Pollution Characteristics, Sources, and Health Risk Assessment of Heavy Metals and Polycyclic Aromatic Hydrocarbons in PM2.5 in the Central Tianshan Mountains: Postprint

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Abstract

To investigate the pollution characteristics of PM2.5 in the Middle Tianshan region, PM2.5 samples were collected in the Wulasitai area of Middle Tianshan from July to September 2019. The concentrations of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in PM2.5 were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatography-mass spectrometry (GC-MS), respectively, and the sources and health effects of heavy metals and PAHs in PM2.5 were studied. The results indicated: (1) The concentrations of heavy metals and PAHs in PM2.5 in the Middle Tianshan region during summer and autumn were generally low; the total average concentration of heavy metals was 238.50 $\mathrm{ng \cdot m^{-3}}$, with the average concentration levels of individual elements following the order Fe > Cu > Zn > Pb > Mn > Cr > As > V > Rb > Ni > Co > Se > Cd > Tl. Except for Fe (139.90 $\mathrm{ng \cdot m^{-3}}$) and Cu (78.72 $\mathrm{ng \cdot m^{-3}}$), the average concentrations of all other elements were below 10 $\mathrm{ng \cdot m^{-3}}$. The total average concentration of PAHs was 1.37 $\mathrm{ng \cdot m^{-3}}$, with the concentration proportions of 3-ring, 4-ring, and 5-7-ring PAHs being 3.59%, 32.34%, and 64.07%, respectively. (2) During the observation period, PM2.5 was primarily influenced by long-range transport from the west and short-range transport from the north and west, and may also have been affected by valley winds and boundary layer variations. (3) Positive matrix factorization (PMF) identified the pollution sources as natural gas combustion and petroleum sources (28.56%), motor vehicle emissions and coal combustion (28.46%), biomass burning and industrial pollution (16.14%), non-ferrous metal smelting (14.32%), and dust (12.52%). (4) Direct inhalation of heavy metals and PAHs in PM2.5 through the respiratory tract posed certain carcinogenic risks to both adults and children, while the non-carcinogenic health risks were low. The individual elements that presented carcinogenic risks were Cr, Co, As, and Se, while the health risks of other substances were low.

Full Text

Preamble

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Pollution Characteristics, Sources, and Health Risk Assessment of Heavy Metals and Polycyclic Aromatic Hydrocarbons in PM2.5 in the Middle Tianshan Mountains

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Abstract

To investigate the pollution characteristics, sources, and health effects of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in PM2.5 in the middle Tianshan Mountains, PM2.5 samples were collected in the Wulasitai region from July to September 2019. Heavy metal contents were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS), and PAHs were analyzed using gas chromatography-mass spectrometry (GC-MS). The results showed that: (1) Concentrations of heavy metals and PAHs in PM2.5 were generally low. The total average concentration of heavy metals was 238.50 $\mathrm{ng \cdot m^{-3}}$, with element concentrations following the order Fe > Cu > Zn > Pb > Mn > Cr > As > V > Rb > Ni > Co > Se > Cd > Tl. Except for Fe (139.90 $\mathrm{ng \cdot m^{-3}}$) and Cu (78.72 $\mathrm{ng \cdot m^{-3}}$), all other elements had average concentrations below 10 $\mathrm{ng \cdot m^{-3}}$. The total average PAHs concentration was 1.37 $\mathrm{ng \cdot m^{-3}}$, with 3-ring, 4-ring, and 5–7 ring PAHs accounting for 3.59%, 32.34%, and 64.07%, respectively. (2) During the observation period, PM2.5 was mainly influenced by long-distance transport from the west and short-distance transport from the north and west, and may also have been affected by valley winds and boundary layer changes.

(3) Positive Matrix Factorization (PMF) analysis identified pollution sources including natural gas combustion and petroleum sources (28.56%), vehicle emissions and coal burning (28.46%), biomass burning and industrial pollution (16.14%), non-ferrous metal smelting (14.32%), and dust (12.52%). (4) Direct inhalation of PM2.5 posed carcinogenic risks to both adults and children due to heavy metals and PAHs, while non-carcinogenic health risks were relatively low. The elements Cr, Co, As, and Se were identified as high-risk substances.

Keywords: PM2.5; heavy metals; polycyclic aromatic hydrocarbons; pollution characteristics; source analysis; middle Tianshan Mountains

Introduction

PM2.5 is one of the major atmospheric pollutants. Due to its small particle size, long atmospheric residence time, and ability to transport over long distances, it can easily enter the human body through respiration and cause harm to human health and the ecological environment. The particle surface can enrich complex and diverse harmful substances from various sources. Heavy metal elements, including V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Cd, and Pb, can adsorb onto PM2.5 and become one of its harmful components. These elements are not easily degraded in the natural environment, accumulate in the body, and have strong toxicity, damaging the nervous system, kidneys, heart, lungs, and other organs. Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants mainly emitted from anthropogenic activities, most of which have carcinogenic and mutagenic effects on humans and can further generate secondary aerosol pollution through environmental transformation.

Xinjiang is located in the hinterland of the Eurasian continent, with an arid climate, low rainfall, frequent dust storms, and frequent radiation inversion. The geographical environment is not conducive to the removal of atmospheric pollutants, resulting in relatively high overall PM2.5 concentrations. The region is rich in petrochemical resources, has many energy production and processing industries, and rapid growth in vehicle ownership, providing numerous potential sources for heavy metal and PAH emissions. Previous studies on heavy metals and PAHs in PM2.5 in Xinjiang have mostly been conducted independently, with few studies combining the two for comprehensive analysis. The middle Tianshan region has high altitude, is a high precipitation area in Xinjiang, and is far from cities with less direct anthropogenic impact, resulting in an atmospheric environment different from urban areas.

This study collected PM2.5 samples at the northern foothills of the middle Tianshan Mountains during summer and autumn, analyzing heavy metals and PAHs to investigate their pollution characteristics, sources, and health risks. Previous studies have shown that in Urumqi, heavy metals in PM2.5 mainly come from vehicle emissions, industrial metallurgy, and coal and oil combustion. In Yining City and surrounding counties, anthropogenic sources emit more elements such as Zn, Pb, and Mn, with heavy metal elements posing carcinogenic risks to adult males, females, and children that exceed negligible levels. Other studies have found that in Urumqi, the annual average concentration of PAHs in PM2.5 was 448.14 $\mathrm{ng \cdot m^{-3}}$, with the highest concentration in winter and the lowest in summer, mainly from petrochemical industry emissions, coal combustion, and vehicle exhaust. In Yining City, PAH concentrations were 16.70 $\mathrm{ng \cdot m^{-3}}$ in urban areas and 14.60 $\mathrm{ng \cdot m^{-3}}$ in suburban areas, mainly from vehicle emissions. In Urumqi, heavy metal concentrations in PM2.5 were high, especially for Pb and Zn, while in Fuyun County, As concentrations were high due to coal combustion emissions.

Although these studies analyzed the characteristics and sources of PM2.5 pollution in Xinjiang, this research attempts to combine heavy metals and PAHs to discuss their potential connections and common sources, providing a more comprehensive understanding of air pollution and health risks in Xinjiang, and offering scientific support for effective air pollution prevention and control strategies.

1. Materials and Methods

1.1 Sample Collection

The sampling site was the Middle Tianshan Grassland Ecosystem Monitoring Station (43.47°N, 87.20°E, 2169 m), located in Wulasitai, Baiyanggou, Urumqi County, Xinjiang Uygur Autonomous Region, approximately 50 km from Urumqi city center. Sampling was conducted from July 15 to September 10, 2019. Due to the influence of rain and snow processes, no samples were collected on some days. Each sample was collected continuously for 23.5 hours from 17:30 to 18:00 the next day, with a total of 31 samples collected. A medium-flow atmospheric particulate sampler (Wuhan Tianhong TH-150C) equipped with a PM2.5 cutter ($D50 = 2.5 \pm 0.2$ m) was used at a flow rate of 100 $\mathrm{L \cdot min^{-1}}$. Quartz fiber filters (diameter $\Phi = 90$ mm) were used as sampling substrates. Before sampling, filters were baked at 800 °C for 3 hours to remove adsorbed organic compounds. After sampling, filters were folded with the particle-laden side inward, wrapped in tin foil, and stored at -20 °C.

Note: Based on the standard map from the Ministry of Natural Resources Standard Map Service website with approval number GS(2023)2767, with no modifications to the base map boundaries.

[Figure 1: see original paper] Location of sampling sites and atmospheric backward trajectory

1.2.1 Heavy Metal Analysis

Following the method of Zhang et al. [?], filter membranes were punched to obtain samples placed in test tubes. 3 mL of 30% H_2O_2 (ultrapure) and 5 mL of 65% HNO_3 (ultrapure) were added, followed by standing at room temperature for 30 minutes. The samples were then heated in a microwave digestion system (Preekem TOPEX) with a temperature gradient of 120 °C for 3 minutes, 160 °C for 3 minutes, and 200 °C for 5 minutes. After cooling, test tube caps were opened and placed in an acid evaporation device (Preekem G-400) at 150 °C for 5 minutes to remove acid. After evaporation, the solution was transferred to a clean test tube, diluted with 1% HNO_3 to 15 mL, and filtered through a polyethersulfone aqueous syringe filter (SCAA-101, 13 mm × 0.45 m). The filtrate was used for determination. Heavy metal ion analysis was performed using an inductively coupled plasma mass spectrometer (Agilent 7850 ICP-MS) in helium collision mode to determine the concentrations of 15 elements. Detection limits were: V (4.92×10^{-3} ng · m^{-3}), Cr (4.50×10^{-3} ng · m^{-3}), Mn (6.40×10^{-3} ng · m^{-3}), Fe (4.22×10^{-3} ng · m^{-3}), Co (3.29×10^{-3} ng · m^{-3}), Ni (9.86×10^{-3} ng · m^{-3}), Cu (1.73×10^{-3} ng · m^{-3}), Zn (7.42×10^{-3} ng · m^{-3}), As (4.02×10^{-3} ng · m^{-3}), Se (3.80×10^{-3} ng · m^{-3}), Rb (3.57×10^{-3} ng · m^{-3}), Cd (3.22×10^{-3} ng · m^{-3}), Tl (4.15×10^{-3} ng · m^{-3}), and Pb (1.34×10^{-3} ng · m^{-3}). Blank contamination for some elements was high, so these were not considered in the study.

1.2.2 PAHs Analysis

Following the method of Santos et al. [?], a simple, comprehensive, and miniaturized solvent extraction method was used. Non-porous filters (Whatman Mini UniPrep) with 0.2 m polytetrafluoroethylene membrane at one end were used. The extraction agent was a liquid mixture of dichloromethane. A small piece of filter membrane was placed in the filter chamber containing 500 L of extraction agent, and the filter was ultrasonically extracted using a desktop ultrasonic cleaner (Kunshan Shumei KQ5200) for 23 minutes. The extract was then manually compressed (Whatman Mini UniPrep G2). A mixed standard solution (J&K Scientific) at 10 mg · L^{-1} was used as the standard working curve, with 0.5 L added to samples as an internal standard. Analysis was performed using gas chromatography-mass spectrometry (Agilent), with an HP-5MS chromatographic column (30 m × 0.25 mm × 0.25 m) and high-purity helium (>99.999%) as carrier gas at 1 mL · min^{-1}. Detection components and limits were: naphthalene (1.63×10^{-3} ng · m^{-3}), acenaphthylene (1.59×10^{-3} ng · m^{-3}), acenaphthene (1.41×10^{-3} ng · m^{-3}), fluorene (1.48×10^{-3} ng · m^{-3}), phenanthrene (3.92×10^{-3} ng · m^{-3}), anthracene (8.98×10^{-3} ng · m^{-3}), fluoranthene (2.24×10^{-3} ng · m^{-3}), pyrene (2.57×10^{-3} ng · m^{-3}), benz[a]anthracene (1.15×10^{-3} ng · m^{-3}), chrysene (2.92×10^{-3} ng · m^{-3}), benzo[b]fluoranthene (1.02×10^{-3} ng · m^{-3}), benzo[k]fluoranthene (1.44×10^{-3} ng · m^{-3}), benzo[a]pyrene

(2.87×10^{-3} $ng \cdot m^{-3}$), indeno[1,2,3-cd]pyrene (1.25×10^{-3} $ng \cdot m^{-3}$), dibenz[a,h]anthracene (9.77×10^{-3} $ng \cdot m^{-3}$), benzo[ghi]perylene (9.80×10^{-3} $ng \cdot m^{-3}$), and coronene (1.75×10^{-3} $ng \cdot m^{-3}$). Concentrations below detection limits were treated as not detected.

1.3 Meteorological Elements and Backward Trajectory Analysis

Meteorological data including temperature, relative humidity, wind speed, and precipitation were obtained from the Urumqi Grassland Meteorological Experimental Station approximately 50 km from the sampling site, with a time resolution of 1 hour. This study calculated the Pearson correlation coefficients between meteorological elements and heavy metals and PAHs concentrations during the sampling period, with significance testing to analyze correlations.

Backward trajectories were analyzed using the MeteoInfo software based on the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [?]. Model data were from the GDAS dataset. The model height was set at 500 m, which accurately reflects the average flow field characteristics of the boundary layer [?]. Backward trajectories reaching the sampling site at four times daily (00:00, 06:00, 12:00, 18:00) were calculated for the sampling period, followed by cluster analysis.

1.4.1 Enrichment Factor

The enrichment factor (EF) is widely used in heavy metal source studies to determine the degree of anthropogenic influence by comparing the content of elements in background environments with their actual content in specific samples [?]. The calculation method is:

$$EF = \frac{(C_{sample}/C_{ref})_{sample}}{(C_{sample}/C_{ref})_{soil\ background}}$$

where C_{sample} and C_{ref} are the concentrations of the studied element and reference element, respectively. The ratio represents the concentration ratio of studied to reference elements in the sample versus soil background. Generally, EF < 10 indicates natural sources, EF > 10 indicates increasing anthropogenic influence, with higher EF values indicating greater anthropogenic contribution. The reference element should be stable in the environmental background; this study selected Fe with low coefficient of variation. Soil background values were taken from "Background Values of Soil Elements in China" for Xinjiang [?], with missing data supplemented by Northwest China land quality geochemical survey data [?].

1.4.2 PAHs Characteristic Ratio Method

Different pollution sources emit different PAH components and concentrations. Calculating the concentration ratios of different components is a simple and rapid method for pollution source analysis. This study calculated Ant/(Ant+Phe), BaA/(BaA+Chr), IcdP/(IcdP+BghiP), and BaP/BghiP ratios, with different ratios representing different pollution sources as shown in Table 1.

Characteristic ratios of PAHs corresponding to different sources

1.4.3 PMF Model

This study used the EPA PMF 5.0 model for source apportionment. The PMF model decomposes source data into source profile distribution matrices and source contribution matrices. After specifying the number of pollution sources, it uses weights to calculate errors for different components, determines the relative contributions of pollution sources using the least squares method, and identifies source types based on source profile data [?]. The basic principle is:

$$X_{ij} = \sum_{k=1}^{P} G_{ik} F_{kj} + E_{ij}$$

where X_{ij} is the concentration of substance j in sample i ($\mathrm{ng} \cdot \mathrm{m}^{-3}$); G_{ik} is the concentration of factor k in sample i ($\mathrm{ng} \cdot \mathrm{m}^{-3}$); F_{kj} is the concentration of substance j in factor k ($\mathrm{ng} \cdot \mathrm{m}^{-3}$); E_{ij} is the residual factor of substance j in sample i ($\mathrm{ng} \cdot \mathrm{m}^{-3}$); and P is the total number of pollution sources.

The main objective is to minimize the objective function Q, making calculated values as close as possible to theoretical values:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{(X_{ij} - \sum_{k=1}^{P} G_{ik} F_{kj})^2}{U_{ij}^2}$$

where U_{ij} is the uncertainty of substance j in sample i.

1.5 Health Risk Assessment Method

Based on the human health risk assessment model recommended by USEPA [?] and the "Technical Guidelines for Health Risk Assessment of Regional Environmental Pollution" [?], this study used an improved algorithm based on inhaled chronic exposure concentration (EC) to calculate carcinogenic and non-carcinogenic risks from direct inhalation of PM2.5.

The exposure concentration is calculated as:

$$EC = \frac{CA \times ET \times EF \times ED}{AT}$$

where CA is the pollutant concentration in air ($\text{g} \cdot \text{m}^{-3}$); ET is exposure time ($\text{h} \cdot \text{d}^{-1}$); EF is exposure frequency ($\text{d} \cdot \text{a}^{-1}$); ED is exposure duration (years); and AT is averaging time (h). Health risk exposure parameters for different populations are shown in Table 2.

Value of health risk exposure parameters of different populations

Non-carcinogenic health risk is assessed using the dimensionless hazard quotient (HQ):

$$HQ = \frac{EC}{Rfc \times 1000}$$

where Rfc is the inhalation reference concentration ($\text{mg} \cdot \text{m}^{-3}$). Generally, HQ > 1 indicates non-carcinogenic health risk, with larger values indicating higher risk. When multiple pollutants are present, total health risk is assessed using the hazard index (HI):

$$HI = \sum HQ$$

Carcinogenic risk is assessed using the dimensionless excess lifetime cancer risk (ECR):

$$ECR = EC \times IUR$$

where IUR is the inhalation unit risk factor ($\text{g}^{-1} \cdot \text{m}^{3}$). Generally, ECR $< 10^{-6}$ indicates no significant carcinogenic risk; $10^{-6} <$ ECR $< 10^{-4}$ indicates some carcinogenic risk; and ECR $> 10^{-4}$ indicates serious carcinogenic risk.

Heavy metal elements with health risks include Cr, Co, As, Se, and Cd [**?**]. The hexavalent form of Cr is the most toxic and representative species, so this study introduced the dimensionless toxic equivalency factor (TEF) to convert concentrations of other species to the health risk equivalent of Cr^{6+}, then summed them to obtain the total toxic equivalency concentration (TQE):

$$TQE = \sum C_i \times TEF_i$$

where C_i is the mass concentration of species i ($\text{ng} \cdot \text{m}^{-3}$) and TEF_i is the toxic equivalency factor relative to Cr^{6+}.

Concentration values of Rfc and IUR of heavy metals

2. Results and Analysis

2.1 Heavy Metal Concentration Characteristics and Enrichment Factors

The concentration levels of 15 heavy metal elements in PM2.5 are shown in Table 4. The total average concentration was 238.50 $\mathrm{ng\cdot m^{-3}}$. The average concentrations of each element followed the order: Fe > Cu > Zn > Pb > Mn > Cr > As > V > Rb > Ni > Co > Se > Cd > Tl. The average concentrations of Fe (139.90 $\mathrm{ng\cdot m^{-3}}$) and Cu (78.72 $\mathrm{ng\cdot m^{-3}}$) were significantly higher than other elements, while the remaining elements were all below 10 $\mathrm{ng\cdot m^{-3}}$. The coefficient of variation for most elements was small, indicating relatively stable concentrations, while Zn, As, Se, and Cd showed larger variation coefficients, indicating greater concentration fluctuations. Compared with other regions in China (Table 5), most heavy metal concentrations in PM2.5, especially Fe and Cu, were significantly lower in the middle Tianshan Mountains. Only Zn and Pb concentrations were relatively high compared to other regions.

Concentration of heavy metals in PM2.5 in middle Tianshan Mountains

Comparison of average concentrations of heavy metals in PM2.5 in China

2.2 PAHs Concentration Characteristics

The average concentration of PAHs in PM2.5 was 1.37 $\mathrm{ng\cdot m^{-3}}$ (Table 6). The highest average concentration was for BghiP (0.47 $\mathrm{ng\cdot m^{-3}}$), followed by BaP (0.23 $\mathrm{ng\cdot m^{-3}}$), IcdP (0.16 $\mathrm{ng\cdot m^{-3}}$), and BbF (0.14 $\mathrm{ng\cdot m^{-3}}$). The average concentration of BaP was 0.10 $\mathrm{ng\cdot m^{-3}}$, far below the limit value in the "Environmental Air Quality Standard" [?]. The lowest average concentration was for Cor (0.01 $\mathrm{ng\cdot m^{-3}}$), also the only component below the detection limit.

PAHs with different ring numbers have different properties. Lower molecular weight PAHs (3-4 rings) are more volatile, while higher molecular weight PAHs (5-7 rings) have lower volatility and longer residence times [?]. The proportions of different ring numbers were: 3-ring 3.59%, 4-ring 32.34%, and 5-7 ring 64.07%. Compared with other regions in China (Table 7), PAH concentrations in PM2.5 at most sites were higher than in the middle Tianshan Mountains. The proportion of 5-7 ring PAHs in the middle Tianshan was significantly higher than at other sites, while the proportion of 3-ring PAHs was relatively high.

Concentration of PAHs in PM2.5 in middle Tianshan Mountains

Comparison of average concentrations of PAHs in PM2.5 in China

2.3 Meteorological Elements and Backward Trajectory Analysis

Based on meteorological data for temperature, relative humidity, precipitation, wind speed, and wind direction during the sampling period (Fig. 2), correlations between meteorological elements and heavy metals and PAHs concentrations were calculated (Fig. 3). Some heavy metals showed negative correlations with relative humidity and precipitation, and positive correlations with wind speed. PAHs showed negative correlations with relative humidity and positive correlations with temperature and wind speed.

[Figure 2: see original paper] Daily variation characteristics of meteorological factors and PM2.5 components in middle Tianshan Mountains

[Figure 3: see original paper] Correlation coefficient between meteorological elements and PM2.5 components in middle Tianshan Mountains

Precipitation during the sampling period mostly occurred in the evening to nighttime, which is already a period with less pollution emission and transport [**?**], so no significant scavenging effect was observed. The negative correlation between PAHs and relative humidity may be related to wet deposition processes, as gaseous PAHs can dissolve in atmospheric droplets during condensation, causing a significant reduction in concentration and leading to transformation from particle phase to gas phase, thereby reducing particle-phase PAHs concentration [**?**]. The positive correlations of PAHs with temperature and wind speed may be related to valley wind transport and boundary layer diffusion. Higher daytime temperatures in mountainous areas strengthen mountain winds, facilitating pollutant transport from low-altitude urban areas to high-altitude mountainous regions. At the same time, high temperatures result in thicker atmospheric boundary layers, making it easier for pollutants to diffuse upward. However, low-ring PAHs are more likely to transform to gas phase at high temperatures, while high-ring PAHs are more stable and more likely to show positive correlations [**?**].

Additionally, based on wind direction during the sampling period, high total heavy metal concentrations occurred more frequently during west-southwest, northwest, and north-northwest winds. For some elements with higher concentrations, the high-value wind directions were relatively consistent with those for total heavy metals. High values of Zn and Pb occurred mainly during northwest and north-northwest winds, while high values of Mn occurred mainly during north-northwest, east-northeast, and east winds. High PAHs concentrations occurred more frequently during west-southwest, northwest, and northeast winds, with high values of BghiP occurring mainly during east-northeast and east winds.

The backward trajectories and cluster analysis during the sampling period are shown in Fig. 1. PM2.5 in the middle Tianshan Mountains was mainly affected by air mass transport from the west and north. Short-distance trajectories from the north accounted for 8.33%, which, although a small proportion, passed through Urumqi, the nearest city, and may have had a significant impact on PM2.5 composition and concentration. Among trajectories from the west, short-distance transport accounted for 8.33%, passing through the Tianshan Mountains and affected by pollution emissions from cities such as Yining; long-distance transport accounted for 83.34%, originating from Central Asia.

Combining backward trajectories with wind directions, both long-distance and short-distance air masses from different directions contributed to heavy metals and PAHs in PM2.5, but their contributions to different components were not consistent. All five air mass trajectories transported significant amounts of Fe and Cu. Some elements such as Zn, Pb, and Mn mainly came from short-distance transport from Urumqi. Different ring-number PAHs also had different sources. Low-ring PAHs are more easily transformed to gas phase or eliminated through reactions with free radicals during long-distance transport [**?**], so they mainly came from short-distance transport from Urumqi with relatively high concentrations. High-ring PAHs are more stable and can reach the middle Tianshan Mountains through long-distance transport from the west.

2.4.1 Enrichment Factors

The average EF values for each element are shown in Fig. 4. The EF values for Cd and Se were the highest, with average values of 89.70 and 74.22, respectively, indicating significant anthropogenic contributions. The EF values for As, Pb, Zn, Cu, and Ni were between 10 and 50, with samples accounting for 96.72%, 86.89%, 50.82%, 39.45%, and 18.20%, respectively, indicating that these elements were predominantly from anthropogenic sources. The EF values for Cr and Co were around 10, with about 50% of samples having EF > 10, indicating some anthropogenic contribution but not completely dominant. The EF values for V, Mn, Rb, and Fe were less than 10, with some samples having EF > 10, indicating minor but existing anthropogenic influence.

[Figure 4: see original paper] Average enrichment factors of heavy metals in PM2.5 in middle Tianshan Mountains

2.4.2 PAHs Characteristic Ratios

The average characteristic ratios of PAHs are shown in Fig. 5. The average Ant/(Ant+Phe) ratio was 0.20, with most samples > 0.10, indicating combustion sources as dominant. The average BaA/(BaA+Chr) ratio was 0.29, with most samples between 0.20-0.35, showing mixed influence from petroleum and combustion sources. The average IcdP/(IcdP+BghiP) ratio was 0.52, with all samples > 0.50, indicating significant influence from coal and biomass combustion. The average BaP/BghiP ratio was 0.49, with most samples > 0.50, indicating vehicle emission sources. Overall, PAHs had diverse sources, dominated by combustion sources including coal, biomass, and liquid fossil fuel combustion, with petroleum sources also having some influence.

[Figure 5: see original paper] Characteristic ratios of PAHs in PM2.5 in middle Tianshan Mountains

2.4.3 PMF Source Apportionment

PMF analysis identified five contributing factors for heavy metals (Fig. 6). Factor 1 had high contributions to V, Ni, and Tl (74.22%, 54.98%, and 41.19%, respectively), with lower contributions to other elements (mostly $< 30\%$). V and Ni are typical tracers of natural gas, and Tl is a chemical marker of industrial petroleum [?], so Factor 1 was identified as natural gas combustion and petrochemical sources, with a total contribution of 28.56%.

Factor 2 had high contributions to Zn, Pb, and Mn (90.01%, 66.73%, and 60.95%, respectively), with contributions to other elements mostly between 20-30%. Zn, Pb, and Mn are typical markers of vehicle emissions [?], and Zn and Pb are also representative elements of coal combustion [?], so Factor 2 was identified as vehicle emissions and coal combustion mixed sources, with a total contribution of 28.46%.

Factor 3 had high contributions to Cd and Se (74.95% and 54.21%, respectively), with contributions to other elements mostly $< 20\%$. Non-ferrous metal mining and smelting processes emit large amounts of Cd and Se [?], so Factor 3 was identified as non-ferrous metal smelting sources, with a total contribution of 14.32%.

Factor 4 had contributions $> 20\%$ to Cr, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Cd, Tl, and Pb, with the highest contribution to Fe (55.07%). Xinjiang has extensive selenium-rich soil, and Urumqi is a concentrated area of selenium-rich farmland [?], so these elements likely originated from agricultural soil. Additionally, Fe, Cu, and Zn are tracers of road dust and construction dust [?], so Factor 4 was identified as dust sources, with a total contribution of 12.52%.

Factor 5 had contributions $> 20\%$ only to Cr and Co (39.45% and 18.20%, respectively). Cr is a representative element of coal combustion [?], and Co is related to industrial production processes such as coking [?], so Factor 5 was identified as biomass combustion and industrial pollution mixed sources, with a total contribution of 16.14%.

Overall, heavy metals and PAHs shared some common sources. The factor identified as vehicle emissions and coal combustion mixed source contributed 39.45% to heavy metals and 18.20% to PAHs, making it the most important common source. Some individual components had higher proportions from the same source, such as the biomass combustion and industrial pollution mixed source factor contributing 49.30% to PAHs and 7.17% to heavy metals.

[Figure 6: see original paper] Ratio of PMF source resolution factors

2.5 Health Risk Assessment

The health risks of heavy metals and PAHs are shown in Table 8. The total non-carcinogenic health risk (HI) for heavy metals was 1.20×10^{-3} for adults and 1.12×10^{-3} for children, both far below 1, indicating low non-carcinogenic health risk. The total carcinogenic risk (ECR) for heavy metals was 6.08×10^{-6} for adults and 1.14×10^{-6} for children. The adult risk exceeded 10^{-6}, indicating some carcinogenic risk, with higher risk for adults. Among individual elements, only Cr had ECR values of 3.17×10^{-6} for adults and 1.69$×10^{-6}$ for children, indicating some carcinogenic risk, while other elements were slightly above 10^{-6}.

The total ECR for PAHs was 2.47$×10^{-8}$ for adults and 8.22$×10^{-9}$ for children, both below the risk threshold. The total HI for PAHs was 6.90$×10^{-4}$ for adults and 4.18$×10^{-4}$ for children. Overall, PAHs had lower carcinogenic and non-carcinogenic health risks than heavy metals. The individual substance BaP had an ECR of 5.18$×10^{-6}$ for adults, indicating some carcinogenic risk, while other PAHs had low health risks.

HQ and ECR for heavy metals and PAHs

3. Conclusions

(1) During summer and autumn in the middle Tianshan Mountains, the total average concentration of heavy metals in PM2.5 was 238.50 $\mathrm{ng \cdot m^{-3}}$, with Fe and Cu having the highest average concentrations, while other elements were below 10 $\mathrm{ng \cdot m^{-3}}$. The total average PAHs concentration was 1.37 $\mathrm{ng \cdot m^{-3}}$, with 3-ring, 4-ring, and 5-7 ring PAHs accounting for 3.59%, 32.34%, and 64.07%, respectively. Heavy metal and PAHs concentrations were significantly lower than in other regions of China, with only Zn and Pb concentrations being relatively high.

(2) In the backward trajectories during the sampling period, short-distance transport from the north accounted for 8.33%, short-distance transport from the west accounted for 8.33%, and long-distance transport from the west accounted for 83.34%. Air masses passing through Urumqi and Yining may have significantly impacted PM2.5 in the middle Tianshan Mountains. Meteorological elements such as temperature, humidity, and wind speed were correlated with concentration changes, possibly affecting PM2.5 through changes in gas-particle partitioning, transformation processes, and transport mechanisms such as valley winds and boundary layer changes.

(3) Heavy metals and PAHs had multiple sources including anthropogenic and natural sources. PMF source apportionment identified pollution sources including natural gas combustion and petroleum sources (28.56%), vehicle emissions and coal combustion (28.46%), biomass combustion and industrial pollution (16.14%), non-ferrous metal smelting (14.32%), and dust (12.52%). Vehicle emissions and coal combustion were the most important common sources of heavy metals and PAHs.

(4) Health risk assessment for direct inhalation of PM2.5 showed that non-carcinogenic health risks for adults and children were low, but some carcinogenic risk existed, with higher risk for adults. Among heavy metals, Cr posed some carcinogenic risk, while other elements had low health risks.

Among PAHs, BaP posed some carcinogenic risk, while other substances had low carcinogenic and non-carcinogenic health risks.

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