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Spatial Distribution, Chemical Speciation and Health Risk of Heavy Metals from Settled Dust in Qingdao Urban Area

Hongxia Xu, Yan Wang, Ruhai Liu *, Mingyu Wang and Yanyan Zhang

Key Lab of Marine Environmental Science and Ecology, Ministry of Education; College of Environment Science and Engineering, Ocean University of China, Qingdao 266100, China; xuhongxia1994@163.com (H.X.); yanjane@ouc.edu.cn (Y.W.); wmy6393@stu.ouc.edu.cn (M.W.); 15589855526@163.com (Y.Z.)

* Correspondence: ruhai@ouc.edu.cn

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Abstract: Settled dust samples were collected from Qingdao urban area to analyze the spatial distribution, chemical speciation and sources of metals, and to evaluate the health risk of metals from atmospheric dust. The average contents of Hg, Cd, Cr, Cu, Ni, Pb and Zn in the atmospheric settled dust of Qingdao were 0.17, 0.75, 153.1, 456.7, 60.9, 176.0 and 708.3 mg/kg, respectively, which were higher than soil background values. The mean exchangeable metal and carbonated-associated fraction proportions of Cd, Zn and Pb were 43.6%, 26.1% and 15%, which implies that they have high mobility and bioavailability. Higher contents of heavy metals appeared in old city areas because of the historical accumulation of metals. Principal component analysis showed that combustion sources partially contributed to Pb, Zn and other trace metals. Hg, Pb and Zn mainly originated from business, human activities and municipal construction. Cd and Cu from settled dust of the old city originated from the erosion and ageing of construction materials. The non-carcinogenic risk rankings for the seven determined heavy metals were ingestion > dermal > inhalation. Cd, Cr and Ni from settled dust showed a low carcinogenic risk. The health risks of Cr, Cu and Pb were higher in old city areas and, therefore, need special attention.

Keywords: heavy metals; chemical speciation; settled dust; spatial distribution; source identification; health risk

1. Introduction

Atmospheric settled dust refers to the particles that settle on the ground as a result of their own gravity. Their particle size is mostly larger than 10 μm, which is an important indicator of air pollution monitoring [1]. Due to the different sources of pollutants and the different effects of the physical and chemical processes, the chemical composition of the settled dust in the atmosphere is complex, including metal particles, inorganic particles and organic particles [2–4]. More pollutants (e.g., heavy metals, polycyclic aromatic hydrocarbons (PAHs)) accumulate in city soil or dust in correlation with human activities [5–8]. Therefore, settled dust is thought to be the carrier and reaction bed of pollutants; it has an important impact on environmental changes, the climate and human health [9–11]. High contents of heavy metals in atmospheric particles have been observed, especially in fine particles [12,13]. The contents of heavy metals in settled dust are much higher than soil background values [4,14]. Metals in dust can enter the human body by inhalation, ingestion, dermal exposure, and they can have a non-carcinogenic risk or carcinogenic risk. Partial metals in surface dust are also dissolved in mega-city acid rain, and are then carried to rivers by runoff and affect the safety of aquatic ecosystems [15,16]. Because of the high content of harmful metals in dust, the health assessment of heavy metals from street/road/park dust collected in different urban functional areas was performed [4,17–20].

The sources of metals in settled dust are complex, including soil, industrial releases, traffic transport, fuel combustion, road, and other human activities. Metal contents in dust are varied in different city functions due to the differences of regional pollutant sources [4,17,18]. The source identification of metals from settled dust is difficult but helpful for pollutant control and the protection of human health in cities with severe air pollution. Multivariate analysis (e.g., principal component analysis (PCA) and factor analysis (FA)) is a common method to identify the source of metals in aerosols, soils and dust [21–23]. Positive matrix factorization (PMF) has been used for road dust [24].

With rapid urbanization, more people will live in cities [25], which will bring more stress on the city environment due to the increased number of vehicles, and the increased industry and domestic activities. Particulate matter (PM) pollution is severe in many cities with rapid urbanization and economic development, and haze weather has often occurred in recent years [19,26], especially during winter periods. The fine atmospheric particles in a haze day can form larger particles by combination, or combine with coarse particles, then settle on the ground or building surfaces as a part of dust [19]. In China, city areas have increased quickly over the last 30 years. Some old factories have been relocated or abandoned. New city areas have been developed and expanded over the recent several decades. However, old factories still affect the environment in many ways. For example, polluted soil is one of the sources of dust. Harbors, railways and some industries are still important in old city areas. Old buildings and old decorated materials face weathering. Atmospheric pollutants are released by scattered coal stoves without treatment because many old houses do not have centralized heating facilities in winter. The pollutants released from the old city areas might be accumulated in the surface dust and might be different from those in the new city areas. This might cause various threats to the health of people located in different places. Without a sufficient number of samples from the whole city area, it is not easy to identify the spatial characteristics of pollutants. At the same time, the toxicity of metals is thought to depend on their mobility and availability [27,28]. However, the amount of research on the species of metals from dust has been relatively low [28]. Dust can affect human health by ingestion, inhalation, and dermal contact.

In this paper, the spatial distribution of heavy metals was provided using 93 sites in the Qingdao main city area based on geographical information system (GIS) capabilities. Chemical species of metals in 34 sites were analyzed using the sequential extraction method [29]. Water-soluble ions come from primary and secondary particles; they are also the main components of dust. Water-soluble ions were also used to identify the source of atmospheric particulate matter [30]. The source of pollutants was identified by the PCA method considering the water-soluble ion and metal contents.

Qingdao is one of the oldest industrial and port cities in China, dating from early in the last century. The port, textile industry, chemical industry and steel industry were established earlier in the old city area and have partly moved out of town in recent years. City areas continue to expand and Qingdao has become a metropolis with a population of more than 9 million. Air pollution and soil pollution problems in the old city area are representative because of the long-term human activities. Although Qian and Liu [31] assessed the health risk of metals from park dust in Qingdao, the speciation of heavy metals in dust was not studied, which is important data for health risk assessments. Research on the dust at the end of the heating period is important to establish the risk of dust on the health of people in the most severe particulate pollution season.

The main objectives of this study were as follows: (1) to analyze the spatial distribution patterns of heavy metals from settled dust and the differences between the old city and the new city areas of Qingdao; (2) to analyze the speciation of metals from settled dust; (3) to identify the sources of metals from settled dust using PCA; (4) to assess the contamination levels and human health risks of heavy metals from settled dust.

2. Materials and Methods

2.1. Sampling and Experimental Setup

Qingdao is a century-old coastal city. The urban areas along Jiaozhou Bay (west part of Shinan (SN), Shibei (SB) and Licang (LC)) are old city areas. There are many old plants in the north-west of the old city areas. The eastern part of the city has been developed over the last 30 years. In March 2017, settled dust samples were collected from Qingdao city. Because street dust is often mixed with the uppermost surface layer of soil, the settled dust samples were collected gently with a brush from the surface of wooden doors and windows without paint or metal shedding. They were then stored in polyethylene bags. In this way, the settled dust samples were not mixed directly with the upper layer of soil. The sampling sites were not close to obvious pollution sources such as point-source and line-source pollution. The sampling height of settled dust was 1.5–2.0 m. The samples were screened by 150 mesh nylon screens, and air dried before analysis. Approximately 93 settled dust samples were collected (Figure 1). Chemical speciation was analyzed for 34 samples.

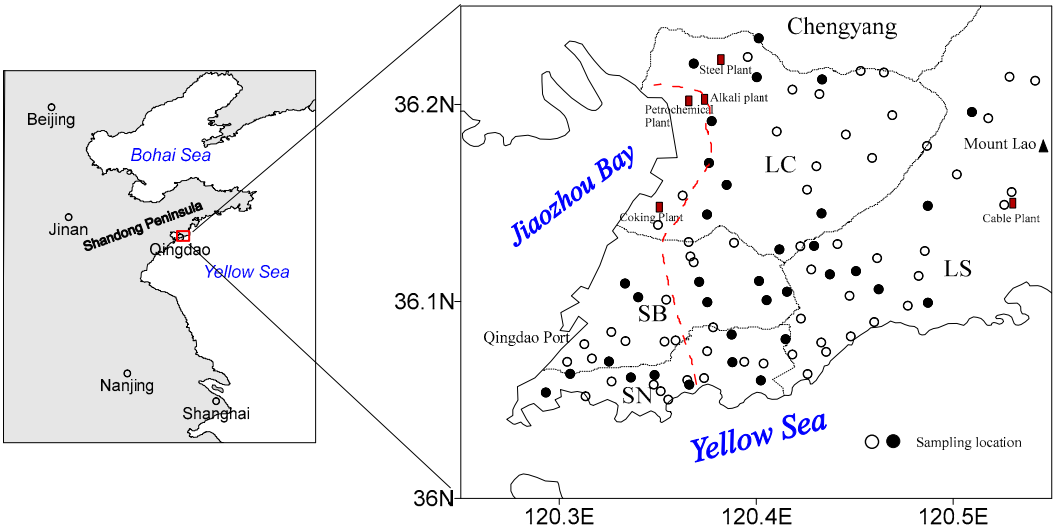

Figure 1. Atmospheric settled dust collection sites in Qingdao, China; Qingdao's main urban area includes Shinan (SN), Shibei (SB), Licang (LC) and Laoshan (LS); west of SN, SB and LC are the old city areas of Qingdao (west of red line); the speciation of metals was analyzed in sites marked with dark solid circles.

2.2. Analysis of Samples

The total contents of trace heavy metals from the settled dust samples such as Hg, Cd, Cr, Cu, Ni, Pb, Zn and other constant elements such as Fe and Al were measured. The samples were digested with aqua regia (6 mL concentrated HCl and 2 mL concentrated HNO_3) to determine Hg by the method of cold vapor atomic fluorescence spectrometry (CVAFS, US EPA1631) using Brooks Rand Model III. The samples were digested to measure other metals with HNO_3 + HF + $HClO_4$ at 180 °C in a Teflon crucible until the solid residue disappeared and the solution was clear. Cd, Cr, Cu, Ni, Pb, Zn, Fe and Al were measured by the method of plasma emission spectrometry (ICAP-6300, Thermo Fisher Scientific, USA).

The exchangeable metal fraction (F1), carbonated-associated fraction (F2), fraction associated with Fe and Mn oxides (F3), fraction bound to organic matter (F4) and residual fraction (F5) of metals in dust were analyzed using five-step sequential extraction [29]. The contents of different metals specifications were measured by the method of plasma emission spectrometry (Thermo, ICAP-6300). Organic carbon was determined using the $K_2Cr_2O_7$ oxidation method (CEPA, HJ615-2011).

Furthermore, major water-soluble ions such as Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} were analyzed. Water-soluble ions in particulate samples were extracted using second-deionized water

by an ultrasonic cleaner (KQ-300E) [30]. The filtrate was used to determine water-soluble ions such as Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} by Ion chromatography (ICS-3000, Diane, USA).

Five standard samples (GBW07315) were tested for each batch of samples to calculate the method of the recovery of heavy metals, and the blanks were also tested to calculate the detection limit. The recovery rate of metals was 84.4–113.5%, and the detection limit of the water-soluble ions is shown in Table S1. In the experiment, samples were randomly selected for parallel analysis and the relative standard deviation was less than 2.6%. Ultrapure water (18.2 MΩ·cm, 25 °C) was used in the analysis.

2.3. Enrichment Factor Analysis

The enrichment factor (EF) is an important index to quantitatively assess the degree of disturbance of human activities on the natural environment. To reduce human influences and ensure the equivalence among the indices of the samples, the reference element is used to normalize the elements in the settled dust samples [32]. The natural, ubiquitous, easily measured and inert elements are used as references. In this paper, Fe is used as a reference element, and the calculation formula is as follows:

$$\mathrm{EF} = \frac{(\mathrm{C}_i/\mathrm{C}_n)_{\mathrm{sample}}}{(\mathrm{C}_i/\mathrm{C}_n)_{\mathrm{background}}} \quad (1)$$

where C_i represents the content of heavy metal element i, C_n represents the content of Fe, and the background value of heavy metal content in the study area comes from the baseline value of Qingdao City provided by Yao et al. [33]. According to the values of the enrichment factor and other research [34], pollution levels are divided into 5 categories (Table 1).

Table 1. Pollution evaluation criteria of the enrichment factor (EF).

Enrichment Factor Index	Pollution Level	Enrichment Degree
$EF < 2$	1	Depleted–minimal
$2 \leq EF < 5$	2	Moderate
$5 \leq EF < 20$	3	Significant
$20 \leq EF < 40$	4	Very high
$EF \geq 40$	5	Extreme

2.4. Health Risk Assessment

The soil risk model was proposed by the US Environmental Protection Agency (US EPA) as a basic framework [35]. It was used to estimate the health risk assessment. Several parameters were revised [36]. The risk assessment includes two types of risks: non-carcinogenic risk and carcinogenic risk. Hg, Cu, Pb, Zn, Cr, Cd, Ni have chronic non-carcinogenic health risks. Cd, Cr and Ni also have carcinogenic health risks, and dust inhalation is the only harmful possibility for humans for carcinogenic heavy metals. People were divided into two groups: children and adults. Ingestion, inhalation, and dermal contact absorption are the main exposure routes. The calculation model of health risk is shown as follows. The meanings and values of the parameters are shown in Table S2.

$$\mathrm{ADD_{ing}} = \mathrm{c} \times \frac{\mathrm{IngR} \times \mathrm{CF} \times \mathrm{EF} \times \mathrm{ED}}{BW \times AT} \quad (2)$$

$$\mathrm{ADD_{inh}} = \mathrm{c} \times \frac{InhR \times EF \times \mathrm{ED}}{\mathrm{PEF} \times \mathrm{BW} \times AT} \quad (3)$$

$$\mathrm{ADD_{derm}} = \mathrm{c} \times \frac{SA \times \mathrm{CF} \times \mathrm{SL} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED}}{BW \times AT} \quad (4)$$

ADD_{ing} is the daily average exposure by ingestion. ADD_{inh} is the daily average exposure by inhalation. ADD_{derm} is the daily average exposure by dermal contact.

$$HQ = ADD/RfD \quad (5)$$

$$HI = \sum HQ_i \quad (6)$$

$$(Risk)_i = ADD_{inh} \times SF \quad (7)$$

HQs (hazard quotients) indicate the non-carcinogenic risk of non-carcinogenic substances. HQs are the ratios of non-carcinogenic exposure to a reference dose (RfD). HI is the hazard index. When HI < 1, the risk can be considered small or negligible; when HI > 1, then there is a non-carcinogenic risk. Risk represents the probability of cancer occurrence [36]. For the risk of cancer (Risk), if it is less than the value of carcinogenic risk (10^{-6}~10^{-4}), then that substance does not carry risk of cancer; otherwise, there is a potential risk of cancer [36]. The total carcinogenic risk is the sum of the carcinogenic risks of each carcinogenic heavy metal.

3. Results and Discussion

3.1. Heavy Metal Contents and its Speciation in Settled Dust

The total mean contents of metals (without outliers) recorded in Qingdao are shown in Table 2. The average contents of Hg, Cd, Cr, Cu, Ni, Pb and Zn in the atmospheric settled dust of Qingdao were 0.17, 0.75, 153.1, 456.7, 60.9, 176.0 and 708.3 mg/kg, meaning 6.86, 4.86, 4.94, 34.6, 4.95, 5.67 and 10.3 times the soil background values, respectively. This indicates the enrichment of heavy metals in settled dust. Excepting Hg and Ni, the mean contents of Cu, Pb, Zn, Cd, Cr were all higher than the Chinese new soil quality guidelines for agricultural land (GB 15618-2018) [37], but lower than the Chinese new soil quality guidelines for residential land (GB 36600-2018) [38]. The largest values of Cu, Pb, Cr, Ni were higher than the guidelines for residential land. Two areas showing high values were found in this study: one area was located in the west south of the city (the oldest part of city), and the other was close to the Hanhe cable factory (Figure 2). Compared to other international standards, the mean values of Cu, Pb, Zn, Cr, Ni were all higher than the Canadian soil quality guidelines for agricultural or residential land. Hg and Cd contents in several sites were higher than Canadian soil quality guidelines for agricultural land.

Cu, Pb, Zn, Cr, Ni contents were higher than in Beijing [24,39], Nanjing [28], Chengdu [4], Jordan [40] and Massachusetts [41] (Table 2). However, Hg, Cu, Pb, Zn and Cr contents were lower than in Krakow [20]. Except for Cu, the metal contents were comparable with those in Shanghai, but most metals were lower than in Hong Kong [14]. The Zn content in Warsaw, the capital of Poland [42], was about twice that of Qingdao, which might be related to the local industrial and historical background of Warsaw. Higher contents of Cu, Pb, Zn, and Cr were recorded in Qingdao, Shanghai [43] and Krakow [20] from surface dust compared with street dust in the other cities excepting Hong Kong. Street dust might contain more coarse soil particles, while particles of the surface dust were finer. Fine particles stick to the skin or enter the stomach from unwashed hands more easily. There were recorded high contents of metals in fine soil, sediment and dust [12,44]. Therefore, the metal contents were higher in the samples collected on the surface of buildings.

Table 2. Comparison of heavy metal contents from settled dust with the soil quality guidelines and other cities.

Cities/Standard	Hg mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Cd mg/kg	Cr mg/kg	Ni mg/kg	Al %	Fe %	Type	Sources
Mean	0.17 *	456.7 *	176.0	708.3 *	0.75 *	153.1 *	60.9	4.63	3.82	Settled dust	This study
Minimum value	0.014	11.3	40.0	109	0.10	32.3	2.99	0.3	0.65		
Maximum value	3.94	5840	666	2595	9.02	2395	368	9.35	11.5		
Median	0.098	218	138	640	0.45	131.3	54.8	4.66	3.85		
Soil background	0.035	13.2	31	69	0.13	31	12.3	6.62	2.72	Soil	[33]
Chinese soil quality guidelines	1.8	50	90	200	0.3	150	70	—	—	Agricultural land	[37]
	8	2000	400	—	20	3 [a]	150	—	—	Residential land	[38]
Canadian soil quality guidelines	6.6	63	70	250	1.4	64	45	—	—	Agricultural land	[45]
	6.6	63	140	250	10	64	45	—	—	Residential land	
Shanghai	—	186.4	212.9	687.3	0.97	218.9	64.9	—	—	Surface dust	[43]
Beijing	0.34	41.5	54	219.2	1.1	73.5	34.1	—	—	Street dust	[39]
	—	83.1	60.8	280	0.59	92.0	32.0	—	2.97	Road dust	[24]
Nanjing	—	102.8	82.7	302.7	4.37	67.1	46.2	0.92	—	Street dust	[28]
Chengdu	—	100	82.3	296	1.66	84.3	24.4	—	—	Street dust	[4]
Hong Kong	0.6	534	240	4024	1.8	324	—	4.66	3.98	Street dust	[14]
Jordan	—	91.9	59.5	639.8	6.36	65.5	—	—	—	Dust, office dust	[40]
Massachusetts	—	105	73	240	—	95	—	—	2.81	Road dust	[41]
Krakow	1.5	—	190	956	6	64	61	0.53	2.17	Park dust	[20]

* Mean value of metals without outliers (value is much higher than the sum of mean and three times standard deviation); [a] shows hexavalent chromium.

The mean contents of five chemical types and their ratios to the total contents in 34 sites are shown in Table 3. In five types, the mean residual fraction (F5) proportion orders of the metals decreased as follows: Al > Fe > Cr > Pb > Cu > Cd > Zn. The proportions of Al, Fe and Cr were the highest, at 82.6%, 81.4% and 69.3%, respectively. High proportions implied the lesser content of the other four fractions. Therefore, Fe, Al and Cr had high stability, and were strongly bound to minerals or the component of the resistant mineral crystal structure. The mean F5 proportion of Pb was 46.3% with the largest proportion in five fractions. The mean proportion of the five fractions for Fe, Al, Cr and Pb decreased in the following order: F5 > F3 > F4 > F2 > F1. This order was similar to Al and Cr from dust in the Nanjing Jiangning area [28]. The F3 proportion of Zn was the highest, at 44.6%. The fraction bound to the organic matter (F4) of Cu, Cd, Zn and Pb was significant, with proportions of 70.2%, 26.3, 18% and 15%, respectively. The content of organic matter in dust was 6.16%, which was much higher than the soil background values. Copper ions combine easily to organic matter in soil and sediment [46]. For Cd, the order was F4 > F1 > F3 ≈ F2 > F5, which was different from other metals. The exchangeable metal (F1) and carbonated-associated fraction (F2) of Cd accounted for 24.6% and 19%, respectively. Because humans can easily absorb F1 and metals in the F2 fraction could be released by gastric acid, the sum of F1 and F2 was used to represent the bioavailability of metals. Therefore, high values of F1+F2 implied high environmental health risks. The mean F1+F2 proportion decreased as follows: Cd > Zn > Pb > Cu > Cr > Fe > Al. The mean F1 + F2 proportions of Cd, Zn and Pb were 43.6%, 26.1% and 15%, which implied that they have high mobility and bioavailability. This characteristic was also found in other street dusts [28,47]. The high mobility and bioavailability of Pb in dust might cause high Pb concentrations in children's blood in heavy polluted cities [48].

Table 3. Content and ratio of each chemical speciation of metals in settled dust.

Metals	F1		F2		F3		F4		F5		F1 + F2	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Cu	4.3	1.9	13.8	6	1.9	0.8	162.2	70.2	49	21.2	18.2	7.9
Pb	3.3	2.3	18.3	12.8	34	23.7	21.5	15	66.3	46.3	21.6	15
Zn	37	9.4	65.9	16.7	175.8	44.6	71.1	18	44.3	11.3	102.8	26.1
Cd	0.12	24.6	0.1	19	0.1	19.2	0.13	26.3	0.06	12	0.22	43.6
Cr	0.41	0.7	0.76	1.3	9.75	17.3	6.37	11.3	39.09	69.3	1.17	2.1
Al	14.5	0.1	220.1	0.9	2526.6	10.5	1417.5	5.9	19,883.6	82.6	234.5	1
Fe	16.1	0.1	81.8	0.5	2213.5	13.4	765.5	4.6	13,430.6	81.4	97.8	0.6

3.2. Spatial Distribution Characteristics of Heavy Metals

The spatial distributions of different heavy metals in urban areas varied significantly. The contents of Cu, Pb, Zn, Ni, Cr and Hg were higher in the southwest of Qingdao (the west of SN and SB districts), where the old city area is (Figure 2). One site located close to the railway station recorded the highest Cr, Pb, Zn, and Cd, which might be influenced by the intensive transport. In this area, there are old residential areas, the harbor, and the railway station. Human activities affected for a long time the accumulation of metals in surface dust. A high-content site of Cu, Pb, Zn and Cd was established in the east of Laoshan, which is potentially polluted by the Hanhe cable factory. High contents of Fe and Ni were revealed in the north of Qingdao city, close to the Qingdao steel plant.

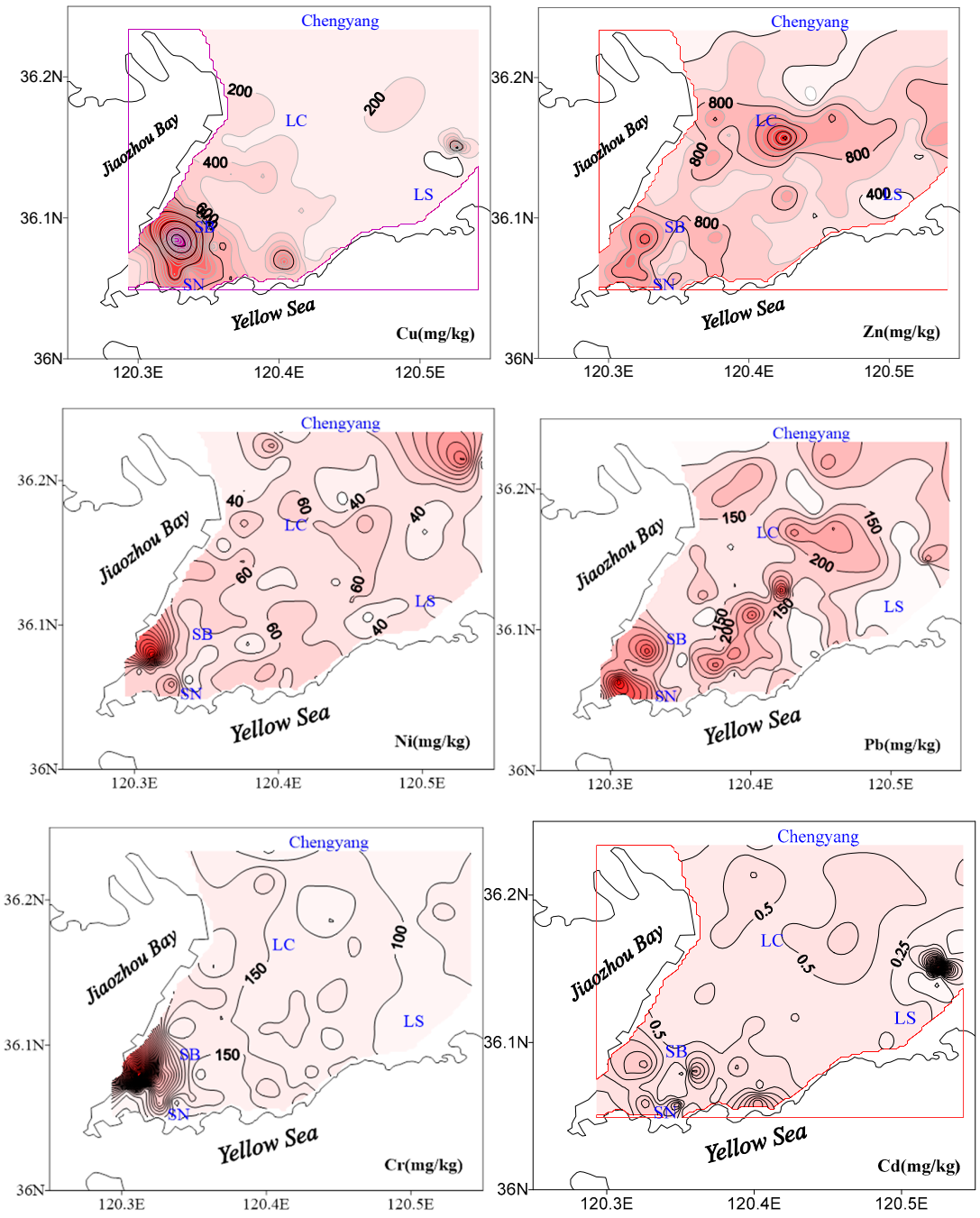

Figure 2. *Cont.*

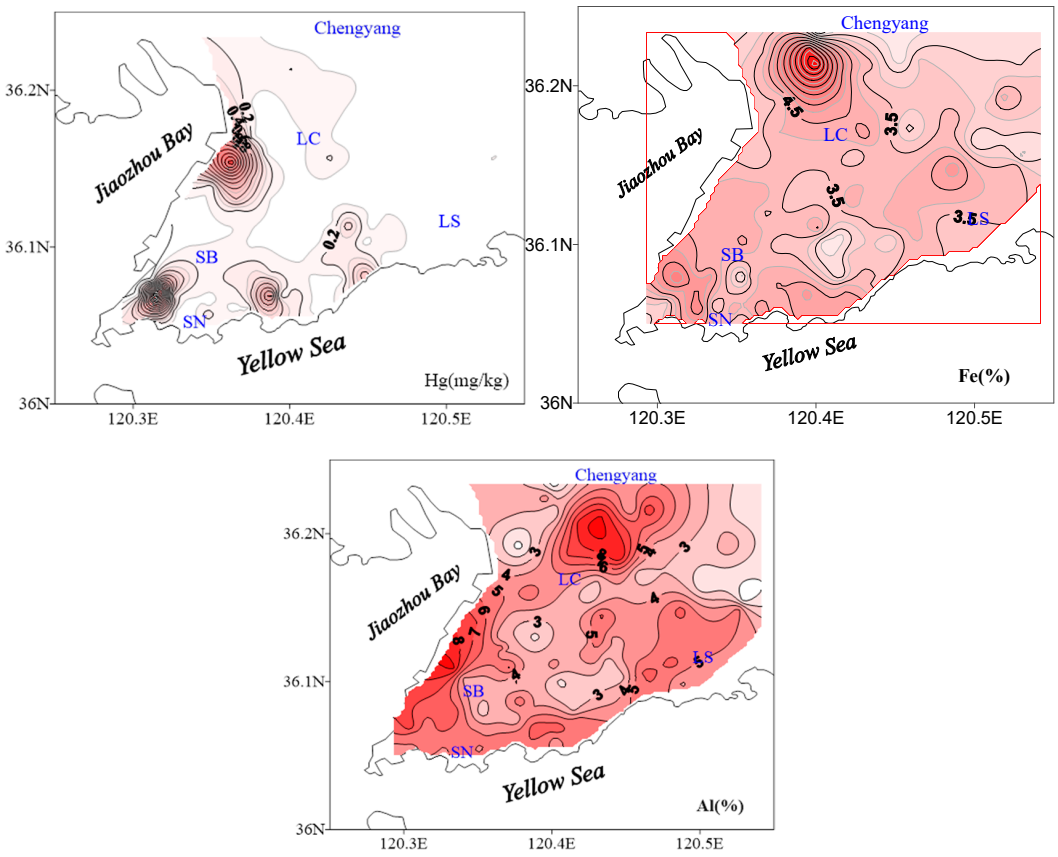

Figure 2. Spatial distribution maps of heavy metals from settled dust in Qingdao.

The spatial distribution differences of Fe and Al were relatively small, but the contents in the coastal area were higher than those inland. A high content of Hg was recorded in the west of LC, which is an old industrial area including the Thai Group coke gas plant, and nearby chemical plants. Coal is the raw material of coke production. Hg in coal is released to the air and adsorbed by dust [49]. Hg contents in business zones between Xianggangzhong Road and Zhongshan Road were higher. Hg might originate from fluorescent lamps and the oil paint used in shop decoration in the past. The lowest Hg content appeared in the northeast of Qingdao, close to Mount Laoshan. The content of Ni in most areas was within the background value range, and human activities had little influence on the content of Ni in settled dust.

The larger variation coefficients of Hg (207%) and Cu (202%) implied large spatial differences influenced by different human activities. The average contents of Al and Fe in the four districts were 4.66% and 3.90%, respectively. The content of Al in Qingdao was lower than the soil background value of Shandong (6.6%) [50].

3.3. Source Identification of Atmospheric Settled Dust

A Pearson correlation was performed, and the results are shown in Table S3. Most of the water-soluble ions correlated significantly with each other. Excepting Al, Fe and Hg, other heavy metals correlated significantly with each other. This suggests that there was a large difference in the main sources between water-soluble ions and heavy metals. We found that several water-soluble ions were correlated significantly with heavy metals. For example, K^+ correlated significantly with Cd, Cr, Cu and Pb.

The sources of settled dust are complex in mega-cities. PCA was used (Table 4) to analyze the source of settled dust using the water-soluble ions and metal contents. The Kaiser–Meyer–Olkin (KMO) value was 0.69, and Bartlett test probability significance level was 0.000; therefore, PCA

was suitable. Five components were extracted because their characteristic values were more than 1, and their cumulative contribution rate was 70.5%. Component 1 mainly reflected the change of water-soluble ions except NH_4^+, and Mg^{2+}, K^+, Na^+, Ca^{2+}, Cl^-, SO_4^{2-} and NO_3^- explained a relatively high positive load in component 1. Na^+ and Cl^- are the ion pairs that reflect the characteristics of the sea source. K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} are also the main components of seawater. In winter, sea fog often appears in Qingdao in the morning and the humidity is high. The diameter of fine particles increases with condensed water, which causes more fine particles to settle on the surface of buildings. SO_4^{2-} and NO_3^- are the main components of secondary aerosols, mainly reflecting the source of fuel combustion [51]. K^+ in aerosol is believed to originate from the biomass combustion [52]. In component 1, Pb, Zn, Ni, Cu, Cr and Cd contribute to a positive load, but these metals are trace components in seawater. Therefore, fuel combustion might be an important source of trace metals. Pb and Zn were found with high values in coal combustion, tire wearing and vehicle exhaust emissions [41,53,54]. In past years, domestic heating depended on dispersed coal-burning stoves in old city areas, and pollutants were released directly to the atmosphere.

Table 4. Analysis and statistics of the main components of atmospheric settled dust in Qingdao.

Elements	Component				
	1	2	3	4	5
Na^+	**0.755**	−0.005	−0.543	−0.009	0.093
NH_4^+	0.354	−0.331	**0.629**	0.291	0.116
K^+	**0.768**	0.126	0.036	−0.254	−0.305
Mg^{2+}	**0.884**	−0.264	−0.12	−0.025	−0.085
Ca^{2+}	**0.697**	−0.438	0.395	0.051	0.037
Cl^-	**0.736**	0.009	−0.539	0.041	0.157
NO_3^-	**0.648**	−0.364	0.287	0.171	0.189
SO_4^{2-}	**0.731**	−0.171	−0.268	0.122	−0.014
Hg	−0.019	0.295	0.053	−0.567	**0.637**
Al	−0.217	0.381	−0.458	**0.360**	0.189
Cd	0.226	**0.594**	0.108	0.026	−0.191
Cr	0.244	**0.785**	0.211	0.103	−0.254
Cu	0.288	**0.760**	0.044	−0.140	−0.312
Fe	−0.139	**0.585**	0.068	**0.481**	0.235
Ni	0.335	0.461	0.125	**0.325**	0.303
Pb	0.48	0.395	0.149	0.064	0.071
Zn	0.382	**0.516**	0.28	−0.366	0.236
Eigenvalue	4.798	3.305	1.699	1.156	1.033
Variance%	28.224	19.441	9.992	6.800	6.076
Cumulative variances%	23.074	35.440	47.716	58.002	67.242

In component 2, Cr, Cu, Cd, Fe, Zn and Ni had higher loads; these elements were widely used in human activities and municipal construction. They are often used in alloy surface preservation on many metal tools or for the decoration of surfaces. Metals are released into the environment due to long-term oxidation and weathering processes. At the same time, Cr and Ni also came from the electroplating of metals and the wearing of brake components [55]. Cd and Cu are widely used in alloy surface preservation. High contents were determined in the old city areas and near the Hanhe cable factory. Therefore, Cd and Cu in the old city areas originated from the corrosion and ageing of construction materials. The wearing of the brake lining not only causes Cd pollution, but also brings Cu pollution in the dust [41,56–58]. In component 4, Al and Fe had higher loads, being constant elements in the soil and parent rock. Fe, Al and Ni had higher positive loadings to component 2 and 4, suggesting that they came from human activities and soil origins. In component 5, Hg had the highest load, being mainly derived from human activities. For example, there was a high Hg content in the commercial district and the hospital of Qingdao determined in this study.

3.4. Enrichment Factors and Health Risk Assessment

Enrichment factors (EFs) of Cd, Cr, Cu, Hg, Ni, Pb and Zn in the settled dust in urban areas of Qingdao are shown in Figure 3. There were large EF differences between different regions of Qingdao, especially for Cu. The EFs of most sites were larger than 2. This indicates that the atmospheric settled dust in the urban areas of Qingdao was predominantly affected by human activities. In urban areas, more than 75% of the EFs of Hg, Cd, Cr, Ni and Pb were less than 5, and more than 50% of the EFs of Hg, Cd, Cr, Ni and Pb were higher than 2.5. This indicates that most of the areas were moderately polluted. Furthermore, 87% of the EFs of Zn were from 5 to 20, and the enrichment of Zn was significant. The EF of Cu was the largest, because 4% of samples were higher than 50, while 57% and 24% of samples were higher than 20 and 40, respectively. Therefore, Cu in settled dust was extremely enriched. Pollution by Cu and Zn in settled dust deserves special attention. Because the differences of Fe were small, the EF values were affected by the concentration of heavy metals. The spatial distribution patterns of EFs were similar to the distribution of metal concentrations (Figure 2).

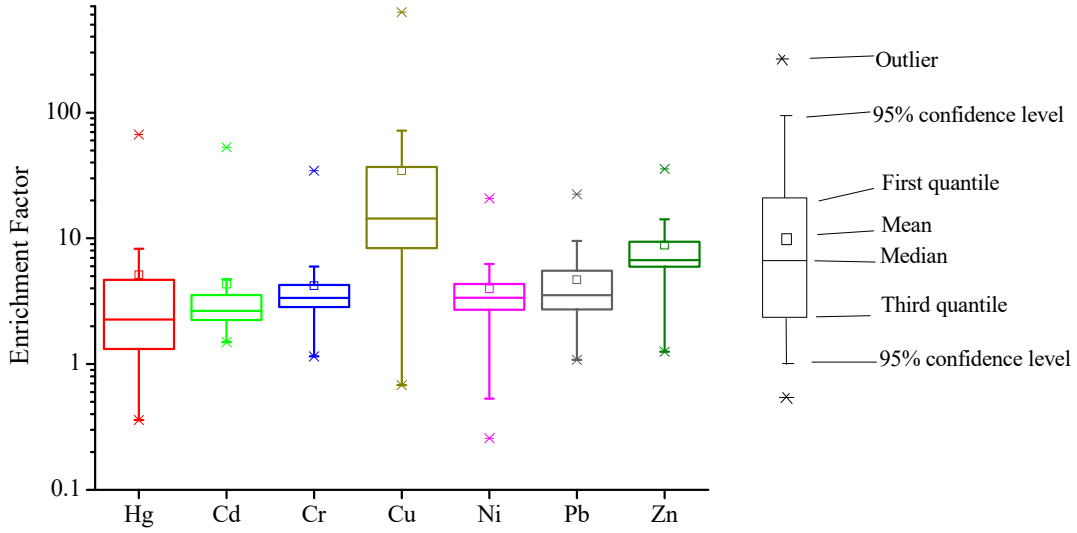

Figure 3. Heavy metal enrichment factors of atmospheric settled dust in Qingdao City.

According to Equations (2)–(4) and the heavy metal exposure parameters presented in Table S2, the exposure doses of the three routes are shown in Tables S4 and S5. The non-carcinogenic heavy metal daily exposure dose of Zn was the highest, followed by Cu and Cr, while the exposure doses of Cd and Hg were lower. The non-carcinogenic exposure doses order from large to small were Zn, Cu, Cr, Pb, Ni, Cd, and Hg. The exposure doses order of different exposure routes was as follows: ingestion > dermal > inhalation. This characteristic was also reported in other cities [4,24]. Therefore, ingestion intake is the main path for exposure in the case of settled dust. The influence on children is considered to be larger than in adults for all three exposure methods. The risk associated with children needs to be more closely studied and mitigation/protection measures should be developed [59].

Based on the estimated exposure doses, the non-carcinogenic risk indices of seven heavy metals and the carcinogenic risk indices of three heavy metals in the atmospheric settled dust of Qingdao are displayed in Table S6. The non-carcinogenic risk sequence was as follows: ingestion > dermal > inhalation. The average values of non-carcinogenic risk were all less than 1. This indicates that the risks of heavy metals to human health are not high in most sites. However, non-carcinogenic risks of Cr, Cu and Pb by ingestion exposure in some sites were higher than 1 (Figure 4), which were significantly higher than that of the inhalation pathway or dermal route. These three metals in several sites may be harmful to human health through the ingestion route of exposure. For children, as a sensitive group, the non-carcinogenic risks are higher than in adults, which is consistent with the research results of Men et al. [24]. The non-carcinogenic risk indices of heavy metals for children and adults through

the ingestion route were as follows: Cr > Pb > Cu > Ni > Zn > Hg > Cd; the non-carcinogenic risk indices through the inhalation route were Cr > Pb > Hg > Cu > Ni > Zn > Cd. The non-carcinogenic risk indices through dermal contact were Cr > Pb > Cd > Cu > Zn > Ni > Hg. The average total risk of the non-carcinogenicity of different heavy metals accumulated in settled dust was less than 1, but the risk indices for children and adults in several sites were greater than 1.

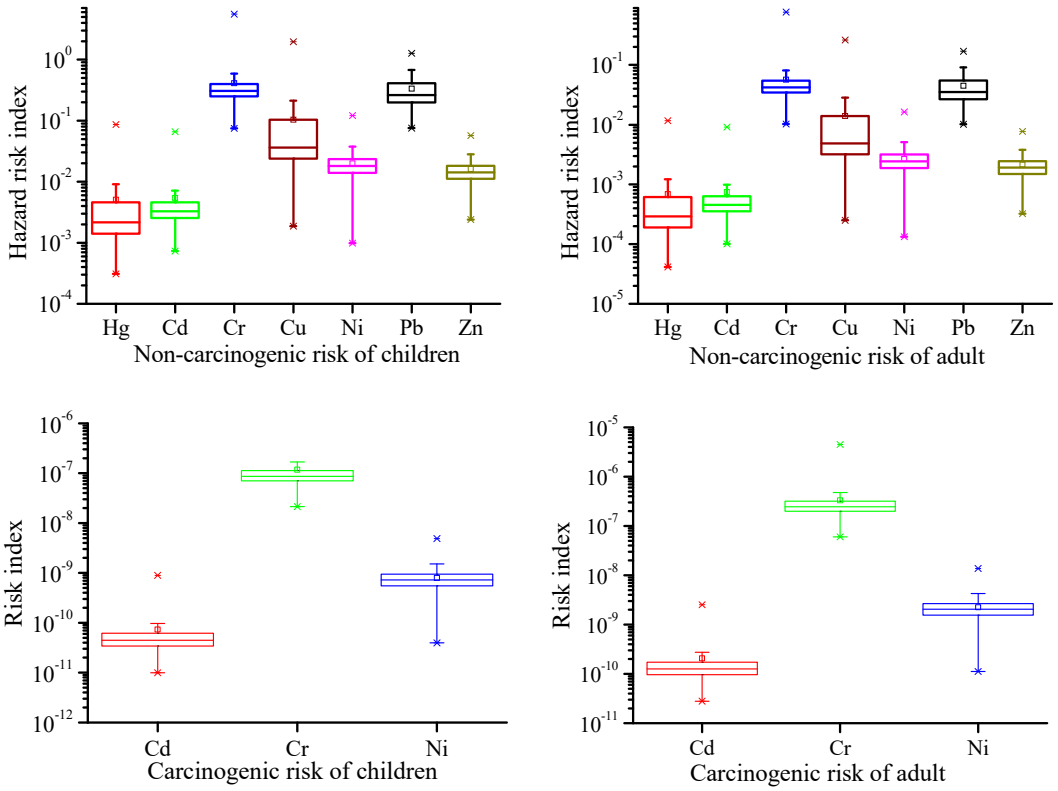

Figure 4. Non-carcinogenic and carcinogenic hazard index for heavy metals from settled dust in Qingdao. The illustration of boxplot is same to Figure 3.

The carcinogenic risk exposure by the inhalation route (Table S6) shows that the carcinogenic risk indices of Cd, Cr and Ni in settled dust were between 10^{-11} and 10^{-7}, lower than the non-carcinogenic risk, which is consistent with the research results of Qian et al. [31]. The carcinogenic exposure doses and carcinogenic risk rankings were in the order of Cr > Ni > Cd, and this shows that risk for adults is lower than for children. The maximum carcinogenic risk indices of Cr in children and adults were 1.58 $\times$ 10^{-6} and 4.48 $\times$ 10^{-6}, respectively.

4. Conclusions

The average contents of Hg, Cd, Cr, Cu, Ni, Pb and Zn in the atmospheric settled dust were 6.86, 4.86, 4.94, 34.6, 4.95, 5.67 and 10.3 times the soil background value, respectively. There were significant spatial distribution differences of heavy metals in settled dust. The contents of Cu, Pb, Zn, Ni, Cr and Hg were higher in the old city areas due to human activities.

The residual fraction proportions of Al, Fe and Cr were highest at 82.6%, 81.4% and 69.3%, respectively. The mean exchangeable metal (F1) and carbonated-associated fraction (F2) proportions decreased as follows: Cd > Zn > Pb > Cu > Cr > Al > Fe. The mean exchangeable metal and carbonated-associated fraction proportions of Cd, Zn and Pb were 43.6%, 26.1% and 15%, respectively, which implies that they have high mobility and bioavailability. The combustion source contributes much to partial water-soluble ions, Pb, Zn and other trace metals. Hg, Pb and Zn are mainly related to business and industry. Cd and Cu in the old city areas originate from the corrosion and ageing of construction materials.

The enrichment coefficients indicate that Cd, Cr, Ni, and Pb reached a moderate level of pollution, Hg and Zn contents reached significant levels of pollution, and Cu was extremely enriched, which requires close attention in some sites of the Qingdao urban area.

The non-carcinogenic risk route was as follows: ingestion > dermal > inhalation. Children are more vulnerable to the environmental health threats than adults. The non-carcinogenic risks of Cr, Cu and Pb by ingestion exposure in several sites were higher than 1, which was significantly higher than that of the inhalation pathway or dermal route. Further, considering the proportion of speciation of F1+F2 in total content, Cr, Cu and Pb in several sites may be harmful to human health through the ingestion route of exposure. Cd, Cr and Ni in settled dust had a low carcinogenic risk. The health risks of Cr, Cu and Pb were higher in the old city areas and therefore need further research.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/10/2/73/s1, Table S1: Standard substance quality control, Table S2: Pollution evaluation criteria of Enrichment factor, Table S3: Pearson correlation of water-soluble ions and heave metals, Table S4: Table S4 Daily average exposure calculation parameters of heavy metals, Table S5: Reference doses of heavy metals in different ways of exposure (RfD) mg/(kg·d), Table S6: Exposure doses of heavy metals in different ways of different populations (ADD) mg/(kg·d), Table S7: Health risks of heavy metals in settled dust.

Author Contributions: H.X., Y.W., and R.L. were involved in the data analysis and discussion of the results; H.X., M.W. and Y.Z. were involved in the sample collection and data determination and validation. R.L. supervised the project and assisted in the interpretation of the results. All of the authors were involved in the preparation, revision and review of the manuscript.

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