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Pollution characteristics, sources, and risk assessment of heavy metals and perfluorinated compounds in $PM_{2.5}$ in the major industrial city of northern Xinjiang, China

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Abstract

At present, research on $PM_{2.5}$ has focused on eastern and central China; little attention has been given to Xinjiang, the most northwestern part of China. Ten kinds of heavy metals (HMs) and 12 kinds of perfluorinated compounds (PFCs) in atmospheric $PM_{2.5}$ are detected by inductively coupled plasma mass spectrometry and high-performance liquid chromatography-mass spectrometry, respectively. Principal component analysis and risk assessment methods are used to study HMs and PFCs and explore their pollution levels and health risks. Results show that HMs and PFCs are prevalent in atmospheric $PM_{2.5}$ of Shihezi and Urumqi. The spatial distributions of HMs and PFCs in four sampling sites are development zone (B1) = industrial park (A1) > factory (A3) > school (A2) and A1 > A3 > B1 > A2, respectively. In the four sampling sites, copper, lead, zinc, and cadmium (Cd) contents are relatively high. Perfluorooctane sulfonate (PFOS), perfluorohexanoic acid (PFHxA), and perfluorooctanoic acid (PFOA) are the most prevalent PFCs. Risk assessment results show that PFCs in the atmosphere will not harm residents, but the Cd and nickel (Ni) in HMs are harmful to humans, especially Cd, which has both carcinogenic and non-carcinogenic risks. These findings indicate that the carcinogenic risk of HMs and PFCs in children is higher than in adults. In addition, HMs and PFCs may cause joint toxicity.

Keywords PFCs · HMs · Source analysis · Risk assessment · Principal component analysis (PCA)

Introduction

$PM_{2.5}$ is one of the most important components of air pollution that has attracted global attention. However, the chemical and physical properties of atmospheric aerosols have yet to be fully understood (Gumede and Savage 2017). Given the small size, complex composition, and strong environmental activity of $PM_{2.5}$, such particles can serve as a carrier of chemicals, heavy metals (HMs), bacteria, toxins, and carcinogens (Coronas et al. 2016; Shi et al. 2014a). The chemical composition of $PM_{2.5}$ is an important factor in determining its health effects. HMs (inorganic substances) and PFCs (organic substances) are difficult to degrade and have a significant impact on human health and the environment. After $PM_{2.5}$ exposure, different HMs preferentially accumulate in different body tissues (Li et al. 2015). In the past decade, many cities in China, such as Xining and Nanjing, have taken measurements of and conducted research of HMs in $PM_{2.5}$ (Shi et al. 2014b; Qi et al. 2016a). Research and development in foreign countries began in the 1990s, and relevant studies have been conducted on the sources, hazards, and transformation of HMs in $PM_{2.5}$ (Van Vliet et al. 1997).

PFCs are hydrophobic and oleophobic organic compounds in which all hydrogen atoms in the carbon chain are replaced by fluorine atoms. PFCs are difficult to degrade, have bioaccumulative and potentially toxic effects, and can be adsorbed onto $PM_{2.5}$. PFCs are widely used in industrial applications and consumer products (Wu et al. 2015), including products for antifouling and water and grease protection. In 2010, PFCs were found in fish collected from alpine lakes in the Tibetan Plateau and found in cattle in Xinjiang (Shi et al. 2010; Wang et al. 2017). Studies on the hazards of PFCs have

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shown that PFCs can enter the body of the elderly and cause diabetes (Lind et al. 2014). PFCs have also been found in the umbilical cord serum of infants, where the concentration increases rapidly during the first few months of life (Fromme et al. 2010). Concerns about PFCs have increased significantly in recent years. However, most regions of the world, especially China, still lack PFC toxicity data.

Therefore, we decided to identify the source and spatial distribution of HMs and PFCs and conduct health risk assessments, laying the foundation for controlling local emissions of HMs and PFCs, and preventing and reducing cancer risk.

Materials and methods

Sampling time and location

According to the characteristics of functional areas with different sources of pollution, environmental carrying capacity and population densities, four sampling sites were selected in Shihezi and Urumqi, as shown in Fig. 1 and Table 1.

The population densities of A1, A2, A3, and B1 are 5300 persons km^{-2}, 6700 persons km^{-2}, 500 persons km^{-2}, and 570 persons km^{-2}, respectively. $PM_{2.5}$ was collected on a 47-mm QMA quartz filter (manufactured by Whatman) using a low-flow $PM_{2.5}$ sampler (manufactured by US BGI). The sampler had a sampling flow rate of 10 L min^{-1}; the sampling time was 23 h from 11:00 p.m. to 10:00 p.m. the next day. Samples were collected on the 1st, 5th, 11th, 15th, 21st, and 25th of each month in order to reduce the amount of experimentation while ensuring that the data are reasonable. The sampling period was from January 1, 2018, to June 30, 2018, for a total of 36 observation days; a total of 144 samples were collected. In Xinjiang, January to March is the cold season, whereas April to June is the hot season. The filter was placed in a muffle furnace at 700 °C for 4 h before sampling to remove carbonaceous contaminants. Then, the collected filter was placed in a sealed bag and stored in a refrigerator at − 18 °C. Disposable gloves were used for each sample to reduce human error in the experimental data.

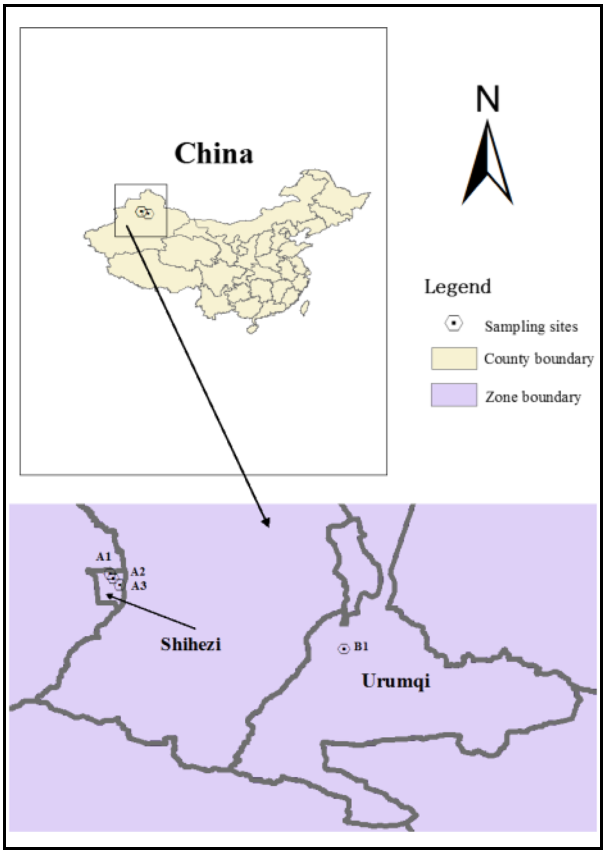

Fig. 1 The sampling sites in Shihezi and Urumqi

HMs analysis

Extraction of HMs

The HNO_3–$HClO_4$–HF digestion system was used for sample pretreatment. The NexIon 350X inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer, USA) was used to analyze the contents of ten elements that are truly classified as HMs in industry: Cu, Pb, Zn, Cd, cobalt (Co), Ni, antimony (Sb), bismuth (Bi), mercury (Hg), and tin (Sn). Specifically, the weighed filter membrane was cut with Teflon scissors and placed in a Teflon digestion tank, and 10 mL nitric acid and 5 mL perchloric acid were poured into it. The tank was covered and heated by a temperature-controlled heating plate. The sample was heated to approximately 180 °C, digested for 4–5 h and cooled to room temperature. Then, 3 mL hydrofluoric acid was added. The temperature rose to approximately 220 °C, and heating and digestion were continued until the sample was nearly dry. After cooling to room temperature, 50 mL ionized water was added and passed through a 0.22-μm filter. The solution was stored in a clean centrifuge tube at 4 °C before analysis.

Determination by ICP-MS

The main working conditions of ICP-MS were as follows: RF power of 1200 W, atomizing gas flow of 0.88 L min^{-1}, carrier gas flow of 18.0 L min^{-1}, auxiliary gas flow of 0.75 L min^{-1}, sampling cone diameter of 1.0 mm, intercept cone diameter of 0.7 mm, super-cut cone diameter of 0.5 mm, scanning method is the jump peak, number of scans is 20, and the number of repetitions is 2.

Analysis of PFCs

A method for determining PFCs in $PM_{2.5}$ was developed. It involves connecting a liquid chromatograph to a triple

Table 1 Descriptions of the four sampling sites

Sampling sites	Environmental characteristics	Type of functional area	Geographic coordinates
A1	North of the Shihezi	Industrial transportation mixed area	44° 33′ N, 86° 04′ E
A2	Central part of the Shihezi	Cultural educational mixed area	44° 30′ N, 86° 06′ E
A3	South of the Shihezi	Industrial transportation mixed area	43° 86′ N, 87° 50′ E
B1	Central part of the Urumqi	Industrial residential mixed area	43° 86′ N, 87° 50′ E

quadrupole tandem mass spectrometry system (LC-MS/MS), which is sensitive and accurate (Zafeiraki et al. 2014). In this study, solid-phase extraction (SPE) was combined with high-performance liquid chromatography-mass spectrometry (SPE-HPLC-MS/MS).

Ultrasonic extraction

The quartz filter was cut with Teflon scissors, placed in a conical flask and soaked in 10 mL methanol for 0.5 h, and then placed in an ultrasonic cleaner for 1 h and rinsed with 2 mL methanol. Finally, the contents of the vial were poured into a clean tube. The entire process was repeated three times in succession.

SPE

The extraction device was connected to the vacuum pump. The SPE column was placed on the device and activated by the addition of 5 mL ultra-pure water and methanol. After the preparation, the solution was poured into the SPE column for filtration extraction, and the flow rate was controlled at 0.3 mL min^{-1}. Finally, 0.5 mL of solution was collected and blown with nitrogen, and the mobile phase was added to the sample until 1.5 mL.

Liquid quality conditions

HPLC analysis

The Agilent Eclipse XDB C18 column (3.5 μm, 2.1 mm × 100 mm) was used with an injection volume of 10 μl and a flow rate of 0.25 mL min^{-1}. The residence time is 12 min while the residence time in the column is 8 min. The gradient elution procedure for mobile phases A (2 m mol L^{-1} aqueous ammonium acetate) and B (acetonitrile) was as follows: (1) 60% A and 40% B at the beginning; (2) 10% A and 90% B at 9 min; and (3) 10% A and 90% B at 12 min.

Mass spectrometry conditions

An electron spray ion source was connected, and the electron multiplying voltage is 600 V. The capillary voltage is 4.0 kV, dry gas temperature is 350 °C, dry gas flow rate is 8 L min^{-1}, and nebulizer pressure is 38 psi. The IS method was used for quantification.

Principal component analysis

Principal component analysis (PCA) is a statistical analysis method that grasps the main components of things. It can analyze the main influencing factors from multiple things, reveal the essence of things, and simplify complex problems (Viana et al. 2006). The software SPSS Statistics 22 (IBM) was used to analyze the principal components.

Risk assessment

Health risks are generally divided into carcinogenic and non-carcinogenic risks. Carcinogenic risk has carcinogenic effects on the human body with no dose threshold; that is, trace amounts will have adverse effects on the human body. According to the US Environmental Protection Agency (EPA), if the carcinogenic risk value is greater than 10^{-6}, then the carcinogenic risk of a pollutant exceeds the acceptable level. Non-carcinogenic risk refers to the risk of non-carcinogenic effects on the human body with a dose threshold. Below the threshold, there is no adverse effect on the human body. When the non-carcinogenic risk value is greater than 1, it exceeds the acceptable level.

$$\mathrm{CDI}_{\mathrm{inhale}} = \left(\mathrm{C} \times \mathrm{IRi} \times \mathrm{EF} \times \mathrm{ED} \times 10^{-6}\right)/(\mathrm{BW} \times \mathrm{AT}), \quad (1)$$

where $\mathrm{CDI}_{\mathrm{inhale}}$ is the oral and nasal exposure dose [mg (kg d)$^{-1}$], C is the mass concentration of the pollutant in $PM_{2.5}$ (μg m^{-3}), IRi is the air intake (8.7 m^{-3} for children, 15.2 m^{-3} for adult males, and 11.3 m^{-3} for adult females), EF is the exposure frequency (365 d a^{-1}), ED is the exposure period (18 a for children, 30 a for adults), CF is the conversion factor (10^{-6} kg mg^{-1}), BW is the body weight (44 kg for children, 62.7 kg for adult males, and 54.4 kg for adult females), and AT is the average time of action (18 × 365 days for children and 30 × 365 days for adults) (US EPA 2004; Duan 2012).

$$HQ = CDI_{inhale}/RfD, \tag{2}$$

$$R = CDI_{inhale} \times SF, \tag{3}$$

where HQ and R are carcinogenic and non-carcinogenic risk values, respectively. RfD is the chronic reference dose, and SF is the carcinogenic slope factor. These values were set by the US EPA (2004).

Quality control and quality assurance

Quality assurance and quality control procedures were applied for ensuring the reliability of experimental data. The target recovery for all elements was in the range of 100% ± 25%. The correlation coefficients of the standard curves were greater than 0.999. The limit of detection (LOD) is the concentration of the signal-to-noise ratio (S/N) of 3. The limit of quantitation (LOQ) is defined as the minimum calibration standard for the S/N. For PFCs, the LOD ranged from 0.03 to 6.20 pg/m^3, the LOQ ranged from 0.07 to 15.98 pg/m^3. For HMs, the LOD ranged from 0.001 to 0.016 μg/m^3, and the LOQ ranged from 0.003 to 0.064 μg/m^3.

Results and discussion

$PM_{2.5}$ mass concentration

As shown in Fig. 2, the average $PM_{2.5}$ mass concentration range of A1 was 14.83–343.26 μg m^{-3}. The maximum value occurred in February, and the minimum value occurred in June, with a mean value of 127.91 ± 122.87 μg m^{-3}. The average $PM_{2.5}$ mass concentration range of A3 was 20.33–277.50 μg m^{-3} which occurred in February, and the minimum value occurred in June, with a mean value of 115.52 ± 100.29 μg m^{-3}. The average $PM_{2.5}$ mass concentration range of B1 was 21.86–207.5 μg m^{-3} which occurred in January, and the minimum occurred in May, with a mean of 95.26 ± 72.42 μg m^{-3}. The average $PM_{2.5}$ mass concentration range of A2 was 21.86–153.31 μg m^{-3} which occurred in February, and the minimum value occurred in May, with a mean value of 80.98 ± 55.19 μg m^{-3}.

The average $PM_{2.5}$ mass concentrations in the four sampling sites were similar to industrial cities in domestic, such as Beijing (125.00 μg m^{-3}) and Yangzhou (104.30 μg m^{-3}) (Ha et al. 2018; Ge et al. 2017). The average value of the four sampling sites decreased in the following order: A1 > A3 > B1 > A2. According to the latest Chinese ambient air quality standard, GB3095-2012, the average $PM_{2.5}$ of the four sampling sites exceeded the daily average secondary standard (75 μg m^{-3}). The maximum values of the three sites in Shihezi occurred in February, indicating a correlation between the three sampling sites. In February, the $PM_{2.5}$ values of the sampling sites were large, and the values of A1 and A3 were

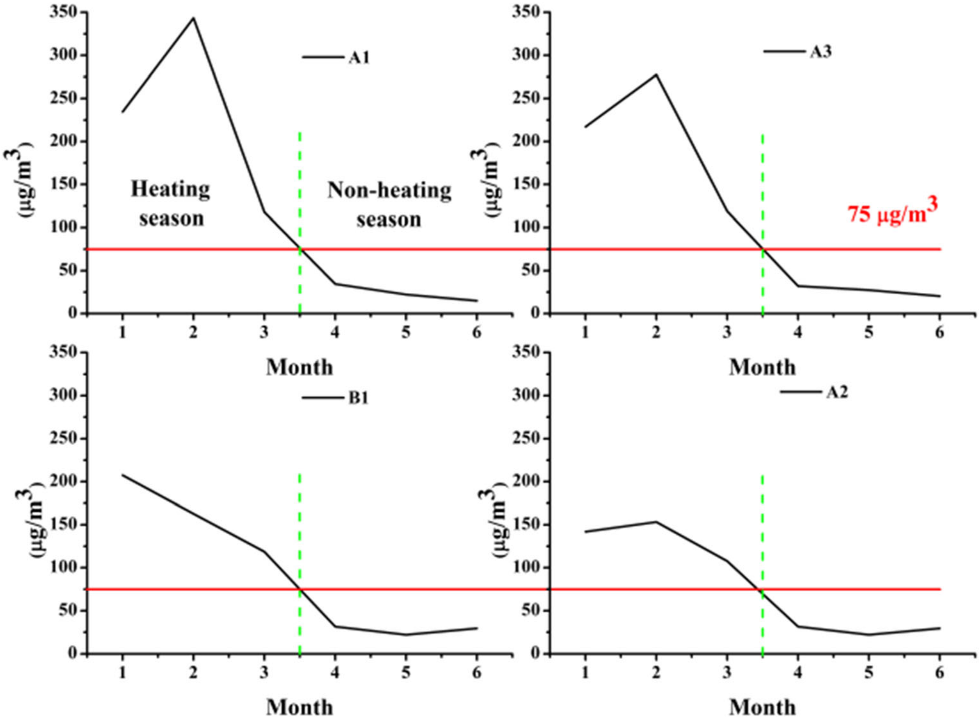

Fig. 2 The monthly average concentration of $PM_{2.5}$ in four sampling sites

significantly larger than those of B1 and A2. In January and March, the $PM_{2.5}$ values of A1, A3, and B1 were similar. In addition, the $PM_{2.5}$ values in January, February, and March were significantly greater than those in April, May, and June, and the $PM_{2.5}$ value of the dividing line (mid-March) is exactly 75 μg m^{-3}; this pattern may be related to heating energy (coal-fired) and heating way (water-heating system) in winter in the two cities (Khanum et al. 2017).

HMs

Concentration levels and composition of HMs

As seen in Fig. 3, among all the HMs detected, Pb, Zn, Cd, and Cu were at a highest level, followed by Hg and Bi; Ni, Sb, Sn, and Co were at the lowest. The percentage of elements in HMs were as follows: Pb (29.3%) > Zn (28.03%) > Cd (20.38%) > Cu (10.19%) > Hg (4.46%) > Bi (3.82%) > Ni (1.27%) = Sb (1.27%) > Sn (0.64%) = Co (0.64%).

The Zn content of A1 was the largest among the HMs, and the Pb content of B1 was also relatively large. According to China's latest GB3095-2012, the reference concentration limits of Pb, Cd, and Hg are 0.5 μg m^{-3}, 0.005 μg m^{-3}, and 0.05 μg m^{-3}, respectively, which the measured values exceed. The distribution of the total average concentration of HMs in the four sampling sites is as follows: A1 (0.20 ± 0.31 μg m^{-3}) = B1 (0.20 ± 0.32 μg m^{-3}) > A3 (0.17 ± 0.21 μg m^{-3}) > A2 (0.07 ± 0.10 μg m^{-3}). The maximum value was detected in B1. The values of A1 and B1 were equal possibly because the two sites were subjected to the same amount of pollution. The value of A3 is slightly lower than A1 and B1, which shows that the source of HM pollution could be industrial emissions. Meanwhile, A2 has the lowest value probably because it is surrounded by commercial and residential areas. Among the total concentrations of the same HM tested, A1, A3, and B1 had larger values than those in Nanjing, which were lower than those in Beijing; however, the gap was not large (Qi et al. 2016b, ; Gao et al. 2016). HM pollution in $PM_{2.5}$ in the areas where the sampling sites are located was at the domestic upper-middle level. A2 is lower than in Nanjing and Beijing, which indicates that the HM pollution in A2 is not serious compared with the other sampling sites.

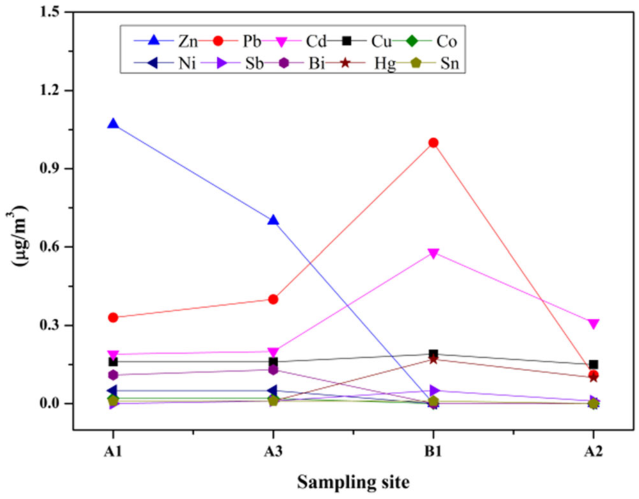

Fig. 3 The concentration levels of HMs in four sampling sites

HMs PCA

The PCA of HMs in four sampling sites is shown in Table 2. Two factors contribute to the HMs in $PM_{2.5}$ in A2. The variation of these two factors accounted for 93.16% of the data variance of the entire group, which is highly correlated with Cr, Hg, and Cu, respectively. Therefore, the source of A2 pollution may come from coal-burning near A1 and A3, and automobile exhaust emissions near A2 (Ye et al. 2017). The HMs in $PM_{2.5}$ in B1 mainly have a single source, which is highly correlated with Cu, Pb, Cr, and Hg, respectively. As a sampling site in metropolis, B1 may be contaminated jointly by coal burning, automobile exhaust, and tire wear. Two main factors contribute to the HMs in $PM_{2.5}$ in A3. The variation of these factors accounted for 88.42% of the data variance of the entire group, which is highly correlated with Bi, Sn, and Ni, respectively. As a sampling site around the factory, the source of A3 pollution may be mainly coal burning emissions from thermal power plants and combustion of flame retardants in textiles and plastics in textile mills. Three main factors contribute to the HMs in $PM_{2.5}$ in A1. The variation of these factors accounted for 95.41% of the variance of the entire data, which is highly correlated with Cu, Pb, Bi, Sn, and Sb. As an industrial transportation mixed area, the pollution sources of A1 may be coal burning, automobile exhaust, tire wear, and burning of flame retardants in textiles and plastics (Talbi et al. 2017). In this work, the sources of HMs in $PM_{2.5}$ at the four sampling sites are mainly coal combustion and automobile exhaust.

Risk assessment of HMs

The risk assessment of HMs in the four sampling sites is summarized in Table 3. A conservative risk of 10^{-6} was set as the target risk value to fully protect human health. The carcinogenic risk values of Cd and Ni exposed to air were greater than 10^{-6}. Therefore, both HMs are toxic. The carcinogenic risk of Cd was slightly larger than that of Ni, indicating that Cd poses a high carcinogenic risk to human health. For non-carcinogenic risks, the non-carcinogenic risk values of various HMs exposed through the respiratory route ranged from 1.83×10^{-4} to 2.69. The non-carcinogenic risk values of all HMs except Cd (HQ > 1) were below the acceptable health risk level (HQ = 1). Thus, the non-carcinogenic health risk of exposure to HMs in the respiratory pathway is insignificant. The non-carcinogenic risk intensity decreases in the following

Table 2 Principal component of HMs in four sampling sites

Sampling site	A1			A3		A2		B1
Element	1	2	3	1	2	1	2	1
Cu	*0.85*	−0.18	−0.34	0.58	0.43	−0.11	*0.99*	*0.97*
Pb	*0.87*	0.10	−0.33	0.83	0.53	0.82	0.38	0.95
Zn	0.75	−0.63	0.12	*0.94*	−0.28	0.23	0.14	0.54
Cd	0.75	0.60	−0.27	*0.90*	0.26	*0.97*	0.15	*0.97*
Co	*0.80*	0.47	−0.35	*0.93*	0.37	0.34	0.47	0.13
Ni	0.69	−0.67	−0.21	−0.28	*0.90*	0.26	0.75	0.53
Bi	0.66	−0.18	*0.71*	0.53	−0.83	−0.61	0.77	−0.68
Sb	0.67	0.69	0.25	*0.97*	0.01	0.24	0.34	0.37
Hg	0.68	−0.59	0.40	0.06	−0.86	*0.95*	0.13	*0.99*
Sn	0.33	*0.70*	0.61	*0.95*	−0.28	0.14	0.27	0.89
Variance%	51.50	28.12	15.78	57.80	30.62	57.95	35.21	83.57
Cumulative%	51.50	79.63	95.41	57.80	88.42	57.95	93.16	83.57

Loads (larger absolute values) are indicated in italic

order: Cd > Hg > Pb > Sb > Cu > Ni > Zn, which is similar to the intensity in Athens, Greece (Valavanidis et al. 2006).

Table 4 shows that Cd exhibits high carcinogenic and non-carcinogenic risks. Cd poisoning can cause osteomalacia, which is called the “pain pain disease” in China. The Cd levels of the four sampling sites were calculated and analyzed, as shown in Table 4. For children, a vulnerable group, the carcinogenic risks are lower than those for adults but are still above the minimum acceptable health risk level (Samek et al. 2017). The non-carcinogenic risks of children are greater than those of adults, and also exceed the minimum acceptable health risk level. The value of (HQ, U1) reached as high as 4.88, indicating that children in B1 were more likely to be Cd-contaminated and carcinogenic than those in the other sites. Cd levels in adult males were relatively higher than in adult females. This finding may be related to weight, spirometry, and similar factors. The value of B1 is much larger than A1, A2, and A3, and this discrepancy may be attributed to differences in the sources of Cd pollution in the two cities. As a city with energy and mining as the pillar industries, Urumqi has more sources of Cd pollution and more related industries than the other sites, such as smelting, calcination of non-ferrous metals, smelting of scrap steel, and incineration of plastic products.

PFCs

Concentration levels and composition of PFCs

As emerging pollutants, PFCs have been intensively researched globally. In this work, 12 PFCs were detected in two major categories: perfluorocarboxylic and perfluorosulfonic acids. Perfluorocarboxylic acids include perfluorobutane sulfonic (PFBS), perfluorohexane sulfonate (PFHxS), perfluorotridecanoic acid (PFTrDA), and perfluorooctane sulfonate (PFOS). Perfluorosulfonic acids include perfluoroheptanoic acid (PFHpA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA), perfluorohexanoic acid (PFHxA), perfluorononanoic acid (PFNA), perfluoropentanoic acid (PFPeA),

Table 3 Risk assessment of HMs in different people

	RfD	HQ (male)	HQ (female)	HQ (child)	SF	R (male)	R (female)	R (child)
Cu	1.20E−02	2.59E−03	1.66E−03	6.40E−03	ND	ND	ND	ND
Pb	3.50E−03	2.56E−02	1.64E−02	6.31E−02	ND	ND	ND	ND
Zn	3.00E−01	2.85E−04	1.83E−04	7.04E−04	ND	ND	ND	ND
Cd	5.71E−05	1.09	0.70	2.69	6.3	1.10E−05	8.19E−06	3.78E−06
Co	ND	ND	ND	ND	ND	ND	ND	ND
Ni	5.40E−03	7.20E−04	4.62E−04	1.78E−03	0.84	5.17E−06	3.84E−06	1.77E−06
Sb	4.00E−04	9.72E−03	6.24E−03	2.40E−02	ND	ND	ND	ND
Bi	ND	ND	ND	ND	ND	ND	ND	ND
Hg	3.00E−04	4.54E−02	2.91E−02	1.12E−01	ND	ND	ND	ND
Sn	ND	ND	ND	ND	ND	ND	ND	ND

Table 4 Risk assessment of Cd in different people at four sampling sites

Sampling site	RfD (Cd)	SF (Cd)	Male		Female		Child	
			(HQ, Cd)	(R, Cd)	(HQ, Cd)	(R, Cd)	(HQ, Cd)	(R, Cd)
A1	5.71E−05	6.3	0.65	6.53E−06	0.42	4.86E−06	1.60	2.24E−06
A3	5.71E−05	6.3	0.68	6.88E−06	0.44	5.12E−06	1.68	2.36E−06
A2	5.71E−05	6.3	1.06	1.07E−05	0.68	7.93E−06	2.61	3.66E−06
B1	5.71E−05	6.3	1.98	1.99E−05	1.27	1.48E−05	4.88	6.85E−06

perfluoroundecanoic acid (PFUdA), and perfluorooctanoic acid (PFOA). The specific concentrations of these substances are shown in Fig. 4. Twelve PFCs were detected in 120 samples, and the detection rate of all samples was 83.33%. In A2 and B1, PFDA, PFPeA, and PFOS were not detected; PFHxS was not detected in A3. All PFCs were detected in A1, indicating that the four sampling sites were contaminated by PFCs. The detection rates of PFHxA and PFOA reached 100% at the four sites. The average percentages of PFCs were as follows: PFOA (50%) > PFOS (24.27%) > PFHxA (18.68%) > PFBHpA (3.74%), PFPeA (1.62%) > PFTrDA (0.5%) > PFBS (0.4%) > PFDoA (0.31%) > PFNA (0.21%) > PFDA (0.16%) > PFHxS (0.07%) > PFUdA (0.04%). PFHxA, PFOS, and PFOA were the most common PFCs, accounting for 92.95% of total PFCs (Rostkowski et al. 2009). PFOA is the most prevalent PFC in the four sampling sites; this result is consistent with other study (Li et al. 2011). The total average concentration of PFCs in the four sampling sites decreased in the following order: A1 (34.54 ± 65.51 ng m^{-3}) > A3 (16.19 ± 28.75 ng m^{-3}) > B1 (5.32 ± 11.11 ng m^{-3}) > A2 (2.20 ± 3.73 ng m^{-3}). The main wind direction in Shihezi is southeast, that is, from A3 to A2 to A1. The lower wind direction of A1 in Shihezi resulted in higher pollution levels than in the other sampling sites. The PFC values of A1 and A3 were approximately 10 times those of B1 and A2; the PFC values of A1 and A3 were greater than A2, and B1 shows that the source of PFC pollution may be traffic emissions. In addition, the low detection rate in B1 and A2 could be attributed to the low value and insufficient sensitivity of the instrument used.

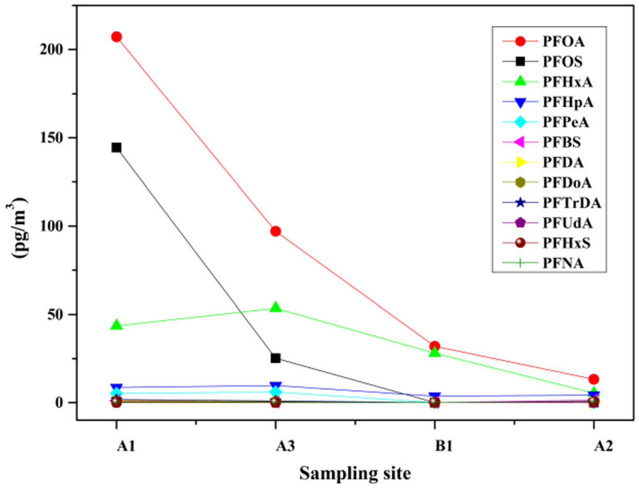

Fig. 4 The concentration levels of PFCs in four sampling sites

PFCs PCA

The PCA results of PFCs in the four sampling sites are shown in Table 5. According to the US EPA emissions statistics, most PFCs are released to the environment at 23% (air), 65% (water), and 12% (soil) (US EPA 2002). According to current research, PFHxA, PFOS, and PFDoA are the major pollutants generated by metal plating, textile, firefighting equipment, PFOS production, and semiconductors (Xie et al. 2013). PFUdA, PFNA, and PFDA are the major pollutants generated by natural and anthropogenic mineral dust and the oxidation of 10:2 FTOHs and 8:2 FTOH (Ellis et al. 2004). PFOS is reportedly one of the components of fire extinguishing media. In addition, PTFE-containing PFOA is widely used in sealant coatings, oil additives, and grease production (Harada et al. 2005). The degradation of long-chain PFCs is a major source of PFPeA (Moriwaki 2005). Thus, traffic density may be the cause of high levels of PFC pollution in northern cities (Sasaki et al. 2003). There are three factors of PFCs in PM$_{2.5}$ that mainly affect A2. The variation of these factors accounted for 96.05% of the variance of the entire data, which is highly correlated with PFNA, PFHpA, PFTrDA, PFUdA, and PFDoA. Therefore, the pollution sources in A2 may be the natural and anthropogenic sources of mineral dust, 10:2 FTOHs and 8:2 FTOH oxidation, dust, and coal combustion. There are two factors of PFCs in PM$_{2.5}$ that mainly affect B1. The variation of these factors accounted for 83.47% of the data variance of the entire group, which is highly correlated with PFHpA, PFOA, and PFDoA, indicating that the pollution source of B1 may be sealant coatings, oil additives and grease production, textiles, and firefighting equipment. There are three factors of PFCs in PM$_{2.5}$ that mainly affect A3. The variation of these factors accounted for 94.71% of the data variance of the entire group, which is highly correlated with PFOA, PFPeA, PFHpA, PFHxA, PFDA, and PFUdA, indicating that the pollution source of A3 may be the natural and anthropogenic sources of mineral dust, 10:2 FTOHs,

Table 5 Principal component of the PFCs in four sampling sites

Sampling site	A1			A3			A2			B1		
Element	1	2	3	4	1	2	3	1	2	3	1	2
PFHpA	0.65	0.57	0.23	0.42	*0.94*	− 0.15	0.20	*0.93*	0.30	− 0.15	*0.98*	0.13
PFBS	− *0.93*	− 0.18	− 0.09	0.30	− 0.09	0.72	− 0.67	0.87	− 0.31	0.09	− 0.60	− 0.07
PFDA	0.36	− 0.37	− 0.26	0.70	− 0.32	*0.93*	− 0.05	0.08	− 0.03	0.34	0.56	− 0.14
PFDoA	0.37	0.60	− 0.05	− 0.39	0.76	0.56	0.34	0.47	− 0.07	*0.87*	0.51	*0.80*
PFHxA	*0.94*	0.10	0.23	0.23	*0.93*	− 0.29	0.08	− 0.42	0.82	0.32	0.89	− 0.43
PFHxS	− 0.53	*0.81*	0.08	0.07	0.15	− 0.08	0.33	0.89	− 0.03	− 0.41	0.07	0.25
PFNA	*0.94*	0.04	0.18	− 0.20	0.72	− 0.01	− 0.61	*0.98*	− 0.05	0.12	0.35	0.66
PFPeA	*0.95*	0.06	0.30	0.01	0.97	0.01	0.04	0.54	0.07	0.17	− 0.60	0.36
PFTrDA	− 0.43	*0.89*	0.08	0.14	0.42	0.87	− 0.05	*0.96*	0.23	− 0.07	0.63	0.66
PFUdA	− 0.04	*0.89*	− 0.41	0.12	− 0.30	0.61	*0.71*	− 0.23	*0.93*	− 0.16	0.00	0.00
PFOS	− 0.59	− 0.05	0.78	0.01	*0.92*	0.19	0.36	0.17	− 0.64	0.33	0.08	0.37
PFOA	− 0.28	0.01	*0.94*	0.10	*0.99*	0.06	0.04	0.86	0.50	0.06	*0.90*	− 0.40
Variance%	42.53	26.05	16.48	8.64	54.17	27.04	13.51	61.30	22.47	12.28	59.53	23.95
Cumulative%	42.53	68.57	85.05	93.70	54.17	81.21	94.71	61.30	83.76	96.05	59.53	83.47

Loads (larger absolute values) are indicated in italic

oxidation of 8:2 FTOH, sealant coatings, oil additives and grease production, and related factors. There are four factors of PFCs in $PM_{2.5}$ that mainly affect A1. The variation of these factors accounted for 93.70% of the data variance of the entire group, which is highly correlated with PFHxA, PFNA, PFPeA, PFTrDA, PFUdA, PFOA, and PFDA. Therefore, the pollution source of A1 may be the degradation of long-chain PFCs, paint sealant coatings, oil additives and grease production, the mineral dust of natural and anthropogenic sources, and the oxidation of 10:2 FTOHs and 8:2 FTOH. Unlike Shihezi, Urumqi is the largest city in Xinjiang, more companies related to the manufacture of perfluorinated compounds were concentrated here, so B1 was mainly derived from the emissions of related industries can be found. In Shihezi, the main source of pollution of three sampling sites was natural and man-made mineral dust.

Risk assessment of PFCs

As shown in Table 6, for PFOS or PFOA, the risk values of the four sampling sites were less than 1, which indicate that there is no direct impact on the body. In addition, children had the largest risk value, followed by adult males and females. Although the values were all less than 1, the risk value of children was large and increasing. Therefore, corresponding measures should be strengthened and implemented to protect children, such as creating a better living environment (e.g., bedrooms, kindergartens, and parks) for them (Rivas et al. 2014). Different sampling sites had different carcinogenicity risks that decreased in the following order: A1 > A3 > B1 > A2. Unlike A3 and B1, the population densities of A1 and A2 are relatively high; hence, the residents of these regions should take precautionary measures.

Table 6 Risk assessment of PFCs in different people at four sampling sites

Sampling	RfD (PFOA)	RfD (PFOS)	Male		Female		Child	
Site			(HQ, PFOA)	(HQ, PFOS)	(HQ, PFOA)	(HQ, PFOS)	(HQ, PFOA)	(HQ, PFOS)
AVE	2.00E−04	8.0E−05	8.49E−05	1.03E−04	5.45E−05	6.61E−05	2.10E−04	2.55E−04
A1	2.00E−04	8.0E−05	2.01E−04	3.51E−04	1.29E−04	2.25E−04	4.98E−04	8.68E−04
A3	2.00E−04	8.0E−05	9.43E−05	6.11E−05	6.05E−05	3.92E−05	2.33E−04	1.51E−04
A2	2.00E−04	8.0E−05	1.28E−05	ND	8.24E−06	ND	3.17E−05	ND
B1	2.00E−04	8.0E−05	3.10E−05	ND	1.99E−05	ND	7.67E−05	ND

Table 7 The correlation between HMs and PFCs

Element	Cu	Pb	Zn	Cd	Ni	Sb	Hg	PFOS	PFOA
Cu	1								
Pb	*0.996***	1							
Zn	− 0.32	− 0.298	1						
Cd	0.837	0.81	− 0.768	1					
Ni	− 0.333	− 0.288	*0.959**	− 0.795	1				
Sb	*0.911*	*0.904*	− 0.676	*0.968**	− 0.651	1			
Hg	0.657	0.619	− 0.892	*0.962**	− 0.93	0.876	1		
PFOS	− 0.236	− 0.257	*0.88*	− 0.579	0.709	− 0.591	− 0.659	1	
PFOA	− 0.202	− 0.201	*0.964**	− 0.637	*0.854*	− 0.586	− 0.762	*0.967**	1

Italic entries indicate "strong" correlations

**0.01 level (both sides) very significant correlation

*0.05 level (both sides) significant correlation

The correlation between HMs and PFCs

Found in Table 7, there was a certain correlation between HMs and HMs, PFCs and PFCs, such as Cu and Pb, PFOS and PFOA. In addition, the correlation between PFOS, PFOA and Zn, Ni can be found. Previous studies have shown that HMs and PFCs may act on organisms at the same time and produce joint toxicity (zhao et al. 2017). In this work, some HMs and PFCs have no carcinogenic risk under the single action, but HMs and PFCs in the atmosphere may cause joint toxicity, and harm to the human body. Therefore, relevant personnel and departments need to pay attention to joint toxicity of HMs and PFCs when dealing with air pollution.

Conclusion

The results showed that HMs and PFCs are prevalent in the $PM_{2.5}$ in Shihezi and Urumqi. Samples were collected from four sampling sites simultaneously for spatial distribution analysis. The spatial distributions of HMs and PFCs were B1 = A1 > A3 > A2 and A1 > A3 > B1 > A2, respectively. Among all the HMs detected, Cu, Pb, Zn, and Cd were at relatively high levels. PFOA (50.00%), PFOS (24.27%), and PFHxA (18.68%) were the most prevalent PFCs. PCA results showed that coal combustion and automobile exhaust are the most dominant sources of HMs according to the concentration level of each HM in $PM_{2.5}$. This result seems to be a feature of most cities in Northern China. The pollution sources of PFCs in $PM_{2.5}$ are mainly metal plating, textile, firefighting equipment, PFOS production, semiconductors, and natural and anthropogenic sources of mineral dust. Risk assessment was conducted to support the research. The hazard assessment of PFCs on humans indicated that no PFCs in the atmosphere can harm Shihezi and Urumqi residents. However, the Cd and Ni in HMs are harmful to humans, especially Cd, which has both carcinogenic and non-carcinogenic risks, and thus must be given sufficient attention by society. In addition, HMs and PFCs may cause joint toxicity.

This study investigated the spatial distribution and sources of HMs and PFCs in atmospheric $PM_{2.5}$ in two major industrial cities in northern Xinjiang, China, to analyze the pollution levels and carcinogenic risks of HMs and PFCs. This study has an important role in controlling the local emissions of HMs and PFCs and preventing cancer.

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