment (20 ≤ EF<40) or extremely enrichment (EF ≥ 40) [30].

Figure 2 shows the enrichment factors of inorganic elements in PM_{2.5}. The EF can be used to identify the potential sources of crustal and anthropogenic components. Among the investigated elements, the enrichment level was extremely enrichment for Pb, Zn, Ni, and Cu, significant enrichment for Na and Cr, moderate enrichment for K, Ca and Mg, minimal enrichment for Mn and Fe. High EF value were obtained for for Pb, Zn, Ni, and Cu, which suggested the predominance of non-crustal sources such as vehicular exhaust and industrial emission. Relatively lower EFs values were observed for Na, Cr, K, Ca, Mg, Mn and Fe, suggesting a lesser contribution from anthropogenic sources.

Table 2 shows Pearson's correlation coefficients between elements in PM_{2.5}. The Pearson's correlation coefficients for element Ca had good relationship with Si, K and Ti, and for Si with Mg, Ca and Fe, and for Ti with Ca, Si and K, and for Na with K and Ti. These indicate they mainly originated from the crustal sources, for they were typical crustal elements. The Pearson's correlation coefficients were 0.855, 0.728 and 0.741 between Al and Pb, Mn and Cu, Mn and Zn, respectively, indicating that these elements were likely related to urban anthropogenic sources, such as traffic sources and coal combustion. Coal analyses have indicated that certain elements (Pb, Cu, Zn, Mn, etc.) are ubiquitous in the matrix, and experiments have indeed demonstrated that coal trace elements, especially for semivolatile elements, such as Cu, Pb, and Zn, are released to the atmosphere in effluents of most combustion processes [31,32].

Carbon species

The exposure concentrations of OC in PM_{2.5} ranged between 50.16 and 98.09 µg/m³, with an average of 67.09 µg/m³, EC between 4.37 and 7.84 µg/m³, with an average of 6.45 µg/m³, while TC between 55.31 and 104.25 µg/m³, with an average of 73.53 µg/m³, respectively.

Turpin et al. [33] pointed that the OC/EC ratio exceeding 2.0-2.2 has been used for identification and evaluation of secondary organic aerosols. In our study, the average OC/EC ratio was 10.71, indicating the possible presence of secondary organic carbon (SOC). Some researcher hold the idea that the value of OC/EC can determine the extent of secondary pollution [34-36].

	Al	Mg	Ca	Fe	Si	K	Ti	Na	Cr	Mn	Ni	Cu	Zn	Pb
Al	1													
Mg	-0.121	1												
Ca	-0.289	0.846	1											
Fe	-0.158	0.535	0.399	1										
Si	-0.28	0.821	0.928	0.77	1									
K	-0.078	0.101	0.727	0.034	0.496	1								
Ti	-0.148	0.542	0.818	0.16	0.855	0.808	1							
Na	-0.3	0.122	0.61	0.106	0.451	0.92	0.798	1						
Cr	0.212	0.312	-0.172	-0.491	-0.217	-0.377	0.089	-0.212	1					
Mn	-0.104	0.094	0.188	0.588	0.146	0.453	0.099	0.519	-0.707	1				
Ni	-0.054	0.605	-0.515	-0.024	-0.21	-0.891	-0.434	-0.827	0.661	-0.642	1			
Cu	-0.353	0.347	0.257	0.795	0.374	-0.323	-0.168	-0.229	-0.639	0.728	-0.187	1		
Zn	0.16	-0.193	-0.495	0.069	-0.634	0.004	-0.166	0.228	0.009	0.741	0.057	0.454	1	
Pb	0.855	0.457	-0.405	0.404	-0.247	-0.439	-0.431	-0.629	-0.037	0.34	0.238	0.247	0.574	1

Table 2: The Pearson's correlation between elements in PM_{2.5}.

Parameter	Definition	Value	References
C	Average concentration(mg/Kg)		
EF	Exposure frequency (days/year)	365	[47]
ED	Exposure duration (years)	24	[48]
BW	Body weight (kg)	62.63	In this study
AT	Averaging time (days)	Non-carcinogens, AT= ED × 365 days/year Carcinogens AT=7 year × 365 days/year	[47] [49]
PEF	Particle emission factor	1.36 × 10 ⁹	[50]
InhR	Inhalation rate(mg/day)	14.95	[51]

Table 3: Reference exposure factor.

Following the Castro's equation [37], the concentration of SOC could be calculated by the experimentally derived equation:

$$SOC = OC_{tot} - EC \times \left(\frac{OC}{EC} \right)_{min} \quad (2)$$

Where SOC for secondary organic carbon, OC_{tot} is the total organic carbon concentration in the sample, EC is the elemental carbon concentration in the sample, $(OC/EC)_{min}$ is the minimum value of OC/EC.

Secondary organic carbon is the formation of gaseous organic pollutants by means of photochemical reaction products. The average SOC results in this study is 23.33 $\mu\text{g}/\text{m}^3$. The proportion of SOC is 34.78% in OC. SOC/OC can be used to characterize the extent of secondary pollution of the atmosphere, the higher the ratio indicates the higher degree of secondary pollution. It shows that the secondary pollution in Tianjin is very serious. The result of SOC is significantly higher than in Dezhou (SOC=3.91 $\mu\text{g}/\text{m}^3$) [38] and in Tianjin (SOC=14.6 $\mu\text{g}/\text{m}^3$) [4] studies of individual exposure levels in Tianjin.

The value of TC/PM_{2.5} is 94.12%, which indicate that by the riding process, people sucked component of PM_{2.5}, the carbon occupies the one of the main parts. The value of OC/PM_{2.5} is 85.87%. OC is the basis of atmospheric photochemical reactions [39]. It is the main component of polycyclic aromatic hydrocarbons, hydrocarbons, acids and ketones, aldehydes, etc. These substances are harmful to human health [40].

PAHs

The exposure concentrations of PHE in PM_{2.5} ranged between 18.93 and 27.31 $\mu\text{g}/\text{m}^3$, with an average of 22.87 $\mu\text{g}/\text{m}^3$, NAP between 6.70 and 16.91 $\mu\text{g}/\text{m}^3$, with an average of 11.83 $\mu\text{g}/\text{m}^3$, FLA between 6.39 and 10.95 $\mu\text{g}/\text{m}^3$, with an average of 8.39 $\mu\text{g}/\text{m}^3$, while ACP between 4.12 and 5.83 $\mu\text{g}/\text{m}^3$, with an average of 4.99 $\mu\text{g}/\text{m}^3$, respectively.

The content of the PAHs from high to low are PHE, NAP, FLA and ACY, the rest of the PAHs did not be obtained, because their concentrations are below the detection line. This phenomenon may be related to exposure time is shorter. This result is consistent with the result of the Tianjin exposed children [41]. This shows that in the summer, the highest content of PAHs is phenanthrene in Tianjin. The data showed relatively high levels of 2-3 ring PAHs and much lower levels for the higher molecular weight species. For particulate phase PAHs, 2-ring and 3-ring compounds such as NAP, PHE and ACY accounted 25%, 48% and 9% of PAHs for the personal exposure for cyclist, respectively. These findings are similar to those discussed by Kuo et al. [42] and Bylina et al. [43].

The main source of PHE, NAP and FLA is coal tar. Coal tar is the production of plastics, synthetic fiber, dye, rubber, medicine, high temperature resistant materials and other important raw materials, which can be used in the synthesis of pesticides, saccharin, dyes, drugs, explosives, and other industrial products. The industrial production of primary form of plastic increased by 14%, chemical fiber increased by 15%, 12% growth chemical pesticide, and the product of sugar growth 7%, which illustrate that the increase of the usage of coal tar in tianjin from 2001 to 2010 in Tianjin [44]. This is the reason that the concentration of the PHE, NAP, FLA and ACY are the highest in our study.

Risk Assessment

There are three ways for the body to absorb heavy metals: handling-oral direct ingestion, skin contact and inhalation through the respiratory system. The personal exposure samplings were conducted in this study. So five heavy metals (Cr, Ni, Cu, Zn and Pb) absorbed by inhalation were analyzed to determine heavy metal non-carcinogenic risk to humans [45,46] (Table 3).

	Cr	Ni	Cu	Zn	Pb	HI
ADD _{inh}	2.99E-08	8.89E-08	5.07E-08	2.73E-07	9.07E-08	
HQ	4.98E-04	1.65E-05	4.23E-06	9.12E-07	2.58E-05	5.45E-04
CR	1.25E-06	7.47E-08				

Table 4: The value of the ADD_{inh}, the value HQ potential non-carcinogenic for individual metals and the risk characterization of heavy metals in PM_{2.5}.

Average daily inhalation exposure (ADD_{inh}):

$$ADD_{inh} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (3)$$

The ADD_{inh} value and the value of HQ for potential non-carcinogenic and for individual metals are in Table 4.

The potential non-carcinogenic for individual metals were calculated as follows:

$$HQ = \frac{ADD}{RfD} \quad (4)$$

$$HI = HQ_1 + HQ_2 + \dots + HQ_n \quad (5)$$

Where RfD is the reference dose (mg·kg⁻¹·d). CSF is the cancer slope factor (mg/kg·d)⁻¹. All the equations used in this research referred to USEPA methods and other documents [52-55].

For RfD-ADD_{inh}, RfD_{Cr}=6.00 × 10⁻⁵ mg·kg⁻¹·d⁻¹, RfD_{Ni}=5.40 × 10⁻³ mg·kg⁻¹·d⁻¹, RfD_{Cu}=1.20 × 10⁻² mg·kg⁻¹·d⁻¹, RfD_{Zn}=3.01 × 10⁻¹ mg·kg⁻¹·d⁻¹, RfD_{Pb}=3.52 × 10⁻³ mg·kg⁻¹·d⁻¹.

The Hazard Index (HI) was used to estimate the total non-carcinogenic health risk of multiple metals: HI is the multi-pollutant non-cancer total risk for multiple routes of exposure, when HQ or HI<1.00, it is less non-carcinogenic risk or negligible. From Table 4, it can be seen that HQ_{inh} value for adults was following the order of Cr>Pb>Ni>Cu>Zn, and all values are less than 1. It showed that it exist less non-carcinogenic risk through three routes of exposure for riding process.

Carcinogenic hazard index for metals is defined as:

$$CR = ADD_{inh} \times CSF_{inh} \quad (6)$$

For RfD-CSF_{inh}, CSF_{Cr}=42 (mg/kg·d)⁻¹, CSF_{Ni}=0.84 (mg/kg·d)⁻¹ [53,54].

The carcinogenic risk level for Ni and Cr were both within the range of 10⁻⁴ to 10⁻⁶. Thus, the carcinogenic risk for the two metals indicates that the carcinogenic risk of Ni for cyclists exposure was an acceptable or tolerable risk in Tianjin. Carcinogenic risk for cyclists of Cr is higher than that of Ni.

The results showed that exposure to trace metals in cycling would not cause serious health impacts in the study areas. However, there is a high degree of uncertainty, for example, the assumptions applied in the models seem too ideal, and there were uncertainties of the exposure parameters and the metal toxicity data, and other metals (i.e., Fe, Mn, etc.) were not considered in this study.

Conclusions

The personal exposure levels to PM_{2.5} for cyclists have been analysed and assessed in Tianjin. The elements of Pb, Zn, Ni, and Cu resulted from anthropogenic sources, but K, Ca, Mg, Mn and Fe mainly influenced by crustal sources or lesser anthropogenic sources. The secondary pollution in Tianjin is very significant. PAHs of 2-ring and 3-ring compounds, such as NAP, PHE and ACY, were predominant.

For non-carcinogenic effects, Hazard index values for all studied metals were lower than the safe level of 1 for cyclists. And, the carcinogenic risk for Cr and Ni were all below the acceptable level (10⁻⁴~10⁻⁶).

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