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Pollution evaluation and health risk assessment of airborne toxic metals in both indoors and outdoors of the Pearl River Delta, China

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ABSTRACT

Background: Industries developed cities in the Pearl River Delta (PRD) are suffering serious atmospheric metals pollution, in which, people's health risks after inhaling particulate matter (PM) with airborne toxic metals might be rising. This study provides the latest and comprehensive pollution profiles of toxic metals both from indoors and outdoors in PRD.
Method: Total 22 pairs of indoor and outdoor total suspended particulates (TSP), PM_{10} and $PM_{2.5}$ samples in residential area were synchronously sampled and investigated in detail within 9 main cities of the PRD, China. The concentrations of the Zn, Pb, Mn, Ni, As, V, Sb and Cd in the samples were measured by inductively coupled plasma mass spectrometry (ICP-MS). Health risk assessment via inhalation of residents was estimated by EPA recommended model with exposure parameters of Chinese population indoor and outdoor activity pattern.
Results: The trends followed as Zn > Pb ≈ Mn > Ni > As > V > Sb ≈ Cd for both indoors and outdoors. Investigated metals were found to be dominantly distributed in $PM_{2.5}$ for both indoors and outdoors. The concentrations of outdoor PM and the most of metals were significantly higher than those of indoors. The results concluded that toxic metals might be from regional emission, such as Pb from ceramic factory, Ni from motor factory and V from oil combustion of ship. In health risk assessments, LCR is higher than 1.00E-06 for adults, while contrary to children in the PRD. Among four carcinogenic metals, LCR of As and Cd are higher than 1.00E-06 in some cities. In addition, HI below one for both adults and children in the PRD.
Conclusions: Outdoor metals concentrations are related to local industry types, while indoor metals are mainly from outdoor. Health risk assessments indicated that adults suffered unsafe cancer risk from metals, especially As and Cd in some cities, while both adults and children did not suffer non-carcinogenic risks.

1. Introduction

The rapid economy development of the Pearl River Delta (PRD) in the past few decades have been accompanied by the deterioration of the environmental air quality and haze weather happened frequently in recent years (Wang et al., 2017; Zhang et al., 2008). Along with economy development, large number of workers flooded into the PRD and became long-term residents. Therefore, large number of people in the PRD have inevitably been threatening by air pollution. It has been demonstrated that human exposure to airborne particulate matter (PM) increased the morbidity and mortality of both cardiovascular and respiratory diseases (Meng et al., 2013; Strak et al., 2012), while recent research had found short-term PM exposure can cause human perturbation of the blood metabolome (Vlaanderen et al., 2017). During 1990–2010, ambient air pollution and household air pollution became the leading causes of Chinese residents' death. Ambient air pollution ranked the fourth and household air pollution ranked the fifth of leading causes of death in China, which were based on age-standardized disability-adjusted life-years rate in 2010 (Yang et al., 2013). Several researches have observed that $PM_{2.5}$ or PM_{10} concentrations in the PRD exceeded the annual average guideline values recommended by World Health Organization (WHO) of 10 and 20 $\mu g/m^3$, respectively (Hagler et al., 2006; Ma et al., 2017; Tao et al., 2017; Wu et al., 2013).

To figure out the composition and formation of PM, many studies were carried out on the individual aerosols recently, especially during haze days (Chen et al., 2017; Li et al., 2016, 2017; Zhang et al., 2017). Results showed that higher level of metals on PM were found in fog and haze days as compared with clear weather (Hu et al., 2015). Furthermore, due to insufficient wind speed among urban dense buildings, air pollutants are difficult to be taken away from the city (Katrinak et al.,

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1993). Thus, airborne metals from various sources are enriched in the urban atmosphere. Moreover, metal-containing aerosols continue to collide and bind each other over a long atmospheric residence time with the change of the forms on PM, resulting in heterogeneous reactions of aerosol in haze weather (Hu et al., 2015).

As far as we known, exposure to the airborne toxic metals would directly cause health impact, especially for respiratory system. Once toxic metals absorbed into blood and enriched in the human organs could cause serious illness or even cancers. For example, arsenic (As) and cadmium (Cd) can affect mothers and children's respiratory system, as well as induce fetal inflammation and immune response (Sanders et al., 2014; Smeester et al., 2017). Lead (Pb) affects children's neurodevelopment at low doses through various exposure pathways (EPA, 2006). In addition, blood Pb might influence airflow limitation of general adult population (Chung et al., 2015). Short-term exposure to PM containing Pb, Ba, Cu, Zn or other metals might influence human blood metabolome (Vlaanderen et al., 2017). Other heavy metals in maternal like manganese (Mn) and vanadium (V), which are not so toxic as, were also reported to affect human low weight birth (Jiang et al., 2016; Xia et al., 2016). Due to the difficulty of large-scale residential sampling and synchronous personal sampling of patients, majority of studies researched human health risk from airborne metals with PM samples collected in nearby outdoor environment, which might ignore the effect of indoor toxic metals. Thus, the different sampling method is needed to be developed to obtain more reliable airborne toxic metal exposure data.

As reported in Chinese activity pattern, Chinese people spend most of their time indoors nowadays (Duan, 2016; Duan et al., 2015). Due to the densely distributed housing in cities of PRD region, residential indoor and outdoor toxic metal emission sources might be different from those in countryside. Urban outdoor toxic metals in the PRD are reported mainly from ship emission (Ni and V), soil dust, coal combustion, nonferrous metal smelting, traffic emissions and others (Tao et al., 2017), while indoor PM and metals might be emitted from activity of smoking, cooking or using printers (Bohlandt et al., 2012; Chen and Zhao, 2011; Rohra et al., 2018). In addition, outdoor PM could enter the room by air flow that mainly through natural ventilation, mechanical ventilation and infiltration (Chen and Zhao, 2011). Thus, metals in outdoor PM would be brought to indoors, which might partially consist of indoor metal pollution sources. Furthermore, secondary suspension of indoor dust could affect the indoor PM and metal levels.

Therefore, in this study, to obtain the more real situation of airborne toxic metal exposure doses of residents, indoor and outdoor pollution level within several residential homes were investigated in the PRD and 22 pairs of indoor and outdoor total suspended particulates (TSP), PM_{10} and $PM_{2.5}$ (particulate matters with aerodynamic diameter less than 10 and 2.5 μm) samples in residential area were synchronously collected in 9 cities of the PRD. Then, the concentrations of eight major toxic metals, including V, Mn, nickel (Ni), zinc (Zn), Pb, Cd, antimony (Sb) and As were determined. Furthermore, the effect of outdoor on indoor toxic metal concentrations as well as possible outdoor sources were evaluated, respectively. And the percentage of metals in $PM_{2.5}$, $PM_{2.5\text{-}10}$ (aerodynamic diameters between 2.5 and 10 μm) and $PM_{>10}$ (aerodynamic diameters more10 μm but less than 100 μm) were calculated, to help infer emission sources due to that $PM_{2.5}$ is usually from anthropogenic sources, while $PM_{2.5\text{-}10}$ is from mechanical wear and $PM_{>10}$ is from geological emission (Xu et al., 2017). The exposure doses of toxic metals in this study are used to assess human health risk via inhalation using U.S. Environmental Protection Agency (EPA) method. The findings of this study can be served as a specific instance for environmental protection departments to control urban pollution sources in the PRD.

2. Materials and methods

Study area and samples collecting procedure were described in previous publications (Zhuo et al., 2019). In this study, outdoor air is related to ambient air, while indoor air is related to household air. Total 22 pairs of TSP/PM_{10}/$PM_{2.5}$ were available to study toxic metals hereafter. The geological position of different cities and ocean lines in PRD are shown in Fig. S1.

2.1. Analysis of metal elements

Acid digestion of particle sample is performed to extract the inorganic metal components. The pre-treatment of elemental analysis was assisted by microwave digestion (MARS6, CEM Inc. USA) with classical mode. 1/8 or 1/4 of filter was cut out of the large one and then cut into pieces with cleaned ceramic scissors. Fragments of sample were put into polytetrafluoroethylene digestion tube, digested with 10–20 mL mixed acid (filters should be immersed by mixed acid and each tube should be equal to volume in one patch). The digestion mixed acid consists of 55.5 mL HNO_3 (Thermo Fisher Scientific, USA, ppb degree) and 167.5 mL HCl (CNW, USA, ppb degree), diluting to 1 L with ultrapure water. The digestion program is shown in Table S1. After microwave digestion, the digested solutions were heated at 100 °C for 2 h to remove part of acids to control the acidity of sample solution, which needs to be less than 5%. The filters were dipped for 30 min with 10 mL ultrapure water and then the digested solution was filtered with 0.45 microporous filter membrane. Finally, the digested solution was diluted to a probably concentrations. Take 10 mL filtrate to disposable polyethylene centrifuge tube (CNW, USA) and stored at 4 °C until analysis. This method was based on the Chinese environmental protection standards (HJ 657–2013) established by Ministry of Environmental Protection (MEP) of China (MEP, 2013).

Inductively coupled plasma mass spectrometry (ICP-MS) (ICPQ, Thermo Inc. USA) was employed to measure the concentrations of eight inorganic metals, including V, Mn, Ni, Zn, As, Cd, Sb and Pb. ICP-MS standard solution was commercial multi-element standard solution (160008-01-01, o2si, USA) and standard curve solution was diluted with 1% HNO_3. All of elements' standard curve correlations were more than 0.999. At the same time, we used peristaltic pump to inject the internal standard solution containing 15 μg/L of Ge, Sc, Y, In, Re and Bi (China Nonferrous Metals and Electronic Materials Analysis and Testing Center) to correct matrix drift in the samples. Element concentration (C_{air}, ng/m^3) was calculated after Eq. (1) (MEP, 2013):

$$C_{air} = (C - C_0) \times V_s \times \frac{n}{V} \tag{1}$$

where C and C_0 (μg/L) represent the metal concentration of sample and blank, respectively. V_s (mL) represents constant volume of digestion solution and V represents sampling air volume (m^3, in actual condition). The n (n = 4 or 8) is the proportion digested of whole large sample filter area.

2.2. Quality assurance and quality control

The experimental water is ultrapure water (resistivity ≥18.25 MΩ cm), and the vessels are all made of plastic. All containers in direct contact with the sample should be soaked overnight with 10% HNO_3, rinsed with ultrapure water for at least three times, and placed in a clean place to dry naturally. Each batch of 24 treated samples includes two whole procedural blanks, at least one field blank and one spiked sample. The sample results were deducted from the blank background value. The spiked recovery rates of eight metals in present study were 88–109% (Fig. S2).

2.3. Statistical analysis

Indoor/outdoor concentration ratio (I/O) of each element on PM was calculated and used to estimate how much outdoor air pollution infiltrate into indoor environment (Lim et al., 2011; Pekey et al., 2010), on the premise of minimizing ventilation. Data of I/O ratio were analyzed based on a normal distribution with One-Sample student-t Test ($n < 30$). The coefficient of correlation (r) between indoor and outdoor samples was used as an indirect indicator of the degree to which PM indoors had been transported via infiltration or natural ventilation from outdoors (Massey et al., 2009). Pairwise-Samples student-t test was used to test the significance of correlations between indoor and outdoor samples. In this study, significant level (α) of 0.05 and 0.01 with $df = 20$ are used to test the significance of correlation coefficients. When $p < 0.05$ and 0.01, the correlation between indoor and outdoor data are significant and extremely significant, respectively.

2.4. Health risk assessment

Residents living in PRD are the potential recipients of various metals in the outdoor and indoor air. Toxic metals on PM could be inhaled through breathing by nose and mouth, which are the directly route of exposure to air (Hu et al., 2012). Inhalation health risk assessment of residents in the PRD was carried out according Risk assessment methodology by EPA (EPA, 1989). Risk assessment includes cancer risk and non-carcinogenic risk assessment in this study. Lifetime cancer risk (LCR) values and hazard quotients (HQ) are the representatives of quantitative evaluation, respectively. LCR is the probability of the chance to cancer when exposure to the toxicant, while HQ or hazard index (HI, the sum of multiple toxicant HQs) less than 1 represents no threat to sensitive population (EPA, 1989). For example, LCR of 1E-04 and 1E-06 indicate probabilities of 1 chance in 10,000 and 1,000,000 of an individual developing cancer, respectively. In addition, LCR of 1.00E-04 and 1.00E-06 are also defined as the tolerable and acceptable risk for government regulatory purposes, respectively (Hu et al., 2012). HQ or HI more than 1 indicate that exposure to the toxicant might cause some non-carcinogenic health impact.

Since superfund program has updated the inhalation risk assessment paradigm of calculation, exposure concentration is calculated by Eq. (2) (EPA, 2009). Risk assessment was carried out for the residents at different life stages: children (< 18 years-old) and adults (> 18 years-old). Human activity pattern refers to Chinese Exposure Manual (Duan, 2016; Duan et al., 2015), which reported Chinese activity pattern based on temporal and spatial distribution. In this study, indoor and outdoor activity time of children and adults are selected from the group of Chinese living in the southern urban in summer. Six years-old for children and 24 years-old for adults are the assessed sub-groups (Hu et al., 2012), because people in 6–24 might spend most of time in school and in the present study we focus on people in residential area.

$$EC = C_{air} \times ET \times \frac{1\ day}{24\ hour} \times EF \times \frac{ED}{AT} \tag{2}$$

where EC is exposure concentration and C_{air} is the concentration of metal in environment air ($\mu g/m^3$); ET represents indoor or outdoor exposure time (hours/day), which are 21.8 and 2 h (120 min) for children, while 20.6 (1239 min) and 3 h (180 min) for adults indoors and outdoors, respectively, based on the Chinese populations activity pattern (Duan, 2016; Duan et al., 2015); EF represents exposure frequency (days/year), 350 day/year for residents; ED represents exposure duration (year), here 6 years for children and 24 years for adults were selected; AT represents average time (day) for exposure, ED × 365 days for non-carcinogens and 70 years × 365 day/year for carcinogens, respectively (Hu et al., 2012).

According to current EPA's inhalation risk assessment methodology, inhalation reference concentrations (RfC) and inhalation unit risk (IUR) from the Integrated Risk Information System (IRIS) are used to calculate LCR and HQ by Eqs. (3) and (4) (EPA, 2009). HI is calculated by Eq. (5) (EPA, 1989).

$$LCR = IUR \times EC \tag{3}$$

$$HQ_i = \frac{EC}{RfC_i \times 1000 \mu g/mg} \tag{4}$$

$$HI = \sum HQ_i \tag{5}$$

where EC is $C_{air\text{-}adj}$ of metals in including $PM_{2.5}$ and PM_{10} but excluding $PM_{>10}$, because $PM_{>10}$ generally do not be inhaled. RfCs and IURs for residents exposure to ambient air can be found on the website (EPA, 2018) and we summarized in Table S2. However, due to data lack of zinc in IRIS, health risk assessment of zinc is not included in this study. The chemical forms of metals in air to select RfCs and IURs are as following: As (inorganic arsenic), Ni (nickel soluble salts), Cd (diet), V (vanadium and compounds), Mn (diet), Sb (antimony trioxide) and Pb (lead phosphate as well as lead acetate and subacetate). The soluble nickel salts are selected as the representative form of airborne nickel because the Ni on the PM was reported that mainly derived from the particles produced by combustion, and most of nickel salts are soluble in water (Okuda et al., 2007).

3. Results and discussions

3.1. Mass concentrations of TSP, PM_{10} and $PM_{2.5}$

The geometric mean concentrations of TSP, PM_{10} and $PM_{2.5}$ of indoor and outdoor samples were discussed by others (Zhuo et al., 2019). To generally evaluate the level of pollution in this study, PM concentrations were compared with the guidelines of Ambient Air quality standards (AQS) in 2012 (35, 70 and 200 $\mu g/m^3$ for $PM_{2.5}$, PM_{10} and TSP, respectively, in category second area including residential area) (MEP, 2012) (Fig. 1). The average concentration of each size of PM were lower than the corresponding guidelines but outdoor $PM_{2.5}$, which was approximately 125% of the Chinese guideline in 35 $\mu g/m^3$. But compared to the WHO corresponding guidelines, $PM_{2.5}$ and PM_{10} concentrations exceeded in both indoors and outdoors (10 and 20 $\mu g/m^3$ for $PM_{2.5}$ and PM_{10} of WHO guidelines, respectively) (WHO, 2000; WHO, 2005). On size distributions, both indoor and outdoor $PM_{2.5}$ were dominant, especially for indoor PM (Fig. 1). Particularly, indoor $PM_{2.5}$ was approximately 90% of TSP in the same sampling space and time. Therefore, composition and source of $PM_{2.5}$ might be the focus.

As shown in Fig. 2, indoor and outdoor PM concentrations vary from place to place. For indoor PM, the highest average PM concentrations were found in Zhongshan, followed by Zhaoqing. Overall, $PM_{2.5}$ is the dominant in indoors, because the PM concentration differences between $PM_{2.5}$ and PM_{10} or $PM_{2.5}$ and TSP are little. As reported, $PM_{2.5}$ is mainly from anthropogenic source (Charron and Harrison, 2005; Wang

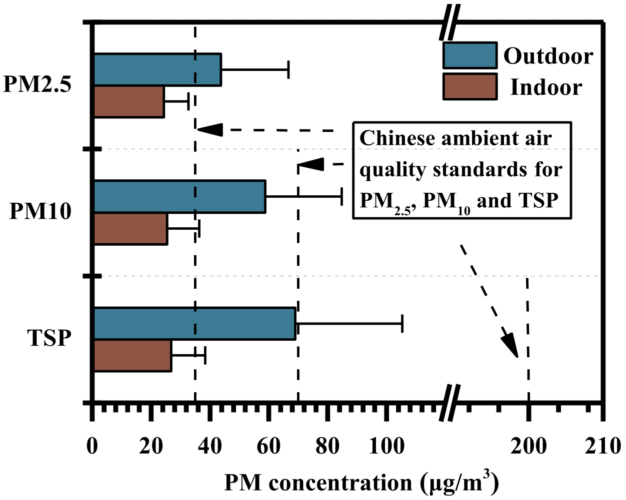

Fig. 1. The mean PM concentrations in the PRD.

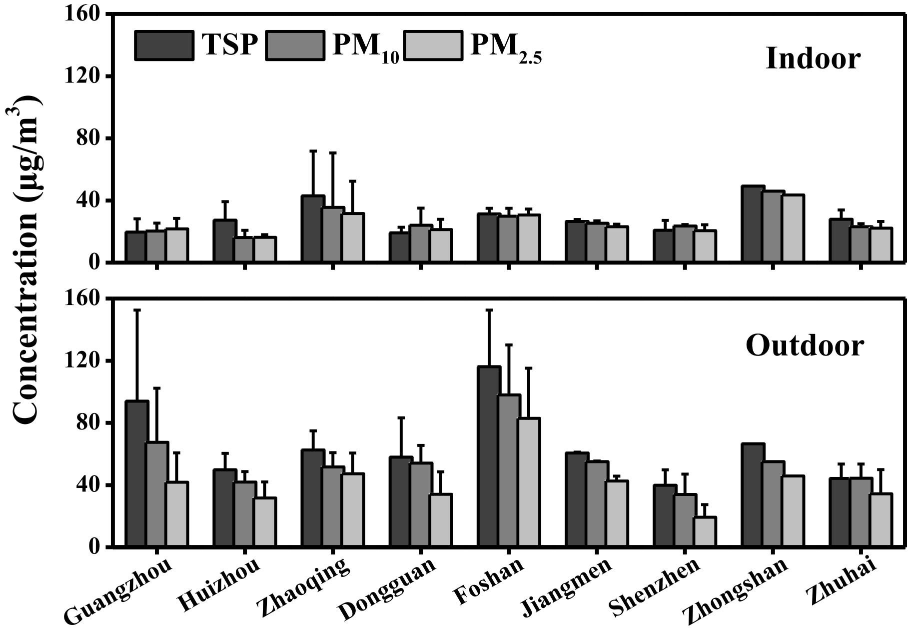

Fig. 2. The indoor and outdoor PM concentration of residential houses in nine cities of the PRD.

et al., 2006; Yeh et al., 2017). For outdoor PM, the highest average PM concentrations were found in Foshan, followed by Guangzhou. As known, Foshan is an industrial developed city in the PRD with wide variety of key industries including ceramics, non-metallic ore processing and household electrical appliances and furniture manufacturing, which are also highly polluting industries (Tan et al., 2016). Whereas, Guangzhou are a rapid economic development city with large population and large energy consumption (Han et al., 2014). As such, the residential area in Foshan and Guangzhou have been affected by local industries and energy consumption. Thus, higher outdoor PM concentrations in Foshan and Guangzhou than other cities were observed as expected in this study. Based on the above analysis, $PM_{2.5}$ is the dominant air pollution, which might be from local industries.

3.2. Metal concentrations in TSP, PM_{10} and $PM_{2.5}$

The mean concentrations of metals analyzed for both indoor and outdoor size segregated PM are presented in Table 1. The trends of indoor and outdoor metal concentrations are both followed by Zn > Pb ≈ Mn > Ni > As > V > Sb ≈ Cd. None of eight metals average concentrations exceeds the guidelines limit of WHO (25, 6.6, 5, 150 and 500 ng/m³ for Ni, As, Cd, Mn and Pb, respectively) (WHO, 2000). As Fig. 3 shows, metals are mainly distributed in $PM_{2.5}$ both indoors and outdoors with the highest percentage of 77% in $PM_{2.5}$ for outdoor V. The proportion of Zn, As, Cd and Pb in outdoor $PM_{2.5}$ are also higher than 70%. However, the proportion of Ni in PM larger than 2.5 μm are higher than other metals, indicating a portion of Ni might be emitted from mechanical abrasion/erosion of metallic surfaces (Okuda et al., 2007).

Further, we found that metal concentrations are quite different among sampling cities. Overall, metal concentrations are significantly higher in outdoor samples than the corresponding samples in indoor ($p < 0.05$ for Cd and $p < 0.01$ for other metals). Eight metal concentrations in indoor and outdoor TSP, PM_{10} and $PM_{2.5}$ are shown in Figs. S3A and S3B, respectively. As mentioned above, Zhongshan and Zhaoqing have higher indoor PM concentrations than other sampling sites but less than in corresponding outdoor PM, which might be caused by higher ventilation rates of the houses (Abt et al., 2000).

Due to the difference in population and industrialization level of each city, outdoor metal distribution is relatively diverse. Foshan has the highest As, Sb, Cd, Zn and Pb concentrations, while Jiangmen has the highest Ni and Mn concentrations and Zn concentration here is just slightly lower than that of Foshan. It is worth noting that V concentrations are the highest in Dongguan and approximately twice higher than those in other cities. However, Shenzhen, Zhuhai and Huizhou have relatively lower metal concentrations. This might be caused by the shower weather in Shenzhen, Zhuhai and Huizhou during sampling period. It is because the rainfall might crush off part of metals

Table 1
Average metal concentrations in indoor and outdoor PM. Unit: ng/m.³.

Metal	Indoor (n = 22) Mean s.d.			Outdoor (n = 22) Mean s.d.			WHO [a] guidelines
	TSP	PM_{10}	$PM_{2.5}$	TSP	PM_{10}	$PM_{2.5}$	
V	0.94 ± 0.68	0.93 ± 0.73	0.87 ± 0.63	4.44 ± 2.30	4.07 ± 2.16	3.83 ± 2.15	-
Mn	6.33 ± 5.72	6.09 ± 5.49	4.97 ± 4.19	25.34 ± 13.12	21.17 ± 12.02	18.20 ± 10.41	150
Ni	1.85 ± 1.46	1.57 ± 1.12	1.46 ± 0.79	7.22 ± 8.98	5.43 ± 5.64	5.14 ± 6.13	25
Zn	31.26 ± 28.33	29.71 ± 26.97	25.74 ± 24.73	106.74 ± 94.96	93.88 ± 86.15	88.60 ± 75.94	-
As	2.01 ± 2.14	1.92 ± 2.05	1.88 ± 2.16	4.80 ± 6.57	4.49 ± 6.31	4.23 ± 5.87	6.6
Cd	0.75 ± 1.32	0.72 ± 1.23	0.69 ± 1.20	0.99 ± 1.29	0.91 ± 1.16	0.92 ± 1.11	5
Sb	0.53 ± 0.45	0.54 ± 0.40	0.47 ± 0.41	1.95 ± 1.16	1.80 ± 1.73	1.39 ± 1.43	-
Pb	7.90 ± 7.71	7.59 ± 4.47	7.52 ± 7.35	27.15 ± 1.11	24.93 ± 28.87	21.23 ± 20.42	500

s.d.: standard deviation.

[a] WHO. Guideline for air quality, 2000.

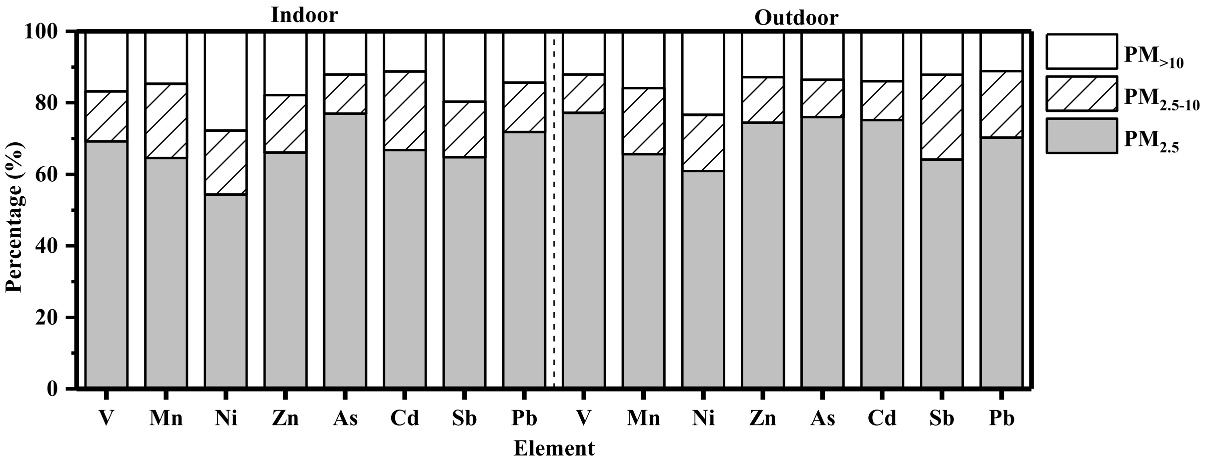

Fig. 3. Metal percentage in size distribution of outdoor and indoor PM.

in air as some forms of metals in air are water-soluble. For example, more than 60% Ni and Zn as well as approximately 40% Pb and Cd are water-soluble in $PM_{2.5}$ (Manousakas et al., 2014).

3.3. I/O ratio and relationship between PM and metal concentrations

Generally, indoor/outdoor (I/O) concentration ratio can reveal the relationship between indoor and outdoor PM level, while the I/O ratio in size distribution might reflect the particle loss in indoor from deposition and generation of those from activities like sweeping the floor and cleaning (Abt et al., 2000). The mean I/O ratios of elements in $PM_{2.5}$, PM_{10} and TSP are presented in Tables 2 and S4. As shown, the pollution of Ni, Zn, As and Cd have significant correlations ($p < 0.05$) between indoor and outdoor samples with R of 0.650, 0.429, 0.539 and 0.768 in $PM_{2.5}$, respectively. As and Cd have the highest R values in $PM_{2.5}$, but Ni and Zn have the highest R values in TSP. Cd have the highest I/O ratio among all metals. However, As, Cd, Ni and Zn have similar R values and I/O ratios in different size of PM. All these indicated that Ni, Zn, As and Cd concentrations outdoors do effect those indoors, but PM deposition occurred infrequently in the sampling houses.

Further investigation found that indoor and outdoor PM concentrations are not significant correlated ($p > 0.05$), but metal concentrations have correlations with PM concentrations (Table S6). Almost all element concentrations had the significant correlations with PM mass concentration ($p < 0.05$). This might tell us that these metals are produced along with other composition in PM, but indoor and outdoor sources are different because not all metals have the similar R values or I/O ratios. However, it is difficult to identify the exact indoor sources of sampling houses in present study, because the ventilation time and permeability of each house are different.

Table 2
Results of student-t test, basic statistics of I/O ratio and correlation coefficient (r) between indoor and outdoor metals in $PM_{2.5}$.

	I/O ratio [a]			Correlation [b]	
	Mean s.d.	Min	Max	R	P-value [c]
$PM_{2.5}$	0.67 ± 0.33	0.52	0.81	0.392	0.071
V	0.29 ± 0.25	0.18	0.40	-0.004	0.985
Mn	0.37 ± 0.41	0.19	0.55	0.393	0.070
Ni	0.46 ± 0.42	0.27	0.65	0.650	0.001
Zn	0.39 ± 0.49	0.17	0.61	0.429	0.046
As	0.58 ± 0.45	0.38	0.78	0.539	0.010
Cd	0.73 ± 1.00	0.29	1.18	0.768	0.000
Sb	0.62 ± 0.72	0.30	0.94	0.241	0.281
Pb	0.57 ± 0.76	0.23	0.90	0.305	0.167

s.d.: standard deviation.
[a] Indoor/outdoor (I/O) concentration ratio of each element and PM.
[b] The coefficient of correlation between indoor and outdoor data.
[c] Single sample student t-test analysis of r in metal and PM concentrations.

In a word, indoor metals including Mn, Ni, Zn and As, are related to outdoor metals, and the metal concentrations are related to corresponding PM concentrations.

3.4. Source analyses of toxic metals based on industrial type in different cities

As concluded above, indoor metals might be from outdoor metals. Therefore, the source of outdoor metals in air need to be investigated. Generally, urban heavy metals in atmosphere are identified as contribution to traffic-related sources and metal-related industries (Duan and Tan, 2013). As mentioned above, Foshan is an industrial city with contribution of 30% to total world ceramics production (Tan et al., 2016). Among various industries, high level of Pb would be emitted during ceramics fabrication process. For instance, Pb is used as ceramic flux to lower the high melting point of silica (Tan et al., 2016). In addition, large amount of coal is used when the ceramic are fired in kiln, emitting high level of As, Cd and Zn (Tian et al., 2010; Zhang et al., 2010). Further, Sb is used in fire retardant (Handa et al., 1982), which might be released by household electrical appliances and furniture manufacturing in Foshan (Tan et al., 2016). All these can explain high concentrations of Pb, Cd, Zn, Sb and As in Foshan air (Fig. S3).

Dongguan is also an industry city in the PRD and famous for its developed manufacturing on electronic information, electrical machinery, textile and clothing. Therefore, higher Sb concentration in Dongguan might be caused by both electrical-related production since fire retardant is needed in the electrical products. Besides Sb, the concentrations of V, Ni, Mn and Zn in outdoor PM are also relatively high in Dongguan. Particularly, V concentrations in Dongguan are approximately twice higher than other cities in the PRD. The possible reason for this is that most of cities in the PRD are costal and have several wharfs. It was reported that ship emission is one of important PM source of the PRD (Tao et al., 2017) and V is the tracer of ship emission (Agrawal et al., 2009; Okuda et al., 2007). Dongguan has a national first-class port, Port of Dongguan, which was used to be called Port of Humen before 2016 and has five subordinate ports, which handle up large amount of cargo ships. The single particle emitted by ship containing Ca, Fe, Ni and V was observed by others (Healy et al., 2009), indicating that higher airborne V in Dongguan might be caused by ship emission.

In addition, Ni is the supplementary tracer of ship emission, because V and Ni are demonstrated as markers for the combustion of heavy fuel oil (Agrawal et al., 2009). When V/Ni ≈ 2, it indicated airborne Ni was mainly caused by combustion of heavy oil, while V/Ni ratio < 2 indicated that there were other Ni source (Okuda et al., 2007). Hence, we calculated all V/Ni in every city studied in this study. We found that Zhuhai had the max V/Ni ratio of 2.06, 1.945 in outdoor PM_{10} and $PM_{2.5}$, respectively. The V/Ni ratio of 1.7 and 1.6 for outdoor $PM_{2.5}$ in Shenzhen and Dongguan, respectively. Complementally, Zhuhai and Shenzhen also have ports and are closer to the South China Sea. All these indicated that V in coastal cities of the PRD are mainly caused by ship emission, which coincided with the surrounding environment investigated. Similar conclusions in Guangzhou and Zhuhai were reported previously (Tao et al., 2017).

As Fig. S3B shows, Jiangmen is also a polluted city. The concentrations of Ni, Mn, Zn, As and Cd in Jiangmen are relatively high and Ni concentration in TSP is approximately 4–9 times higher than other cities in the PRD, exceeding the guideline of WHO. There was a serious nickel pollution event in Jiangmen, although few references reported about that. Manufacturing plays an important role in economy of Jiangmen, among which, manufacturing of motorcycles, household appliances, electronics, paper, food processing, synthetic fibers and garments are the chief industries. In general, nickel is used as coating for plating, which format rust preventive layer. Manufacturing of motorcycles uses large amount of Ni to produce rust preventive products, which might be the dominant cause of ambient Ni in Jiangmen. Besides, diversified manufacturing and large amount of energy consumption might cause elevation of Zn, As and Cd concentrations in the air (Cheng et al., 2015; Tian et al., 2010). Regardless of crustal emission, Mn along with Zn and Pb might be produced by textile industry, because high concentrations of Mn, Pb and Zn can also be found in printing and dyeing sludge (Islam et al., 2009). At the same time, Port of Jiangmen is the second largest port in Guangdong province, which might cause regional metal pollution in Jiangmen along with manufacturing industry.

Vehicle-related emissions and energy consumption might be the leading sources of toxic metals in Guangzhou (Tao et al., 2017). Zhongshan and Zhaoqing are also the cities with developed manufacturing. Zhongshan's major industries are furniture, light fixtures, locks and hardware and the famous electronic acoustics, while Zhaoqing has pillar industries of building materials, electronics, textile and garments. As a tourist city, Zhuhai has the lowest airborne toxic metal concentrations during this sampling time, except V, for its source of ship emission.

3.5. *Health risk assessment via inhalation*

LCR results of toxic metal levels in $PM_{2.5}$ and PM_{10} are shown in Tables 3 and 4, respectively. LCR were affected by metal toxicity and the exposure doses. Exposure doses depend on indoor/outdoor metal concentrations and corresponding exposure time for children and adults (see Eq. (3)). As seen in Tables 3 and 4, LCR of adults are higher than children both in $PM_{2.5}$ and PM_{10}, indicating that adults in the PRD suffered higher cancer risks than children. But LCR of toxic metals in PM_{10} are slightly higher than in $PM_{2.5}$, indicating that cancer risk differences between metals in $PM_{2.5}$ and PM_{10} are little. In other words, cancer risks are mainly from carcinogenic metals in $PM_{2.5}$. Sum of LCR exceeded 1.00E-06 for adults in the PRD, indicating that total pollution of As, Cd, Ni and Pb posed health impact to adults. Among four investigated carcinogenic metals, LCR of As exceed 1.00E-06 as well, which might indicate As is the dominant contributor of health impact. To a certain extent, the LCR in this study might reflect the general health risk for urban residents in the PRD. However, more samples are needed investigation in the further study to get more information about human health risk.

LCR values are various from city to city in the PRD. LCR in $PM_{2.5}$ are followed as in Zhongshan > Foshan > Jiangmen > Guangzhou > Zhaoqing > Shenzhen > Dongguan > Zhuhai > Huizhou for both children and adults. Almost all sum of four carcinogenic metals' LCR in cities exceeded the acceptable level, except for Zhuhai and Huizhou. LCR of As is the highest among four carcinogenic metals in all cities, with maximum of 3.34E-06 and 1.31E-05 for children and adults in Zhongshan, respectively. Following As, Cd is the second threatening metals, with LCR of adults in Foshan and Zhongshan exceeded the acceptable level. However, Ni and Pb in the PRD did not pose a threatening risk to residents. Furthermore, the situation in PM_{10} is slightly more serious. Similar with LCR of $PM_{2.5}$, As in Jiangmen for children, in Zhaoqing for adults and Cd in Jiangmen for adults exceeded the acceptable level of human health. These indicated that except in Huizhou and Zhuhai, the carcinogenic metals in $PM_{2.5}$ and PM_{10} affect human health in the PRD. As and Cd are the major pollution, which need to be monitored and controlled.

As seen in Tables 5 and 6, HQ of V, Mn, Ni, As, Cd and Sb in $PM_{2.5}$ and PM_{10} in cities are less than 1, showing that no threat to sensitive population from individual non-carcinogenic metal (EPA, 1989). But in Zhongshan, the HI, sum of HQs, were more than 1 in $PM_{2.5}$ and PM_{10} for both children and adults, which indicating that total metals might posed non-carcinogenic risks to residents (EPA, 1989; Hu et al., 2012). HI for adults are slightly higher than children in almost cities, but the result is contrary in Zhongshan (Tables 5 and 6). What led to different results in Zhongshan were higher indoor metal concentrations (Fig. S3A) and longer corresponding activity time, especially for children. Thus, the higher indoor airborne toxic metals pollution would be the cause of the greater non-carcinogenic health risk for children.

In short, residents didn't suffer cancer risk or non-carcinogenic risk in the urban residential areas of the PRD. However, risk assessment in the present study might have some uncertainties. We did not conclude all carcinogenic metals (such as Cu, Fe, Zn, Hg, Co, etc.) as well as other

Table 3
Life cancer risk (LCR) assessment in $PM_{2.5}$.

City	CR									
	Children					Adult				
	Ni	As	Cd	Pb	SUM	Ni	As	Cd	Pb	SUM
Guangzhou	3.43E-08	9.46E-07	3.92E-08	8.83E-09	1.03E-06	1.48E-07	3.87E-06	1.62E-07	7.52E-09	4.18E-06
Shenzhen	2.24E-08	2.12E-07	1.87E-08	5.19E-09	2.58E-07	9.14E-08	8.71E-07	8.04E-08	5.49E-09	1.05E-06
Foshan	2.97E-08	1.43E-06	2.78E-07	1.53E-08	1.75E-06	1.28E-07	6.26E-06	1.12E-06	2.50E-08	7.53E-06
Zhongshan	4.43E-08	3.34E-06	4.41E-07	3.04E-08	3.86E-06	1.77E-07	1.31E-05	1.68E-06	6.61E-09	1.50E-05
Jiangmen	1.02E-07	9.72E-07	2.43E-07	8.52E-09	1.33E-06	4.78E-07	4.05E-06	9.59E-07	1.10E-08	5.50E-06
Zhaoqing	2.28E-08	4.79E-07	8.53E-08	1.02E-08	5.97E-07	9.83E-08	1.97E-06	3.57E-07	1.57E-08	2.44E-06
Huizhou	1.70E-08	1.39E-07	1.16E-08	3.29E-09	1.70E-07	7.16E-08	5.81E-07	5.21E-08	8.21E-09	7.13E-07
Zhuhai	3.44E-08	1.71E-07	8.49E-09	1.43E-09	2.15E-07	1.36E-07	6.89E-07	3.47E-08	2.20E-09	8.62E-07
Dongguan	4.48E-08	1.56E-07	2.63E-08	4.09E-09	2.31E-07	1.90E-07	7.08E-07	1.17E-07	8.76E-09	1.02E-06
The PRD	4.03E-08	7.74E-07	1.05E-07	8.94E-09	9.28E-07	1.75E-07	3.20E-06	4.20E-07	3.76E-08	3.84E-06

Table 4
Life cancer risk assessment in PM_{10}.

City	LCR									
	Children					Adult				
	Ni	As	Cd	Pb	SUM	Ni	As	Cd	Pb	SUM
Guangzhou	3.51E-08	8.42E-07	3.72E-08	9.00E-09	9.23E-07	1.49E-07	3.45E-06	1.53E-07	7.79E-09	3.75E-06
Shenzhen	1.95E-08	2.22E-07	1.79E-08	4.81E-09	2.64E-07	8.01E-08	9.08E-07	7.50E-08	4.27E-09	1.07E-06
Foshan	3.77E-08	1.46E-06	2.57E-07	1.47E-08	1.77E-06	1.66E-07	6.47E-06	1.04E-06	3.29E-08	7.72E-06
Zhongshan	4.90E-08	3.07E-06	3.68E-07	3.00E-08	3.52E-06	1.97E-07	1.21E-05	1.41E-06	7.04E-09	1.37E-05
Jiangmen	1.27E-07	1.10E-06	3.16E-07	9.09E-09	1.55E-06	5.65E-07	4.49E-06	1.23E-06	1.18E-08	6.29E-06
Zhaoqing	4.01E-08	7.38E-07	1.43E-07	1.50E-08	9.36E-07	1.66E-07	2.97E-06	5.77E-07	2.07E-08	3.73E-06
Huizhou	1.98E-08	1.50E-07	1.23E-08	3.41E-09	1.86E-07	8.31E-08	6.51E-07	5.67E-08	9.21E-09	8.00E-07
Zhuhai	1.91E-08	1.74E-07	7.75E-09	1.58E-09	2.02E-07	7.92E-08	7.13E-07	3.22E-08	2.81E-09	8.27E-07
Dongguan	3.53E-08	2.06E-07	2.23E-08	3.88E-09	2.67E-07	1.58E-07	9.17E-07	1.02E-07	9.70E-09	1.19E-06
The PRD	4.41E-08	7.96E-07	1.09E-07	9.32E-09	9.59E-07	1.92E-07	3.30E-06	4.39E-07	3.98E-08	3.97E-06

Table 5
Non-carcinogenic risk assessment in $PM_{2.5}$.

City	HQ													
	Children							Adult						
	V	Mn	Ni	As	Cd	Sb	HI	V	Mn	Ni	As	Cd	Sb	HI
Guangzhou	9.22E-03	1.45E-01	1.71E-02	1.71E-01	2.54E-02	2.95E-03	3.71E-01	9.88E-03	1.56E-01	1.84E-02	1.75E-01	2.62E-02	3.02E-03	3.89E-01
Shenzhen	1.23E-02	8.53E-02	1.12E-02	3.84E-02	1.21E-02	1.77E-03	1.61E-01	1.29E-02	9.25E-02	1.14E-02	3.94E-02	1.30E-02	1.82E-03	1.71E-01
Foshan	1.26E-02	1.42E-01	1.48E-02	2.58E-01	1.80E-01	4.89E-03	6.13E-01	1.34E-02	1.56E-01	1.59E-02	2.83E-01	1.81E-01	5.47E-03	6.55E-01
Zhongshan	1.24E-02	3.25E-01	2.21E-02	6.05E-01	2.86E-01	8.65E-03	1.26 E+00	1.27E-02	3.19E-01	2.20E-02	5.93E-01	2.73E-01	8.42E-03	1.23 E+00
Jiangmen	7.38E-03	2.35E-01	5.08E-02	1.76E-01	1.58E-01	2.81E-03	6.30E-01	8.42E-03	2.58E-01	5.96E-02	1.83E-01	1.55E-01	2.94E-03	6.67E-01
Zhaoqing	1.07E-02	7.89E-02	1.14E-02	8.67E-02	5.53E-02	1.21E-03	2.44E-01	1.15E-02	8.61E-02	1.23E-02	8.90E-02	5.78E-02	1.28E-03	2.58E-01
Huizhou	4.39E-03	3.51E-02	8.46E-03	2.51E-02	7.50E-03	1.64E-03	8.22E-02	5.54E-03	4.25E-02	8.92E-03	2.63E-02	8.45E-03	1.88E-03	9.36E-02
Zhuhai	8.01E-03	5.03E-02	1.71E-02	3.10E-02	5.50E-03	8.51E-04	1.13E-01	8.88E-03	5.37E-02	1.69E-02	3.11E-02	5.62E-03	9.00E-04	1.17E-01
Dongguan	1.57E-02	5.34E-02	2.24E-02	2.82E-02	1.70E-02	1.30E-03	1.38E-01	1.88E-02	6.56E-02	2.37E-02	3.20E-02	1.89E-02	1.54E-03	1.61E-01
The PRD	1.18E-02	1.38E-01	2.01E-02	1.40E-01	6.78E-02	3.02E-03	3.81E-01	1.30E-02	1.49E-01	2.18E-02	1.45E-01	6.81E-02	3.20E-03	4.00E-01

Table 6
Non-carcinogenic risk assessment in PM_{10}.

City	HQ													
	Children							Adult						
	V	Mn	Ni	As	Cd	Sb	HI	V	Mn	Ni	As	Cd	Sb	HI
Guangzhou	9.32E-03	1.55E-01	1.75E-02	1.52E-01	2.41E-02	3.33E-03	3.61E-01	9.91E-03	1.66E-01	1.86E-02	1.56E-01	2.48E-02	3.46E-03	3.78E-01
Shenzhen	1.15E-02	8.45E-02	9.72E-03	4.02E-02	1.16E-02	1.94E-03	1.59E-01	1.19E-02	9.12E-02	9.99E-03	4.11E-02	1.21E-02	2.04E-03	1.68E-01
Foshan	1.37E-02	1.68E-01	1.88E-02	2.63E-01	1.67E-01	5.73E-03	6.36E-01	1.48E-02	1.87E-01	2.07E-02	2.93E-01	1.69E-01	6.46E-03	6.91E-01
Zhongshan	1.40E-02	3.95E-01	2.44E-02	5.56E-01	2.39E-01	8.16E-03	1.24 E+00	1.43E-02	3.89E-01	2.46E-02	5.48E-01	2.29E-01	7.99E-03	1.21 E+00
Jiangmen	8.51E-03	2.79E-01	6.34E-02	1.99E-01	2.05E-01	3.26E-03	7.58E-01	9.46E-03	2.98E-01	7.04E-02	2.03E-01	1.99E-01	3.33E-03	7.83E-01
Zhaoqing	1.71E-02	1.70E-01	2.00E-02	1.33E-01	9.26E-02	2.26E-03	4.35E-01	1.78E-02	1.75E-01	2.07E-02	1.34E-01	9.35E-02	2.32E-03	4.44E-01
Huizhou	4.82E-03	5.09E-02	9.89E-03	2.72E-02	7.95E-03	1.81E-03	1.03E-01	6.20E-03	6.11E-02	1.04E-02	2.95E-02	9.19E-03	2.08E-03	1.18E-01
Zhuhai	8.03E-03	5.46E-02	9.53E-03	3.14E-02	5.02E-03	1.38E-03	1.10E-01	9.20E-03	6.04E-02	9.88E-03	3.23E-02	5.22E-03	1.47E-03	1.18E-01
Dongguan	1.50E-02	6.52E-02	1.76E-02	3.73E-02	1.45E-02	1.98E-03	1.51E-01	1.81E-02	8.00E-02	1.96E-02	4.15E-02	1.64E-02	2.39E-03	1.78E-01
The PRD	1.27E-02	1.66E-01	2.20E-02	1.44E-01	7.09E-02	3.57E-03	4.19E-01	1.40E-02	1.78E-01	2.39E-02	1.49E-01	7.11E-02	3.82E-03	4.40E-01

exposure routes, such as dermal and ingestion exposure (Hu et al., 2012; Liu et al., 2015). Therefore, residents of urban areas in the PRD may still be affected by other metals in the atmosphere.

4. Conclusion

The indoors and outdoors concentrations of V, Mn, Ni, Zn, As, Cd, Sb and Pb on $PM_{2.5}$/PM_{10}/TSP in urban residential areas of PRD were analyzed in detail in this work. Most of metal concentrations were found to be higher in outdoor than that of indoor. I/O ratios of As, Cd and Pb were higher than that of V, Mn, Ni, Zn and Sb with minimum of 30% and maximum of 80%. All studied toxic metals in this study dominantly distributed in $PM_{2.5}$ with more than 60% in outdoor $PM_{2.5}$ and more than 53% in indoors. Similar distribution characteristics of elements was found in $PM_{2.5\text{-}10}$ and $PM_{>10}$, accounting for 10%–23% of TSP. Furthermore, residents in the PRD were affected by airborne metals mainly through $PM_{2.5}$ inhalation both from indoors and outdoors. As nickel used as antirust coating, Ni distributed in PM more than 2.5 µm for 39% and 46% outdoors and indoors, respectively. I/O ratios of toxic metals are varied significantly, with the highest I/O for Cd in $PM_{2.5}$. The source identification showed that outdoor toxic metals might be from regional emission, such as Pb from ceramic factory in Foshan, Ni from motor factory in Jiangmen, V from oil combustion of ship in coastal cities. Health risk assessment indicated that most urban residents in the PRD were suffered unsafe but tolerable carcinogenic risk of airborne carcinogenic metals. LCRs in Zhongshan were the highest and the main contributor is As for all cities. Though residents in most cities did not suffer non-carcinogenic risk, HI in Zhongshan were also the highest, with HI larger than 1 for $PM_{2.5}$, indicating that the sensitive population in Zhongshan might be posed non-carcinogenic risk. However, the amounts of samples in these nine cities are still very small, especially for indoor sample, which might lead to differences from other research of PRD.

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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