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Original Research

The Levels and Risks of Heavy Metals, Polycyclic Aromatic Hydrocarbons, and Polychlorinated Biphenyls in Hun River in Northeastern China

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Abstract

The Hun River Basin is one of the most important heavy industrial and agricultural production bases of China. Its pollution level has exerted negative effects on human health. In order to investigate pollution levels and estimate the cancer risk of water in the river, water samples were collected in both the flood and dry periods. Pollution indicators were detected in terms of heavy metals, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). The mean concentrations of chromium (Cr), cadmium (Cd), PAHs, and PCBs were, respectively, 7.96 μg/L, 0.08 μg/L, 2597.22, and 21.21 ng/L in the flood period, and 19.02 μg/L, 1.10 μg/L, 1212.91, and 16.69 ng/L in the dry period. The concentrations of heavy metals were lower in the flood period than those in the dry period. However, in the meantime, contamination by PAHs and PCBs was heavier in the flood period than those in the dry period – the most abundant being four-ring PAHs and three-Cl PCBs in the flood period, and three-ring PAHs, four-ring PAHs, and four-Cl PCBs in the dry period. The carcinogenic contribution rate was in the order: Cr> PAHs >PCBs >Cd. The mean lifetime value of carcinogenic risk was 8.200×10^{-4}, which indicated that there was a risk of cancer associated with drinking Hun River water.

Keywords: polycyclic aromatic hydrocarbons, polychlorinated biphenyls, heavy metals, cancer risk, Hun River

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Introduction

Heavy metals (e.g., Cr and Cd), PAHs, and PCBs are toxic chemicals that ubiquitously exist in the environment [1-5]. In ecological systems, heavy metals are usually in low concentrations, for most of them exist in steady status. However, in aquatic systems they can be quickly transported and transformed from both natural and anthropogenic activities such as direct input from agricultural and industrial activities, atmospheric deposition, mining locations, and surface runoff [6-8]. In aquatic environments, heavy metals have drawn people's attention as one of the most dangerous and persistent pollutants due to their carcinogenic properties, nonbiodegradation, and biocondensation [9-14]. Likewise, as typical persistent organic pollutants (POPs), PAHs and PCBs are adverse to human health and the ecosystem. Besides natural sources, PAHs were mainly formed from the direct release of fossil oil due to incomplete combustion of carbonaceous materials and industrial production [15-17]. Due to its relevance with some human cancers [18-19], PAHs have been listed as prority pollutants in many countries [20-21]. PCBs, which constitute an industrial liquid used in transformers, capacitors, fire retardant, paint, plasticizers, and heat transport systems [22-25], have been banned. Due to persistence, fat-solubility, carcinogenesis, and bioamplification, PCBs have had harmful effects on the human immune, reproductive, and nervous systems [22]. Generally, surface water is an important freshwater source for drinking, industrial use, and crop production in most countries. This is why research on heavy metals, PAHs, and PCBs in surface water must be conducted.

The Hun River, an important anabranch of the Liao River Basin, is located in northeastern China. Its mainstream is 415 km long, and its catchment area is 11,481 km^2 [26]. It runs through Fushun City, Shenyang City, Liaoyang City, and Anshan City, and joins together with the Taizi River into the Daliaohe River. It flows through central Liaoning Province, which is one of the most important heavy industrial and agricultural production bases in China. The situation of its pollution – caused by heavy metals and organic pollution (PAHs and PCBs) – is serious. The concentrations of Cd and Cr in Hun River sediment was 12-fold and 2-fold, respectively, the average concentrations of sediment in China [26]. As a heavy industrial and agricultural production base, lots of wastewater from industry and crops – including all kinds of PAHs and PCBs – are being discharged into Hun surface water, which has resulted in negative effects on human health. However, few studies have comprehensively investigated the pollution levels and cancer risk of heavy metal, PAHs, and PCBs in Hun surface water. Therefore, in this study samples were collected from Hun surface water in the dry period of May and the flood period of August, and Cd, Cr, PAHs, and PCBs were determined. The purpose of the present work is:

1. Determine the levels of heavy-metal Cd and Cr, PAHs, and PCBs.
2. Evaluate the potential cancer risk for humans in Hun River surface water using the Bap-equivalent concentration (Bap_{eq}) and Incremental Lifetime Cancer Risk (ILCR) values.

Our aim is to provide enough data on the pollution level and cancer risk of heavy-metal Cd and Cr, PAHs, and PCBs in the Hun to serve as a reference for improving environmental management of the northeastern Chinese river.

Materials and Methods

Samples Collection

Based on the ecological function zone and the importance of tributaries, 14 sampling points were selected in the main Hun and its tributaries. Six sites were set in the main stream of the Liao River: Ajipu (M1), Gebuqiao (M2), Donglingdaqiao (M3), Shashan (M4), Qitaizhi (M5) and Yujiafang (M6); and eight sites were set in its tributaries: Beizhamu (T1), Gulou (T2), Haixinhe (T3), Oujiahekou (T4), Jiangjunhe (T5), Guchenghe (T6), Lishihe (T7), and Yutai (T8). The distribution of Hun sampling sites is shown in Fig. 1. The water samples were collected from 1 foot depth below the surface of running water in the dry period of May and the flood period of August, and filtered with a 0.45 μm micropore membrane. One sample was stored using a glass bottle for PAH and PCB analysis, and another sample was stored using acid-leached polythene bottles and preserved with concentrated HNO_3 for heavy metals analysis. The samples were stored in an ice box and refrigerated at 4ºC until they were analyzed in the laboratory [27-30].

Chemicals, Reagents, and Instruments

A Mill-Q system Elix 5 (Millipore Co. USA) was used to produce the deionized water. An atomic absorption spectrophotometer (VARIAN AA220) was used to analyze the heavy metal, a high-performance liquid chromatograph (HPLC Angillent 1100) was used to analyze PAHs, and a gas chromatograph (Varian CP3800) was used to analyze PCBs. The analytical grade and HPLC-grade solvents (i.e., hexane, acetonitrile, acetone, methanol, and dichloromethane) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The standard solutions of Cd and Cr also were purchased from Sinopharm Chemical Reagent Co., Ltd. We used stock standard solutions of PAHs, including: Nap, naphthalene; Ace, acenapthene; Acy, acenapthylene; Fl, fluorene; Phe, phenanthrene; Ant, anthrancene; Flu, fluoranthene; Pyr, pyrene; Baa, benz[a]anthracene; Chr, chrysene; Bbf, benzo[b]fluoranthene; Bkf, benzo[k]fluoranthene; Bap, benzo[a]pyrene; Daha, dibenz[a,h]anthracene; and Bgp, benzo[g;h;i]perylene; Inp, indeno[1,2,3-cd]pyrene; plus PCBs (PCB028, PCB052, PCB101, PCB153, PCB138, and PCB180) purchased from Accustandard Inc. (USA).

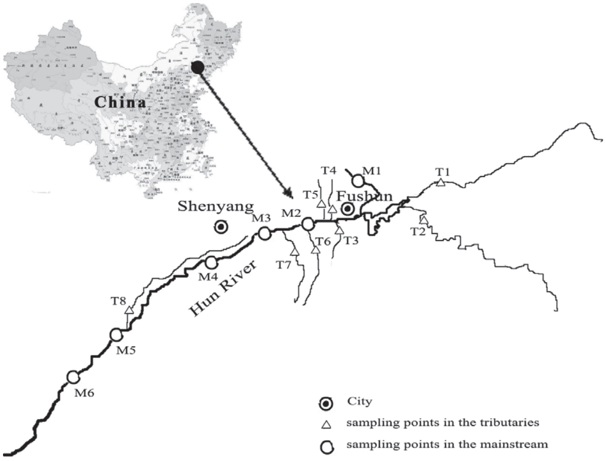

Fig. 1. Locations of sampling sites along the Hun River in China.

Analytical Methods

Heavy metals: The samples were diluted with bidistilled water. Analysis of Cd and Cr was carried out using atomic absorption spectrometry and the standard solutions of the respective metals were used for quantifying the samples [31].

PAHs: The water samples were extracted using an alumina/silica (v/v 1:2) gel column. 25 ml of hexane was used to remove the aliphatic hydrocarbons, and then 75 ml of hexane/dichloromethane (v/v 1:1) was used to extract PAHs [30]. The extracting solution with PAHs was evaporated, and constant in 1 ml acetonitrile (HPLC grade). Finally, analysis of PAHs was performed using a high-performance liquid chromatograph (HPLC Angillent 1100) [30, 32].

PCBs: The 1L water samples were extracted by a C18 gel column washed by dichloromethane, activated by methanol, and washed by deionized water before use. PCBs were extracted using 6mL acetone once and 6mL acetonitrile twice. Then the extracting solution with PCBs was dried and 1 ml hexane was added (HPLC grade), followed by analysis using a gas chromatograph (Varian CP3800).

Quality Control and Statistical Analysis

Standard solution and reagent blanks were inserted randomly to control analytical quality and precision, and the device was re-calibrated when the deviation was >10%. Recovery was also conducted and the recovery rates were 82.5-103.4%. EXCEL 2007 was used to plot the experimental data, and Adobe Photoshop CS6 was used to draw the sampling site map.

Cancer Risk Assessment

Cancer Risks of the Heavy Metals

As a heavy industrial and agricultural production area, Cr and Cd ubiquitously exist in the Hun surface water, and pollution by Cr and Cd was serious. So Cr and Cd were mainly considered to be the carcinogens in this study. The cancer risks can be calculated using the following model [33-35]:

$$Rc = \sum_{i=1}^{k} Rc_{ig}$$

$$Rc_{ig} = \frac{1 - \exp(-\dfrac{IR \times C_i \times Q_{ig}}{\mathrm{BW}})}{AT} \tag{1}$$

…where Rc is cancer risk from heavy metals, Rc_{ig} is average annual cancer risk for individuals through drinking water with heavy metal i, IR is the ingestion rate of water (L/day), BW is body weight (kg), C_i is the concentration of heavy metal i, Q_{ig} is the strength coefficient of the carcinogenic effect through drinking water with chemical carcinogens i ($mg \cdot kg^{-1} \cdot d^{-1}$, Q_{ig} of Cd, As and Cr were 6.1, 15, and 41 $mg \cdot kg^{-1} \cdot d^{-1}$) [34, 26-37], and AT is the average lifespan (for this study AT was set at 70) [30].

Cancer Risks of PAHs and PCBs

In this study, the cancer risks of PAHs and PCBs in Hun surface water of were estimated by Incremental Lifetime Cancer Risk (ILCR), which quantitatively assesses the health risk of PAHs [19, 38-39].
ILCR was calculated using equation (2):

$$ILCR = CSF \times \frac{C_j \times IR \times EF \times ED}{BW \times AT \times 365} \tag{2}$$

…where for PCBs, C_j is the concentration of PCBs (mg/L), and for PAHs, C_j is the benzo[a]pyrene toxic equivalent (TEQ) of the carcinogenic PAHs. TEQ was calculated with the following equation [20, 38-39]:

$$TEQ = \sum_{i} C_k \times TEF_k \tag{3}$$

…where C_k is the concentration of the PAH k (mg/L), and TEF_k is the toxic equivalence factors (TEFs) of the PAH k relative to Bap (mg/L). The carcinogenic PAHs include BaP, BaA, BbF, BkF, ChR, DahA, and InP, and TEFs were 1, 0.1, 0.1, 0.01, 0.001,1 and 0.1, respectively [20, 40]. CSF is the carcinogenic slope factor for Bap and PCB, and the value of CSF is 7.3 and 2.0 mg/(kg·day) [39]; EF is the exposure frequency, in this study EF = 365 day/year; and ED is the exposure duration (year). The lifetime has been divided into two age groups [20]: a child aged 0-15 years (where IR is 1 L/d, BW is 15 kg, and ED is 15 years) and an adult aged 15-70 (where IR is 2.2 L/d, BW is 70 kg, and ED is 55 years).

Results and Discussion

The Concentrations and Characters of Heavy Metals, PAHs, and PCBs in Hun Surface Water

The concentrations of heavy metals (Cr and Cd), 16 PAHs, and 6 PCBs in Hun surface water are presented in Table 1. Heavy metals can be detected in most water samples. The concentrations of Cr in the water samples were detected in the range of ND to 157.51 μg/L, with an overall mean of 13.48 μg/L, and Cd ranged from 0.003 to 4.41 μg/L, with a mean concentration of 0.59 μg/L. Compared to Level III of Environmental quality standards for surface water of China (GB3838-2002) (Cr, 50μg/L; Cd, 5 μg/L), the mean concentrations of Cr and Cd were in the safe ranges. There was no standard value to evaluate the cancer risk for surface water in China. The mean concentrations of Cr and Cd were lower in the wet period (7.96 and 0.08 μg/L) than in the dry period (19.02 and 1.10 μg/L). One possible reason for this phenomenon is that the Hun River Basin is located in a semi-humid continental monsoon climate zone, and precipitation was obviously less in the dry period than in the wet period [15]. The mean concentrations of the heavy metals Cr and Cd at 14 sites varied from 2.74 to 81.75 μg/L, and from 0.086 to 2.243 μg/L, respectively (Fig. 2a). Among the 14 monitoring sites, the spatial differences of the concentrations of Cr and Cd were markedly large, and the highest concentrations of Cr (81.76 μg/L) and Cd (2.243 μg/L) were both observed at site T5. The mean concentrations of Cr and Cd were higher in the tributary (18.53 and 0.653 μg/L) than those in the main stream (6.77 and 0.510 μg/L) because lots of the untreated wastewater, including all kinds of heavy metals from non-point and industrial sources, had been discharged into the tributary.

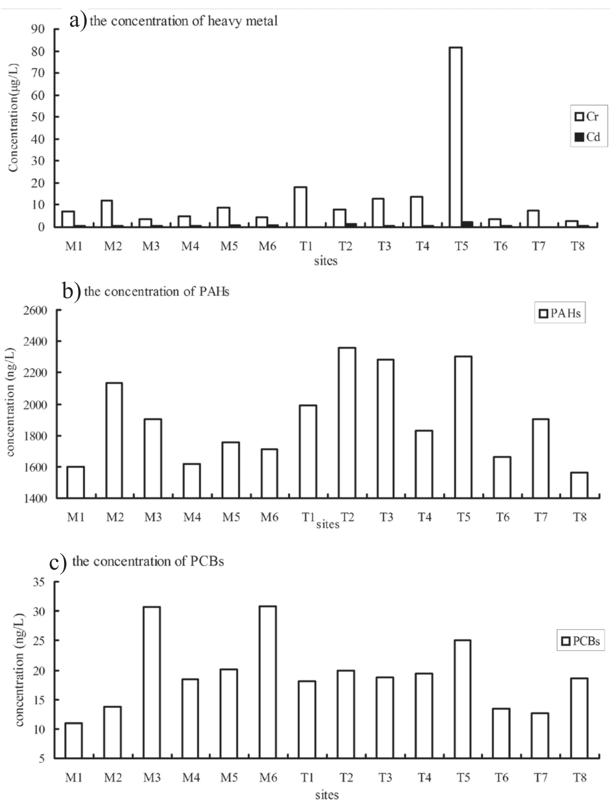

Fig. 2. Spatial distributions of heavy metals, PAHs, and PCBs in Hun River surface water a) heavy metals, b) PAHs, and c) PCBs..

The concentrations of PAHs in Hun surface water are shown in Table 1; except for Ace and Acy, other PAHs could be detected in a majority of water samples. The concentrations of PAHs ranged from 1,996.86 ng/L to 3,549.78 ng/L, with a mean concentration of 2,587.22 ng/L in the flood period; and 595.97-1,834.51 ng/L, with a mean concentration of 1,212.91 ng/L in the dry period. So contaminations by 16 PAHs was heavier in the flood period than in the dry period. The concentrations of PAHs changed markedly in different sites, and the highest PAHs were detected at T2 (Fig. 2b). The mean concentration of PAHs was higher in the tributary than in the mainstream, and the tributary was one important origin of PAHs in the surface water. Compared to other rivers, such as the Tiber River in Italy (43.4 ng/L) [41], the Jinjiang River in China (53.23 ng/L) [40], the Jiangsu section of the Yangtze River (925 ng/L) [42], and Quanzhou Bay (39.63 ng/L) [40], the concentration of PAHs was higher in the surface water of the Hun. The concentrations of Bap in the Hun in the wet and dry periods were 2.09- and 13.68-fold the environmental quality standards for surface water of China (GB3838-2002) (Bap: 2.8 ng/L). Therefore, the pollution degree of PAHs was severe in both the wet and dry periods. The wastewater and atmospheric fallout containing PAHs from oil, chemical, and steel factories of Shenyang and Fushun discharged wastewater into Hun surface water, which is a vital reason for the heavy pollution by PAHs in the Hun [30, 43].

The distribution of PAHs by ring number in Hun surface water is shown in Figs 3a-b, and the samples were dominated by three-ring and four-ring PAHs. The most abundant PAH was four-ring (62.60-75.36%) with a mean value of 70.56% in the flood period; meanwhile, there were three-ring PAHs (36.88-52.31%) and four-ring PAHs (34.61-44.65%), with a mean of 43.87% and 39.50%, respectively, in the dry period. One of reasons is that the concentrations of different ring PAHs in the surface water were affected by the hydrophobicity of PAHs, and the hydrophobicity of high-ring PAHs (five- and six-ring PAHs) was more than the low-ring PAHs (two-, three-, and four-ring PAHs) [44]. When Ant/(Ant + Phe) < 0.1, the PAHs originated from petroleum, while at > 0.1, PAHs came from a combustion source [15, 40, 45]. In this study, Ant/(Ant + Phe) ranged from 0.046 to 0.067 in the flood period, and from 0.145 to 0.197 in the dry period. So PAHs mainly came from petroleum origin in the flood period, while it came from a combustion source in the dry period.

The concentrations of PCBs in Hun surface water are shown in Table 1, and PCB028, PCB052, PCB101, PCB138, PCB153, and PCB180 were detected. The con-

Table 1. Concentrations of heavy metals, PAHs, and PCBs in Taizi River surface in the flood and the dry periods (heavy metals in µg/L; PAHs and PCBs in ng/L).

Pollutant	Flood period		Dry period	
	Mean±SD[a]	Range	Mean±SD	Range
Cr	7.96±7.88	ND-29.00	19.02±40.42	ND[b]-157.51
Cd	0.08±0.12	0.003-0.47	1.10±1.14	0.15-4.41
Nap	311.99±73.25	156.27-442.51	83.70±61.36	8.42-248.82
Ace	ND	ND	ND	ND
Acy	ND	ND	ND	ND
Fl	48.78±14.66	30.50-79.35	65.19±24.27	18.30-112.97
Phe	312.17±69.18	209.76-430.43	382.86±113.07	165.08-557.22
Ant	17.90±4.12	11.23-24.02	82.16±27.24	36.43-135.18
Flu	71.76±10.01	58.82-98.52	220.61±58.21	136.75-326.39
Pyr	49.67±14.79	24.26-86.24	186.90±58.04	102.77-296.42
Baa	1,266.46±276.53	884.69-1833.34	37.15±42.78	8.56-158.61
Chr	442.42±131.14	253.33-709.13	35.10±29.81	ND-89.61
Bbf	15.39±4.74	4.43-23.08	33.25±11.16	17.15-54.05
Bkf	1.19±0.90	0.30-3.04	19.73±6.87	9.33-32.50
Bap	5.85±1.92	2.23-9.18	38.31±14.68	17.53-66.15
Daha	8.69±3.07	2.55-15.93	2.20±1.05	0.61-4.21
Bgp	11.30±4.44	4.85-19.80	21.48±8.59	8.71-35.94
Inp	23.81±10.65	6.57-52.59	4.27±5.60	ND-15.60
PAHs	2,587.22±527.96	1,996.86-3,549.78	1,212.91±377.87	595.97-1,834.51
PCB028	9.77±8.41	1.34-27.08	1.07±0.38	0.65-2.09
PCB052	4.92±6.62	0.13-20.56	9.14±0.86	7.34-10.23
PCB101	4.26±2.69	0.43-10.53	4.04±2.07	0.24-6.94
PCB153	1.00±1.00	ND-2.65	1.14±0.15	0.94-1.45
PCB138	1.75±3.57	0.05-13.00	1.24±0.30	0.68-1.80
PCB180	0.34±0.43	ND-1.25	0.71±0.66	0.34-2.88
PCBs	21.21±13.02	3.81-45.11	16.69±3.13	9.86-20.76

[a]Arithmetic mean ±standard deviations
[b]ND is not detected

centrations of the six PCBs in Hun surface water were determined, ranging from 3.81 to 45.11 ng/L with a mean value of 21.21 ng/L in the flood period, and from 9.86 to 20.76 ng/L with a mean value of 16.69 ng/L in the dry period, respectively. The contaminations of PCBs were heavier in the flood period than in the dry period. The concentrations of PCBs have markedly changed between different sites, and the highest PCB level was detected at M6 (Fig. 2c). The PCBs were beyond the standard of PCBs (14 ng/L) according to water quality criteria of USEPA [46]. Distributions of three-, four-, five-, six-, and seven-CL of PCBs in the Hun surface water are shown in Figs 3c-d. The mean percentage of three-CL PCBs was the most in the flood period (42.81%), and it was four-CL PCBs in the dry period (50.87%). The metabolic rate of PCBs decreased with the increase of chlorine atoms [47], so it was indispensable to enhance the monitoring of PCBs in the dry period even if the concentration of PCBs was lower in the dry period than in the flood period.

Cancer Risk Assessment

The carcinogenic risk values of heavy metals, PAHs, and PCBs in Hun surface water for children and adults by ingestion are shown in Table 2. The cancer risk in children ranged from 1.532×10^{-4} to 2.942×10^{-3}, with a mean

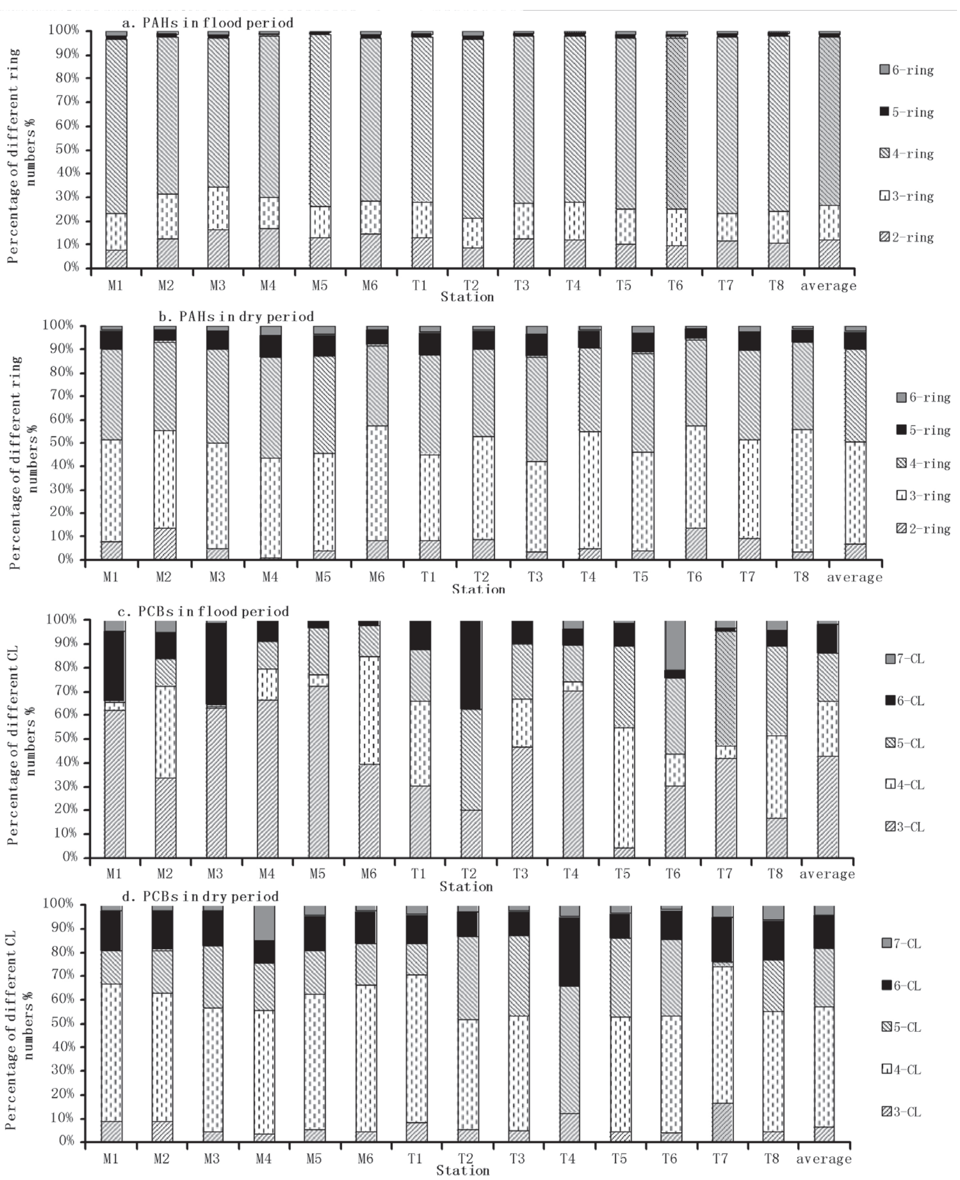

Fig. 3. Distributions of two-, three-, four-, five-, and six-rings PAHs and of three-, four-, five-, six-, and seven-CL of PCBs in Hun River surface water: a) PAHs in flood period, b) PAHs in dry period, c) PCBs in flood period, and d) PCBs in dry period.

of 5.564×10^{-4}; and 6.777×10^{-5} to 1.460×10^{-3}, with a mean of 2.636×10^{-4} for adults. Risk values $> 10^{-4}$ meant that there was a high potential of cancer induction to people, while there was a lower potential cancer risk when the value was between 10^{-6} and 10^{-4} [43]. The carcinogenic risks were beyond the standard value in both the children and adult groups. Under such circumstance, there were probable carcinogenic risks to the two groups. The carcinogenic risk was higher for children, mainly due to the value of IR/BW being greater in children than adults. The value of IR/BW is the ingestion rate of water of per unit body weight, meaning that the demand of water was larger with the increase of IR/BW. The mean value of IR/BW of children was 0.067, and meanwhile 0.031 for adults. The amount of pollutants was greater for the children's group than for the adults. Therefore, probable carcinogenic risk was greater for children under the same conditions. More attention should been paid to the influence of these pollutants on the health of children. The lifetime carcinogenic risk was the sum of the children and adults, and the mean lifetime carcinogenic risk value was 8.200×10^{-4}, ranging from 2.210×10^{-4} to 4.402×10^{-3}. In this study, the lifetime mean risk values were greater than 10^{-4}, which indicated that the potential cancer risk was high and it was not suitable to drink water without effective water treatment.

The distribution of carcinogenic risk in the Hun among different sites is shown in Fig. 4. Though the carcinogenic risks varied in size among different sites, the carcinogenic risks of heavy metals Cr, Cd, PAHs, and PCBs ubiquitously existed in the Hun. By comparing the cancer risk among different sites, the highest cancer risk of heavy metals was detected at site T5, for PAHs at T2, and for PCBs at M6. By comparing the carcinogenic risk values of heavy metals, PAHs, and PCBs among different sites and different groups, the carcinogenic contribution rate was in the order: Cr> PAHs >PCBs >Cd. The carcinogenic risks of Cr and Cd (ranging from 1.59×10^{-4} to 4.31×10^{-3}) were larger than 10^{-4}. There were the potential cancer risks of heavy metals, but these ran counter to the results that the mean concentrations of Cr and Cd were in the safe ranges based on environmental quality standards for surface waters of China (GB3838-2002). Therefore, concentration monitoring had not been enough to describe the environmental status, and it is essential that cancer risk assessment be carried out as part of environment management.

It must be noted that the results of cancer risk assessment were underestimated, because there were other exposure pathways besides ingestion and lots of other carcinogenic chemicals in the Hun surface water, such as arsenic and nitrites, which were not included in this study. In this regard it is necessary to pay more attention to other potential pollution risks in the surface water of the Hun River.

Conclusions

This is a study of heavy metals, PAHs, and PCBs together, and to assess the potential cancer risk in Hun surface water. Our results revealed that the concentrations of heavy metals were lower in the flood period than the dry period, and the mean concentrations of Cr and Cd were

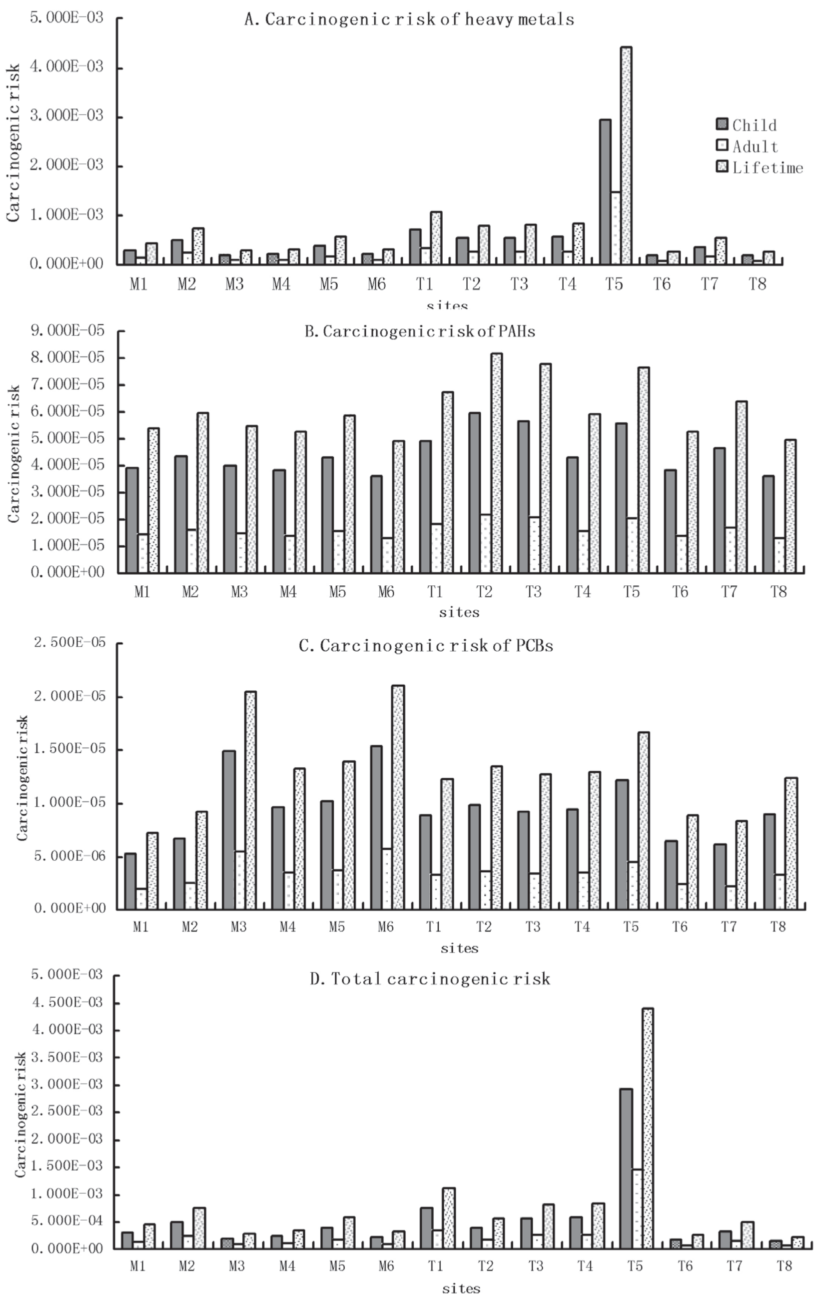

Fig. 4. Distribution of carcinogenic risk in Hun River surface water among different sites: a) Carcinogenic risk of heavy metals, b) Carcinogenic risk of PAHs, c) Carcinogenic risk of PCBs, and d) Total carcinogenic risk.

higher in the tributary than in the main river. In comparison to other rivers, contamination by PAHs was heavier in the Hun, and the samples were dominated by three-ring and four-ring PAHs according to the distribution of PAHs by ring number. PAHs mainly came from petroleum origin in the flood period, and they came from combustion sources in the dry period. The PCBs were beyond the standard of PCBs (14 ng/L) according to water quality criteria of the U.S. Environmental Protection Agency, and three-CL and four-CL PCBs were the dominant PCBs. The mean lifetime carcinogenic risk value was 8.200×10^{-4}, and the ingestion of heavy metals, PAHs, and HCBs from surface water poses a probable cancer risk to residents along the Hun. The carcinogenic contribution rate was in the order: Cr> PAHs >PCBs >Cd. The mean concentrations of Cr and Cd were in the safe ranges based on environmental quality standards for surface water of China (GB3838-2002), but there were the potential cancer risks of heavy metals. It is essential that cancer risk assessment be carried out as part of environment management.

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