Seasonal concentration distribution of PM1.0 and PM2.5 and a risk assessment of bound trace metals in Harbin, China: Effect of the species distribution of heavy metals and heat supply

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To clarify the potential carcinogenic/noncarcinogenic risk posed by particulate matter (PM) in Harbin, a city in China with the typical heat supply, the concentrations of PM1.0 and PM2.5 were analyzed from Nov. 2014 to Nov. 2015, and the compositions of heavy metals and water-soluble ions (WSIs) were determined. The continuous heat supply from October to April led to serious air pollution in Harbin, thus leading to a significant increase in particle numbers (especially for PM1.0). Specifically, coal combustion under heat supply conditions led to significant emissions of PM1.0 and PM2.5, especially heavy metals and secondary atmospheric pollutants, including SO4^2−, NO3−, and NH4+. Natural occurrences such as dust storms in April and May, as well as straw combustion in October, also contributed to the increase in WSIs and heavy metals. The exposure risk assessment results demonstrated that Zn was the main contributor to the average daily dose through ingestion and inhalation, ADDing and ADDinh, respectively, among the 8 heavy metals, accounting for 51.7–52.5% of the ADDing values and 52.5% of the ADDinh values. The contribution of Zn was followed by those of Pb, Cr, Cu and Mn, while those of Ni, Cd, and Co were quite low (<2.2%).

Outdoor air pollution caused by unreasonable energy consumption, rapid industrialization and urbanization ranks among the most critical environmental issues in China1,2. Specifically, atmospheric particulate matter (PM), known as PM1.0, PM2.5, and PM10, has drawn much attention because of its acute and chronic effects on human health (such as cardiovascular and lung cancer mortality)3–5. Traditionally, a decrease in the aerodynamic diameter has always led to a significant increase in the chemical reactivity of PM for virus and trace heavy metal adsorption, undoubtedly enhancing the toxicity/health risk of those atmospheric particulates6,7.

PM consists of a mixture of chemical components, which may be directly emitted from primary sources or formed through complex atmospheric processes8. Generally, primary PM is always released into the atmosphere via wind, combustion processes and anthropogenic activities (including fossil/agricultural energy combustion, industrial processes, construction, etc.), whereas photochemical reactions (O3 oxidation, solar irradiation) and other chemical processes lead to the significant formation of secondary PM, such as sulfate, nitrate, ammonium, and secondary organic aerosols (SOAs)9. Due to the considerable dependence on fossil fuel, air pollution in northern China is more severe than that in the southern regions, especially in the heating season10,11. A report by the Ministry of Environmental Protection of China revealed that 33 cities were seriously polluted in January 2013, and the most polluted regions were mainly located in the northern region of China, including the Beijing-Tianjin-Hebei region, central and southern Hebei, southwestern Heilongjiang, western Shandong, and

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central Liaoning and Henan provinces\(^1,2,13\). Specifically, primary emissions originating from fossil/agricultural waste combustion, power generation, industrial processes, and road traffic were the main reasons for atmospheric pollution\(^1,14\).

Inorganic water-soluble ions (WSIs) are among the predominant chemical constituents of the atmospheric pollutants of PM, which play a substantial role in the Earth’s radiation balance and are related to atmospheric particle formation, growth and transformation\(^15\). Recent publications by Sun et al. and Cheng et al. demonstrated that as much as 45.0\%–55.5\% of atmospheric PM was attributed to WSIs\(^16,17\), in which the inorganic WSIs SO\(_4^{2−}\), NO\(_3^{−}\), and NH\(_4^{+}\) have a substantial effect on the atmospheric extinction coefficient and subsequently decrease urban visibility\(^18\). In addition, heavy metals are the essential toxic components of PM, and these nonbiodegradable elements can severely affect human health via three routes of exposure: food intake, skin contact and inhalation\(^19,20\). Among these hazardous heavy metals, Cu, Cr, Fe, Ni, Pb, Zn, V, Cd, and Mn, are the metals of the most immediate concern because of their detection frequency. Exposure to these metals has been associated with cardiovascular diseases, cancer and many other adverse health effects\(^21\), and their specific effects within different age groups varied widely\(^22\). Since the mobility, stability and solubility of heavy metals depend on their speciation characteristics\(^23\), sequential fractionation technology has been used for toxicity analysis\(^24\). However, few studies have addressed the association between the concentrations of aerosolized metallic elements in PM\(_{1.0}\) and PM\(_{2.5}\) and the adverse health impacts on local residents, especially the effect of heavy metal species from the long-term heat supply.

Here, we examined the total mass and species distribution of typical heavy metals and WSIs in PM\(_{2.5}\) and PM\(_{1.0}\) in Harbin and analyzed the variation in these species throughout the year. The concentrations in the periods with and without heat supply were compared. Moreover, the possible health risks posed by heavy metals, especially different metal species, when children and adults were exposed to them were assessed.

**Results and discussion**

**Mass concentration variations in the PM\(_{2.5}\) and PM\(_{1.0}\) of Harbin.** The mass concentrations of PM\(_{2.5}\) and PM\(_{1.0}\), shown in Fig. 1, of the samples in the port of Harbin were analyzed. Overall, the concentration distribution trend of PM\(_{1.0}\) was similar to that of PM\(_{2.5}\). Both exhibited a plateau during the periods of Oct. to Apr. The average mass concentrations of PM\(_{2.5}\) and PM\(_{1.0}\) ranged from 14.1 to 161.4 μg·m\(^{-3}\) and 11.2 to 125.3 μg·m\(^{-3}\), respectively, with the highest value found in January and the lowest in August. Generally, the average PM\(_{2.5}\) value in Oct., Nov., Dec., Jan., Feb., Mar. and Apr. was 1.14–2.15 times greater than the threshold limit values (75 μg/m\(^3\) for PM\(_{2.5}\)) in the Air Quality Standard of China.

Because PM\(_{1.0}\) has a larger specific surface area than PM\(_{2.5}\), toxic pollutants can be more easily adsorbed onto PM\(_{1.0}\) and pose a greater threat to human health\(^20,25\). Monthly distributions of PM\(_{1.0}\)/PM\(_{2.5}\) (Fig. 1) were calculated and varied widely during the continuous 12 months of detection. A higher PM\(_{1.0}\)/PM\(_{2.5}\) ratio (0.61–0.91) implied that fine particle PM\(_{1.0}\) was the predominant component of the PM. In addition, a higher PM\(_{1.0}\)/PM\(_{1.0}\) ratio for the heat supply periods (average ratio of 0.832) than the PM\(_{1.0}\)/PM\(_{2.5}\) ratio for the months with no heat supply (average ratio of 0.769) was related to the coal combustion and pollutants produced from the physical/chemical reactions of atmospheric ions.

**Monthly variation in particle number concentrations.** The variation in the particle numbers of PM\(_{1.0}\) was similar to that of PM\(_{2.5}\); thus, the particle distribution of PM\(_{1.0}\) was selected as an example and is discussed here. Overall, the particle numbers of PM\(_{1.0}\) were much higher in the heat supply period than in the period with no heat supply (see Supplementary Fig. S1), with a maximum value (in particle number/cm\(^3\)) of 50714 in December and a minimum in August (9312). Moreover, the difference between the maximum value and minimum value of the particle number, observed in the heat supply periods, is quite significant, whereas that in the period with no heat supply is not significant (42367 vs 6188). The main reason for this finding might be that (1) the higher humidity observed in the period with no heat supply than in the period with heat supply enhanced the precipitation and settlement of PM and (2) the continuous heat supply in winter led to a more significant
The mass concentration of SO$_4^{2-}$ was selected as an example and discussed (PM$_{1.0}$ in Table 1 and PM$_{2.5}$ in Table S2). Of the inland city Harbin was insignificantly affected by sea salt, the WSIs of Na$_2$O particles originated from industrial emissions and natural sources. Sodium as WSIs within PM$_{2.5}$ and PM$_{1.0}$ obtained from different months, were analyzed, and the distribution of the typical trace elements of PM$_{1.0}$ varied throughout the year, mainly originating from natural emissions and human activities. By contrast, the existence of Pb and Zn, specifically in summer, was partially ascribed to automobile exhaust (Pb emission in particulates during the whole year, mainly originating from natural emissions and human activities. Similarly, elemental Na ranked as the second-highest concentration among all 18 non-WSIs, which is related to its wide application in building materials. Specifically, Na$_2$O contributed to the higher emissions of S, As, Si to the atmosphere, which was mainly ascribed to the heat supply period was also related to coal combustion. In addition, the continuous heat supply in Dec., Jan., and Feb. contributed to the higher emissions of S, As, Si to the atmosphere, which was mainly ascribed to coal combustion. Among all 9 selected WSIs, the secondary atmospheric ions of SO$_4^{2-}$, NO$_3^{-}$, NH$_4^{+}$ were predominant in the fine particles, which originated mainly from physical/chemical reactions. Generally, WSIs were higher in the heat supply period than in the seasons with no heat supply, both for PM$_{1.0}$ and PM$_{2.5}$ (Fig. 2). For example, the mass concentration of SO$_4^{2-}$ reached its maximum value in Jan., with an average value of 28.21 μg/m$^3$ for PM$_{1.0}$ and 33.88 μg/m$^3$ for PM$_{2.5}$. Similarly, the highest values of NO$_3^{-}$ and NH$_4^{+}$ were observed in Feb., exhibiting maximum concentrations (in μg/m$^3$) of 15.86 and 14.25 for PM$_{1.0}$, respectively. Since the atmospheric condition of the inland city Harbin was insignificantly affected by sea salt, the WSIs of Na$^{+}$, Mg$^{2+}$, and Cl$^{-}$ in the collected particles originated from industrial emissions and natural sources. Na$^{+}$ ions, mainly originating from crustal particulate emission. Similar observations were reported by Jones and Harrison. The ratio of the mass concentration/particle number of PM$_{1.0}$ for the samples observed from the heat supply period is lower than that from the months with no heat supply (Supplementary Table S1), implying that the predominant particles in the collected PM$_{1.0}$ in the heat supply period existed as fine particles (smaller average diameter), ascribed to the effective removal of the larger particles by dust removal equipment.

### Table 1. Concentrations of inorganic/metal elements and WSIs in PM$_{1.0}$ in different months from Nov. 2014 to Oct. 2015 (unit: μg/m$^3$)

| Element | Dec | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ca      | 8.63 | 6.28 | 8.16 | 9.09 | 15.28 | 9.12 | 5.20 | 5.36 | 2.98 | 4.21 | 5.77 | 5.97 |
| K       | 2.06 | 1.22 | 3.32 | 3.03 | 1.59 | 1.84 | 1.11 | 1.15 | 0.75 | 1.88 | 4.36 | 4.95 |
| Mg      | 0.76 | 0.54 | 1.20 | 0.89 | 1.54 | 1.17 | 0.45 | 0.85 | 0.32 | 0.55 | 0.76 | 0.72 |
| Na      | 12.13 | 9.87 | 8.18 | 7.26 | 11.54 | 13.26 | 5.97 | 7.29 | 4.66 | 10.19 | 10.53 | 7.17 |
| Ca$^{2+}$ | 2.61 | 6.26 | 2.94 | 2.85 | 1.45 | 1.07 | 1.01 | 0.64 | 0.96 | 1.78 | 1.69 |
| K$^{+}$ | 1.14 | 0.68 | 1.20 | 1.42 | 1.05 | 0.77 | 0.60 | 0.45 | 0.37 | 0.63 | 1.71 | 1.84 |
| Mg$^{2+}$ | 0.11 | 0.33 | 0.66 | 0.37 | 0.27 | 0.17 | 0.13 | 0.18 | 0.06 | 0.15 | 0.29 | 0.15 |
| Na$^{+}$ | 1.35 | 0.29 | 1.61 | 0.56 | 4.24 | 2.30 | 1.33 | 2.01 | 0.69 | 2.31 | 3.19 | 1.16 |
| F$^{-}$ | 0.19 | 0.24 | 0.49 | 0.35 | 0.30 | 0.06 | 0.03 | 0.14 | 0.04 | 0.06 | 0.22 | 0.25 |
| NH$_4^{+}$ | 6.6125 | 7.024 | 14.25 | 6.2425 | 4.1322 | 3.8895 | 2.2441 | 3.7991 | 2.7721 | 3.5617 | 4.0365 | 3.95 |
| Cl$^{-}$ | 2.7185 | 3.275 | 8.1525 | 6.6005 | 3.29 | 1.1883 | 0.778 | 0.3789 | 0.2883 | 0.132 | 2.5133 | 3.8765 |
| SO$_4^{2-}$ | 9.3525 | 28.206 | 13.72 | 22.337 | 9.007 | 5.146 | 4.8 | 1.6506 | 1.5023 | 3.104 | 4.1973 | 4.4915 |
| NO$_3^{-}$ | 6.4345 | 14.536 | 15.863 | 6.1905 | 4.9025 | 2.94 | 3.9575 | 1.5781 | 1.2122 | 0.475 | 6.4512 | 8.504 |
| Σ$^{1}$ | 63.32 | 99.42 | 97.33 | 76.18 | 68.57 | 54.01 | 35.32 | 33.44 | 19.95 | 35.04 | 53.57 | 52.38 |
found that the top five significant contributors to PM10 in Chengdu were vehicle exhaust (28.71%), coal combustion (24.45%), resuspended dust (19.24%), secondary sulfate (13.29%), and vehicular emissions (11.47%).

The contributions of each source/group of sources were predicted according to Bhuyan et al. and are listed in Table S3, in which principal factors with eigenvalues >0.8 were chosen by extracting the eigenvalues and eigenvectors. Factor 1, with higher loadings of Cu, Fe, Mn, Ni and Pb, was typically explained to apply the characteristics of road dust. Factor 2 explained 17.1% of the variance with high loadings of NO3−, SO42−, WSOC and NH4+, indicating the influence of secondary aerosol sources over the site. Factor 3 represented the construction materials, with high loadings of Ca, Mg, Na+ and Cl−, closely related to the cement manufacturing processes and to the end usage at construction sites. Factor 4 showed high loadings of SO42−, NO3−, Na+, NH4+, K+ and organic carbon (OC), indicating combustion sources, biomass burning (SO42−, NO3−, Na+, NH4+, K+) and vehicular emissions (OC, NO3−). Factor 5 was characterized by high loadings of Al, Na, K and Si, which points to crust/soil emissions. Factor 6, characterized by a high F− loading, is related to fossil fuel (especially coal) combustion emissions.

The seasonal percentage distribution of 18 elements for particles PM1.0 and PM2.5 varied widely (in Fig. S2). Since the concentrations of Zn, Ti, Pb, As, Cu, Cr and Ni in the chemical composition of PM1.0/PM2.5 are quite low, the sum of those proportions are defined as other concentrations. K mainly originated from the burning of biomass; thus, K was higher (>14%) in autumn for both PM1.0 and PM2.5 than in the other three seasons. S mainly originated from coal combustion and exhibited the highest value in winter. For comparison, Ca was highest in spring, which is related to the windy weather and dust emissions from building materials. Although Si basically originates from natural sources, coal combustion in winter contributed a significant amount of emissions into the atmosphere; thus, a higher concentration in winter than in the other seasons was finally observed. As shown in Table S3, the majority of the elements in PM1.0 and PM2.5 existed as inorganic matters regardless of the seasonal variation (≥58.0%), except for S and Si in spring. It should be noted that most of the inorganic elements in PM1.0 are highly enriched, demonstrating that the majority of those inorganic particles were attached to PM1.0, and the seasonal variation insignificantly affected their distribution.

Sources in Harbin, exhibited the highest value of 4.24 μg/m³ in Apr., ascribed to the resuspended road dust, soil dust, and construction dust due to the strong wind in spring (average speed of 3.7 m/s). Correspondingly, the highest concentration of K+ in Nov. for PM1.0 (1.84 μg/m³) is mainly ascribed to straw combustion in Heilongjiang Province in autumn, whereas Feb. had the highest levels of Cl− (8.15 μg/m³ for PM1.0). The average Cl− in PM1.0 during the periods with and without heat supply was 4.65 μg/m³ and 0.88 μg/m³, respectively, which is usually considered to be from coal combustion.

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**Source apportionment analysis of PM2.5 and PM1.0 in different seasons.** Potential sources of PM2.5 and PM1.0 in Harbin were evaluated based on the chemical constituent analysis of 150 PM2.5 and PM1.0 samples via principal component analysis-multiple linear regression (PCA-MLR) model utilization. In total, 6 components were resolved from the PCA according to Bhuyan et al. and Cusack et al., in which principal factors with eigenvalues >0.8 were chosen by extracting the eigenvalues and eigenvectors. Factor 1, with higher loadings of Cu, Fe, Mn, Ni and Pb, was typically explained to apply the characteristics of road dust. Factor 2 explained 17.1% of the variance with high loadings of NO3−, SO42−, WSOC and NH4+, indicating the influence of secondary aerosol sources over the site. Factor 3 represented the construction materials, with high loadings of Ca, Mg, Na+ and Cl−, closely related to the cement manufacturing processes and to the end usage at construction sites. Factor 4 showed high loadings of SO42−, NO3−, Na+, NH4+, K+ and organic carbon (OC), indicating combustion sources, biomass burning (SO42−, NO3−, Na+, NH4+, K+) and vehicular emissions (OC, NO3−). Factor 5 was characterized by high loadings of Al, Na, K and Si, which points to crust/soil emissions. Factor 6, characterized by a high F− loading, is related to fossil fuel (especially coal) combustion emissions.

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Overall, the percentage contributions of the six main PM$_{2.5}$ sources of Harbin in the heat supply period were distributed as secondary formation (22.0%) > fossil fuel combustion (21.2%) > combustion (biomass burning + vehicles) (17.6%) > road dust (14.6%) > soil/crust (12.5%) > construction contribution (12.0%). By contrast, the contributions of secondary formation and fossil fuel combustion (coal) decreased to 16.1% and 15.1%, respectively, in the periods with no heat supply. Based on the above analysis, we conclude that coal combustion and secondary aerosols were the main sources of PM pollution in Harbin, especially in seasons with heat supply. Moreover, PM$_{1.0}$ is the most important fine PM emitted for most pollution sources. Thus, prevention and control measures should be urgently developed.

Figure 3. Time-evolved source contributions to different PM$_{2.5}$ (a) and PM$_{1.0}$ (b) samples obtained from the PCA-MLR results (μg·m$^{-3}$).
Speciation characteristics of heavy metals in PM$_{2.5}$. Excess heavy metals in PM$_{2.5}$, especially the weakly bonded exchangeable fractions, endanger natural systems and human health$^{37}$. Speciation distributions of heavy metals in PM$_{2.5}$ were characterized, and the corresponding speciation information is given in Fig. 4. Overall, the majority of the eight selected metals preferentially existed as a residual fraction (mineral crystal lattice), followed by water- and acid-exchangeable phases, while the reducible, oxidizable fractions had substantially lower contents. Briefly, the residual fraction of Cr, accounting for as much as 71.5% of the bulk Cr, was the highest among all eight metals, followed by Cu (41.1%), Zn (33.1%), Cd (31.1%), Mn (29.5%), Co (24.0%), Pb (17.0%), and elemental Ni (9.6%). For comparison, the water-exchangeable fraction of eight elements decreased in the order of Pb (40.3%) > Zn (33.6%) > Cd (29.7%) > Co (29.4%) > Mn (22.3%) > Cu (11.3%) > Ni (8.0%) > Cr (3.2%). Overall, Cd, Co, Pb, Mn and Zn exhibited a higher percentage distribution in the water/acid-exchangeable fractions (>46.4%) than in the other fractions.

According to Sabiene et al.$^{38}$, residual, oxidizable and reducible heavy metals are quite refractory and are generally recognized as a stable fraction due to their weak bioavailability and low solubility, while water/acid-exchangeable heavy metals are defined as a labile fraction$^{39}$. As shown in Fig. 4, Pb was the most labile element among all eight heavy metals in PM$_{2.5}$, accounting for 40.3% as water-exchangeable forms and 27.7% as acid-exchangeable forms. Zn was the second-most labile heavy metal in PM, exhibiting a relatively high percentage distribution of water- and acid-exchangeable fractions (33.6% and 22.1%, respectively). By contrast, Ni, Cu and Cr showed a lower percentage of labile fractions (<34.1%). Overall, Cr was the most refractory metal in PM$_{2.5}$ (3.2% for water- and 9.2% for acid-exchangeable Cr). Based on the binding strength and solubility in different geochemical fractions of heavy metals, the potential toxicity of different heavy metal fractions is expected to decrease in the following order: exchangeable (F$_1$) > carbonates (F$_2$) > reducible (F$_3$) > oxidizable (F$_4$) > residual heavy metal phase (F$_5$)$^{40}$. Thus, we concluded that the elements Ni, Cu and Cr in PM$_{2.5}$ had a low hazard potential. For comparison, elemental Pb exhibited a converse trend, with the highest percentage ratio for F1 and F2 (40.3% and 27.7%, respectively).

Metal fractionation occurring in PM$_{2.5}$ and PM$_{1.0}$ is, in turn, likely to influence metal toxicity$^{41}$. Toxicities of heavy metals in PM can be calculated according to the distribution of the fractional species. The equations for the risk assessment code (RAC) calculation can be summarized as follows:

$$\text{RAC} = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times 100\%$$

(1)

$$C_f = \left( \frac{F_1 + F_2 + F_3 + F_4}{F_5} \right) / F_5$$

(2)

where RAC is the risk assessment code (%) of heavy metal pollution. A value of RAC < 1% usually demonstrates no risk; values of 1% ≤ RAC < 10% and 10% < RAC < 30% refer to low and medium risk, respectively; and an RAC ≥ 30% indicates a high risk, especially when RAC > 50% (very high risk). $F_1$, $F_2$, $F_3$, $F_4$ and $F_5$ represent the percentage distributions of the water-, acid-, reducible-, oxidizable- and residual heavy metal fractions in PM$_{2.5}$, respectively. $C_f$ refers to the pollution coefficient.

As shown in Fig. 5, the results obtained from the RAC calculation demonstrated that Pb, Zn, Co and Cd in PM$_{2.5}$ were at a very high-risk level, which decreased in the order of Pb (68.0%) > Zn (55.7%) > Co (54.7%) > Cd (50.2%). For comparison, the elements Mn (46.4%), Ni (34.1%) and Cu (31.9%) were at a high level, whereas the RAC of elemental Cr was at a medium risk level (RAC = 12.4%). The distribution trend of $C_f$ was quite different from that of RAC and decreased in the order of Ni(9.39) > Pb(4.88) > Co(3.18) > Mn(2.39) > Cd(2.23) > Zn(2.02) > Cu (1.43) > Cr(0.40). Although Ni was at a low concentration level in PM$_{2.5}$, its high RAC pollution potential implied that we should be highly concerned. In addition, the higher toxicities of Cd, Co, Pb, and Zn demonstrated that the emissions from coal combustion, the electroplating industry, metallurgy, the chemical industry and private cars in Harbin City should definitely be controlled, especially in the winter season.

Figure 4. Species distribution of eight heavy metals in PM$_{2.5}$ in heat supply periods (a) and in periods with no heat supply (b).
The distribution of the fractional species of heavy metals obtained from the periods with no heat supply was similar to the distribution in the heat supply periods (see in Fig. 5). Specifically, the RAC of Cu, Co, Ni and Zn exhibited a slight increase during the periods with no heat supply compared to that during the heat supply period (<12%), and that of Cd, Mn and Pb increased significantly (41.5%-64.6%). The higher concentration of Cr observed in the heat supply period (listed in Table 1), as well as the corresponding higher RAC value, implied that the hazardous element Cr within the particles should be given more attention. All the tested heavy metals except Pb exhibited an increased Ca value (especially for Cd, Mn and Co) during the period with no heat supply, implying that coal combustion during heat supply periods contributed to the emission/production of the residual fraction of heavy metals.

**Risk assessment.** A carcinogenic and noncarcinogenic risk assessment for Cr, Ni, Cd, Co, Pb, Cu, Zn, and Mn in PM_{2.5} samples was performed using the health risk assessment model of the US EPA, and three exposure pathways, namely, ingestion, inhalation, and dermal contact, were separately studied (Table 2). In general, the hazard quotient results demonstrated that the three exposure pathways had the same trends of ingestion > dermal contact > inhalation, implying that ingestion was the most health-threatening exposure route for heavy metals in PM_{2.5}. Moreover, children suffered from a higher risk from ingestion and dermal contact from PM_{2.5} inhalation, implying that ingestion was the most health-threatening exposure route for heavy metals in Harbin City.

| Elements | Children | Females | Males | Children | Females | Males | Children | Females | Males |
|---------|---------|---------|-------|---------|---------|-------|---------|---------|-------|
| Cr      | 1.33 × 10^{-2} | 1.83 × 10^{-3} | 1.77 × 10^{-3} | 7.16 × 10^{-3} | 4.88 × 10^{-3} | 5.23 × 10^{-3} | 9.26 × 10^{-4} | 1.92 × 10^{-7} | 2.22 × 10^{-7} |
| Ni      | 2.62 × 10^{-3} | 3.61 × 10^{-4} | 3.50 × 10^{-4} | 1.41 × 10^{-4} | 9.65 × 10^{-4} | 1.03 × 10^{-4} | 1.83 × 10^{-8} | 3.79 × 10^{-8} | 4.38 × 10^{-8} |
| Cd      | 1.21 × 10^{-3} | 1.67 × 10^{-4} | 1.61 × 10^{-4} | 6.52 × 10^{-5} | 4.45 × 10^{-5} | 4.77 × 10^{-5} | 8.44 × 10^{-9} | 1.75 × 10^{-9} | 2.20 × 10^{-9} |
| Co      | 5.71 × 10^{-4} | 7.87 × 10^{-5} | 7.62 × 10^{-5} | 3.08 × 10^{-4} | 2.10 × 10^{-4} | 2.25 × 10^{-4} | 3.99 × 10^{-8} | 8.25 × 10^{-8} | 9.54 × 10^{-8} |
| Pb      | 2.14 × 10^{-2} | 2.95 × 10^{-3} | 2.56 × 10^{-3} | 4.62 × 10^{-3} | 7.89 × 10^{-3} | 7.56 × 10^{-3} | 1.50 × 10^{-7} | 3.10 × 10^{-7} | 3.58 × 10^{-7} |
| Cu      | 1.13 × 10^{-2} | 1.56 × 10^{-3} | 1.35 × 10^{-3} | 2.44 × 10^{-3} | 4.17 × 10^{-3} | 3.99 × 10^{-3} | 7.90 × 10^{-8} | 1.64 × 10^{-7} | 1.89 × 10^{-7} |
| Zn      | 6.73 × 10^{-3} | 9.28 × 10^{-3} | 8.05 × 10^{-3} | 1.45 × 10^{-3} | 2.48 × 10^{-3} | 2.38 × 10^{-3} | 4.70 × 10^{-7} | 9.74 × 10^{-7} | 1.13 × 10^{-7} |
| Mn      | 1.05 × 10^{-2} | 1.45 × 10^{-3} | 1.26 × 10^{-3} | 2.27 × 10^{-4} | 3.88 × 10^{-4} | 3.72 × 10^{-4} | 7.35 × 10^{-8} | 1.52 × 10^{-7} | 1.76 × 10^{-7} |
| Σ       | 1.28 × 10^{-1} | 1.77 × 10^{-2} | 1.56 × 10^{-2} | 6.64 × 10^{-3} | 1.18 × 10^{-3} | 1.14 × 10^{-3} | 8.96 × 10^{-7} | 1.95 × 10^{-6} | 2.14 × 10^{-6} |

Table 2. Ingestion, inhalation, and dermal contact exposure risks of eight heavy metals in PM_{1.0} and PM_{2.5} in Harbin City.
respectively, while the ADD\textsubscript{ing} values of Ni, Cd, Co were quite low (<2.2%). Similarly, Zn was also the predominant source of the ADD\textsubscript{inh} risk and accounted for 52.5% of the bulk ADD\textsubscript{inh} risk. Pb was the second highest risk source, and Cr ranked third, accounting for 16.7% and 10.3%, respectively. Cu and Mn were also important sources of the ADD\textsubscript{inh} risk and contributed 8.8% and 8.2% of the bulk risk, respectively. For comparison, Pb played the most important role in ADD\textsubscript{norm} risk and accounted for 66.5–69.7% of the bulk ADD\textsubscript{norm} risk, followed by Zn (20.9–21.9%), while the ADD\textsubscript{norm} risk of Cr, Ni, Cd, Co, Cu and Mn was quite low. In addition, Pb, Cu, Zn and Mn exhibited a higher ADD\textsubscript{norm} risk for adults than for children, while the ADD\textsubscript{norm} of Cr, Ni, Cd, and Co was significantly lower (especially for Cr and Ni). From the above, we can conclude that Zn and Pb in the PM\textsubscript{2.5} pollutants of Harbin City should be preferentially considered for their high environmental risk and RAC value; Cr, Cu, and Mn should be controlled first, while the environmental risk of Ni, Cd and Co was quite low.

Because the toxicity of the heavy metals was significantly affected by the fractional species distribution of the heavy metals, the risk assessments were further combined and analyzed with the fractional results. Compared to the periods with no heat supply, the RAC value of Cr, as well as the C\textsubscript{r} value of Pb, both exhibited a noticeable increase during the heat supply periods; thus, the pollution of Cr and Pb from coal combustion in heat supply periods should be of great concern. In contrast, Zn, Cu, Co and Mn from street dust should also be at a high level of concern in periods with no heat supply for controlling health risks\textsuperscript{45} due to their high C\textsubscript{r} value and high ecological risk.

Conclusions

(1) The continuous heat supply from Oct. to Apr. led to serious air pollution in Harbin. The tremendous amount of emissions of the fine particle PM\textsubscript{1.0} during the heat supply period led to a higher PM\textsubscript{1.0}/PM\textsubscript{2.5} value of 0.832 than that during the months with no heat supply. The PM\textsubscript{1.0} particle number was highest in Dec. (50714/cm\textsuperscript{3}), which was 4.91 times higher than the minimum value found in August.

(2) The concentrations of the majority of the 9 selected WSIs in PM\textsubscript{1.0} and PM\textsubscript{2.5} were higher in the heat supply period than in the seasons with no heat supply. Specifically, the WSI of SO\textsubscript{4}\textsuperscript{2–} reached the maximum value in Jan.; NO\textsubscript{3}–, NH\textsubscript{4}+, and Cl\textsuperscript{–} in Feb.; Ca\textsuperscript{2+}, K\textsuperscript{+} and F\textsuperscript{–} in Apr.; and Na\textsuperscript{+} in May.

(3) The percentage contributions of the six main PM\textsubscript{2.5} sources in Harbin in the heat supply period were distributed as secondary formation (22.0%) > fossil fuel combustion (21.2%) > combustion (biomass burning + vehicles) (17.6%) > road dust (14.6%) > soil/crust (12.5%) > construction (12.0%). The contributions of secondary formation and coal combustion decreased to 16.1% and 15.1%, respectively, in the periods with no heat supply.

(4) The RAC results demonstrated that Pb, Zn, Co and Cd in PM\textsubscript{2.5} created very high risk levels; Mn, Ni and Cu created a high risk level, while Cr was at a medium risk level (highest residual fraction of 71.5%). The supply increased the RAC value of Cr and the C\textsubscript{r} value of Pb. Ingestion was the most health-threatening exposure route for heavy metals in PM\textsubscript{2.5} in Harbin. Zn was the main contributor to the ADD\textsubscript{ing} and ADD\textsubscript{inh} among the 8 heavy metals, followed by Pb, Cr, Cu and Mn.

Materials and methods

Description of the city of Harbin. Harbin, one of the ten most populated cities in China, is the capital of Heilongjiang Province and is the commercial, industrial, and transportation center of Northeast China. The city is situated on the Songnen Plain, surrounded by mountain chains (the Lesser Khingan Mountains, the Changbai Mountains and the Higher Lesser Khingan Mountains in the north, east and west, respectively, to form a low-lying center), so special geographical and meteorological factors slow the wind speed. The mean annual temperature in Harbin is 3.5 °C; thus, heat supply is necessary during the period of Oct. 20 to Apr. 20\textsuperscript{1}. In 2015, the air quality of Harbin had levels of 24.1% excellent, 38.4% good, 19.7%, 5.5%, 8.5% and 3.8% light, moderate, severe and serious pollution, respectively (http://www.hljdep.gov.cn/hjgl/hjzc/hjzlc/2016/01/11891.html).

PM sample collection and sampling site description. As shown in Fig. 6, atmospheric PM was sampled on the roof of the School of Environment (14 m high) of the Harbin Institute of Technology (HIT) (longitude 126.691°E and latitude 45.763°N). The sampling site was close to Songshan Road and Huanghe Road (with dense vehicular traffic) and surrounded by numerous commercial centers, residential quarters, and power plants. Approximately 9000 residents live on the campus of HIT (second campus, approximately 0.35 km\textsuperscript{2}). Twenty-four-hour PM\textsubscript{1.0} and PM\textsubscript{2.5} sampling was conducted every 7 days during the normal periods and every day during the polluted days from Nov. 2014 to Feb. 2015, using a fine particulate dust sampler (TH-150CIII and TH-150A, Mingxuan Company, Chengdu, China). The fine particulate dust sampler ran at a constant flow rate of 100 L/min. The 47-mm Teflon filters, with low inherent contaminants, were purchased from Pall Company (USA) and were dried/balanced to a constant weight (accuracy of 0.0001 g) at 298 K for 24 h before sampling. Filters were handled with tweezers coated with Teflon tape to reduce the possibility of contamination. In total, more than 150 samples were collected during the whole observation period. Number concentrations of PM\textsubscript{1.0} and PM\textsubscript{2.5} were collected by hand-held number concentration meters (TSI Company, USA), accompanied by the sampling of fine particles. Samples were taken three times a day (8:00 am., 12:00 am and 4:00 pm), each time for 5 min.

Chemical analysis. After weighing, the filters were sectioned, and one-fourth of the filter was cut into small pieces and soaked in a 60 mL polytetrafluoroethylene (PTFE) vial. The WSIs of the PM were obtained by ultrasonating the filters for 150 min in 50 mL deionized water and then filtering the water extracts through a 0.45-μm cellulose acetate filter before chemical ion analysis. Concentrations of the cations (K\textsuperscript{+}, Na\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}) were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES); the anions (SO\textsubscript{4}\textsuperscript{2–}, NO\textsubscript{3}–, Cl\textsuperscript{–},
F\(^-\) were determined using an ion chromatograph (Dionex 4500i, USA); and NH\(_4^+\) was determined by Nessler’s reagent spectrophotometry.

To detect the species concentration distribution of the heavy metals within the atmospheric PM, one-quarter of the sampling filters was cut into small pieces, and the metals within the PM were extracted and analyzed according to Hu \textit{et al.}\textsuperscript{16}. Briefly, one-quarter of the sampling filters was cut into small pieces and immersed in a 15 mL digestion solution of concentrated HNO\(_3\) and concentrated HClO\(_4\) (3:1) for 10 h in a fume hood. Then, the beaker was baked with the temperature maintained at 100 °C until white smoke appeared, and the temperature was increased to 150 °C to volatilize the acid. When the sample solution had evaporated to near dryness, 2 mL of 2% nitric acid was added three times with continued heating. After being digested and cooled, the remaining solution was transferred to a 50 mL volumetric flask. In the next step, the flask was brought to the final volume by employing 2% HNO\(_3\). After filtration, the filtrate was stored in a 15-mL centrifugal tube and subjected to ICP-OES (VISTAMPX, US) for Al, Ca, Fe, K, Mg, Na, S and Si detection and ICP-mass spectrometry (MS) (VG PQ ExCell, Thermo Fisher Scientific Inc., USA) for Ti, Cr, Mn, Ni, Cu, Zn, As, Sr, Ba and Pb analysis.

Chemical–mineralogical speciation of heavy metals in the collected PM\(_{1.0}\) and PM\(_{2.5}\) samples was operatively measured by a five-step sequential chemical extraction procedure, which followed the extraction methods proposed by Tessier \textit{et al.}\textsuperscript{20} Specifically, sequential chemical extraction was carried out with 50 mL polypropylene centrifuge bottles. The water-exchangeable metal species were extracted with 20 mL MgCl\(_2\) (1 M, pH 7.0) and with oscillation at 25 ± 5 °C for 16 h, after which the extracted solutions were separated from the filters by centrifugation at 4000 rpm for 10 min. Similarly, the acid-exchangeable, reducible, oxidizable and residual heavy metal fractions were extracted using NaOAC (1 M, pH 5.0), NH\(_2\)OH·HCl (0.04 M), H\(_2\)O\(_2\) (8.8 M) and HF-HClO\(_4\) mixtures, respectively. The combined supernatants were heated until 1–2 mL of solution remained, and then they were diluted to a volume of 10 mL with 2% HNO\(_3\) to be stored in a polyethylene bottle at 4 °C before analysis.

**Source apportionment analysis.** To understand the probable contributions from local point sources, PCA-MLR and the chemical mass balance (CMB) model were applied for air pollution source apportionment, according to the previous studies of Shi \textit{et al.}\textsuperscript{35} and Bhuyan \textit{et al.}\textsuperscript{34}. The CMB model was freely available for use on the US EPA official website. Seasonal pollution sources of PM\(_{2.5}\) and PM\(_{1.0}\) were analyzed and measured (Mar., Apr. and May were regarded as spring; Jun., Jul. and Aug. as summer; Sep., Oct. and Nov. as autumn; and Dec., Jan. and Feb. as winter).

**Risk assessment.** The risk assessment model developed by the US EPA was applied to evaluate the health risks posed by heavy metals in PM\(_{1.0}\) and PM\(_{2.5}\). Considering the variety of physiological characteristics and lifestyles of Harbin City residents, we divided them into three groups: male (>16 years), female (>16 years) and children (<16 years). Since metal exposure can occur through direct inhalation, ingestion, and dermal contact, the average daily dose (in mg·kg\(^{-1}\)·d\(^{-1}\)) through ingestion (\(ADD_{\text{ing}}\)), inhalation (\(ADD_{\text{inh}}\)), and dermal contact (\(ADD_{\text{derm}}\)) can be calculated as follows\textsuperscript{27,44}:

\[
ADD_{\text{ing}} = \frac{C \times \text{IngR} \times \text{CF} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (3)
\]

\[
ADD_{\text{inh}} = \frac{C \times \text{InhR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}} \quad (4)
\]
\[ ADD_{\text{dern}} = \frac{C \times SA \times CF \times SL \times ABS \times EF \times ED}{BW \times AT} \]  

where \( C \) stands for the concentration of the contaminant in PM\(_{2.5} \) (mg/kg for \( ADD_{\text{ing}} \) and \( ADD_{\text{dern}} \) fg/m\(^3\) for \( ADD_{\text{inh}} \)). For ingestion, the intake rate (ingR) was 100, 100 and 200 mg/day for males, females and children, respectively. For inhalation, InhR was 15.2 m\(^3\)/day for males, females and children, respectively. SA, the surface area of the skin that contacts the airborne particles (cm\(^2\)), was 4220, 3820 and 2160 for males, females and children, respectively. \( SL \) is the skin adherence factor for airborne particulates (mg/cm\(^2\)), which was 0.07, 0.07 and 0.2 for males, females and children, respectively. \( PEF \) refers to the particle emission factor and was \( 1.36 \times 10^{-3} \) mg/cm\(^2\)/day, 240 days. \( EF \) is the exposure frequency in days/year, and was 180 days. \( ED \) is the exposure duration in years, equal to 24, 24 and 6 years for males, females and children, respectively. \( AT \) stands for exposure time, 24 h/day. \( BW \) refers to the average body weight, was 62.7, 54.4 and 15 kg for males, females and children, respectively.

**Data availability**

The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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Author contributions
L.L. Wei, Q.L. Zhao and K. Wang conceived and designed the experiments; W.Y. Wang, L.L. Li and L.J. Hong performed the experiments; L.L. Wei, J.J. Li, and W.Q. Chi analyzed the data; L.L. Wei, and J.Q. Jiang wrote the manuscript; L.L. Wei contributed reagents and materials; and all authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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