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Levels, Inventory, and Risk Assessment of Heavy Metals in Wetland Ecosystem, Northeast China: Implications for Snow Cover Monitoring

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Abstract: Snow cover is a unique environmental medium in cold regions that can cause potential risks to the ecological environment, due to the release of pollutants that are stored in it. In this study, the Qixing River wetland, located in the Sanjiang Plain of China, was taken as the target research area. Heavy metals in snow cover, including Cu, Ni, Cr, Cd, Pb, and Zn were measured at 19 sampling sites. The results showed that the average concentrations of heavy metals were: Zn (103.46 ± 39.16) > Pb (13.08 ± 4.99) > Cr (11.97 ± 2.82) > Ni (9.55 ± 4.96) > Cu (6.19 ± 1.79) > Cd (0.55 ± 0.25) $\mu g \cdot L^{-1}$. Cr and Zn were between Class I and Class II in the "Environmental Quality Standards for Surface Water" of China (GB3838-2002). Pb in snow exceeded the upper limit of Class II, and was significantly higher than concentrations measured in water samples from the Qixing River wetland ($p < 0.05$), indicating that atmospheric deposition during winter was the major source of Pb. The water pollution index (*WPI*) indicated that 61.0% of samples could be considered of "clean" status, while the contribution of Zn, Pb, and Cr to *WPI* were 33.3%, 21.0%, and 19.3%, respectively. A preliminary evaluation of heavy metal inventory in snow cover showed that the residue level of Zn was the highest (2313.57 ± 1194.67 $\mu g \cdot m^{-2}$), while Cd was the lowest (13.91 ± 10.45 $\mu g \cdot m^{-2}$). The areas with high residues of heavy metals were all located near the buffer zone of the wetland (except for Zn), where snow depth tended to be greatest. Exposure analysis indicated that the risks to winter resident birds from snow ingestion was minimal, but it should be noted that the exposure risk was higher in birds with lower bodyweights. This study provides important information and scientific knowledge on the pollution characteristics and residue inventory of heavy metals in wetland ecosystems, while the results can also provide a monitoring method, reflecting atmospheric environmental quality at a local or regional scale.

Keywords: wetland; snow cover; heavy metals; residue inventory; risk assessment

1. Introduction

Heavy metal pollution has become one of the most serious environmental problems due to its persistence, toxicity, bioaccumulation, and extensive sources [1]. It is extremely recalcitrant and long-lasting, with many contemporary problems originating from past eras [2]. Rapid economic development, accelerated urbanization and agricultural production, accompanied by a large amount of emitted pollutants, has led to a significant decline in air quality [3,4]. Most pollutants have a short time of existence in the atmosphere [5], for example, heavy metals tend to adsorb into the surface of suspended particulate matter and fall to the ground during dry and wet deposition processes. Compared to rainfall, snow has a relatively large specific surface area, and a longer contact time with the pollutants in the atmosphere during the deposition; thus, snowfall plays an important role in removing atmospheric pollutants [6]. Sansalone and Buchberger showed that the contents of suspended particles in snowmelt are several orders of magnitude higher than those of rainfall [7]. Compared with the fresh snow, snow cover will be re-polluted by the surrounding environment and atmospheric dry deposition, due to its long existence [8]. Thus, exploring the contamination levels and occurrence of heavy metals in snow cover can effectively reflect the ambient atmospheric pollution conditions [9].

Sanjiang Plain, as the largest region of freshwater swamps in China, has important ecological significance [10]. With the gradual expansion of agricultural production, the consumption of water resources used for irrigation has also increased. Approximately 85% of the world's freshwater resources are used for agricultural irrigation [11], which leads to pressure on surface water sources, hence, wetland ecosystems are facing serious ecological degradation, especially in arid and semi-arid regions [12]. In the Sanjiang Plain, the thickness of snow cover can reach 40–80 mm. Zou et al. proposed to explore the reasonable use of regional snowmelt, which will effectively alleviate the conflict of water use [13]. However, the primary task is to clarify the potential risks of using snowmelt, which could contain pollutants including heavy metals. In 1969, Murozumi and co-workers studied the Pb content in snow from Greenland and Antarctica, which created the prelude to the identification of heavy metal pollution characteristics in snow [14]. Westerlund and Viklander found that snowmelt contains a significant load of particulate matter and heavy metals [15], indicating that snow can be used as a relatively stable medium for monitoring atmospheric heavy metal pollution. The estimation of pollutant residues in snow can comprehensively reflect the regional air pollution status [9], this is especially so during cold periods. The freezing of rivers interrupts fresh water inputs from upstream, thus increasing the relative importance of atmospheric deposition as a pollution source. Therefore, the residue inventory of heavy metals in snow cover can almost fully reflect their input flux from short-range atmospheric transport.

Heavy metals are usually emitted from coal and biomass combustion during the period of heating in wintertime, and then stored in snow cover through atmospheric deposition [5]. Subsequently, these heavy metals can enter into the soil or wetland ecosystem during the snowmelt period, harming the health of wildlife via oral ingestion, dermal contact, and inhalation [16,17]. Fáncsi and Kertész found that wild duck eggs soaked in Cr^{3+} solution for 30 min resulted in a deformity rate of up to 30% after hatching [18]. While this level of exposure is far greater than what would usually be experienced in an environmental setting, it is still indicative of harm. Meanwhile, heavy metals can significantly reduce the growth rate of body weight and wing length of nestlings, and can even lead to death [19]. Suljevic and co-workers evaluated the tissue-specific accumulation of Cr^{6+} in Japanese quail (*Coturnix japonica*) and the induction mechanism of adverse physiological reactions, which indicated that exposure to a Cr^{6+} contaminated environment significantly reduced the immunity of Japanese quail [20]. Additionally, some studies have also quantitatively evaluated the exposure risk of heavy metals to migratory birds, based on an external measurement model [21–23]. Given the characteristics of water freezing during the winter, snow has become the main source of drinking water for winter resident birds. Therefore, exposure risk assessment of heavy metal to migratory birds by considering the snow ingestion pathway could reflect the adverse effects of air pollution on the wildlife in a wetland ecosystem.

As one of the most typical natural freshwater wetlands in Sanjiang Plain, the Qixing River wetland provides significant ecological service functions, such as water conservation, hydrological regulation, and biodiversity maintenance [22], and is also one of the most important breeding grounds for migratory birds in Northeast Asia. The snow cover thickness during the freezing period is 50–200 mm. To remedy the lack of research on the characteristics of heavy metal pollution in the snow cover from a wetland ecosystem, the objectives of the present study are to (1) reveal the contamination levels and occurrence of heavy metals in snow cover in this setting; (2) estimate the inventory of heavy metal residues in the snow cover during the freezing period, and quantify the input flux from the atmospheric deposition; (3) evaluate the heavy metal exposure risk to winter resident birds, by considering the snow ingestion pathway.

2. Materials and Methods

2.1. Study Area

Qixing River wetland is located in the middle and lower reaches of the Qixing River, with the geographical coordinates between: 132°00′22″~132°24′46″ E and 46°39′45″~46°48′24″ N. The total area of Qixing River wetland is 20,000 ha, of which the reed marsh accounts for 70% [24]. Qixing River wetland is one of the most representative epitomes of the virgin landscape of Sanjiang Plain, the best preserved natural freshwater wetlands in China, and the most important breeding grounds for water birds in Northeast Asia. Due to its high ecological significance regionally, nationally, and globally, it has been listed as an internationally significant wetland by the Ramsar Convention in 2011 [25]. Under the temperate continental monsoon climate, the temperature drops sharply during autumn, and the winter is cold and dry, with an average temperature of −17.5 °C in January and an annual average frozen water depth of 94 cm. Snow cover thickness measured in February 2018 was from 50 mm to 200 mm.

2.2. Sample Collection and Analyses

In February 2018, a total of 19 snow cover samples were collected from the Qixing River wetland, and the thickness and densities of the snow cover were tested in the field. Each sample comprised a mixture of three sub-samples, taken 5 m apart at each sampling location. All the samples were stored in 10 L acid-washed polyethylene bottles, and transported to the laboratory as soon as possible in the absence of light. As far as we know, there was no heavy snowfall event that happened after the sampling period, thus the snow cover samples can reflect the annual snowfall amount approximately. The locations of the sampling sites are illustrated in Figure 1.

The process for determining heavy metals has been described in detail in our previous study [9,10]. In brief, 10 mL nitric acid was added to the 500 mL snowmelt water sample. Heated concentrated samples were transported to Teflon crucibles on a hot plate, digested by wet digestion (HCl-HNO_3-$HClO_4$-HF), until there were no solid particles and no white acid smoke escaped. The crucibles were then removed from the hot plate (cooled to room temperature) and diluted to 50 mL using deionized water. The concentrations of heavy metals in the digested samples were determined using the ICE 3500 atomic absorption spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA); Cd and Pb were detected using the graphite furnace portion, and the flame portion was used for the measurement of Cu, Cr, Ni, and Zn. The detection limits were 0.11 $\mu g \cdot L^{-1}$ for Cr, 0.16 $\mu g \cdot L^{-1}$ for Cu and Ni, 0.01 $\mu g \cdot L^{-1}$ for Cd and Pb, and 0.93 $\mu g \cdot L^{-1}$ for Zn.

2.3. Quality Assurance/Quality Control

Strict quality assurance and control of all analytical processes were conducted. All polyethylene bottles and glass vessels used were soaked in 10% HNO_3 for 24 h, then washed with deionized water, and all the reagents used in the digestion procedure were a guaranteed analytical grade. Blank and parallel samples were analyzed by one per each set of five samples. The standard deviation between duplicates was less than 8%, and the concentrations of heavy metals in blank samples were always below the detection limits. The correlation coefficients of calibration curves of the target metals were greater than the minimum permissible limit for the instrument test (greater than 0.995).

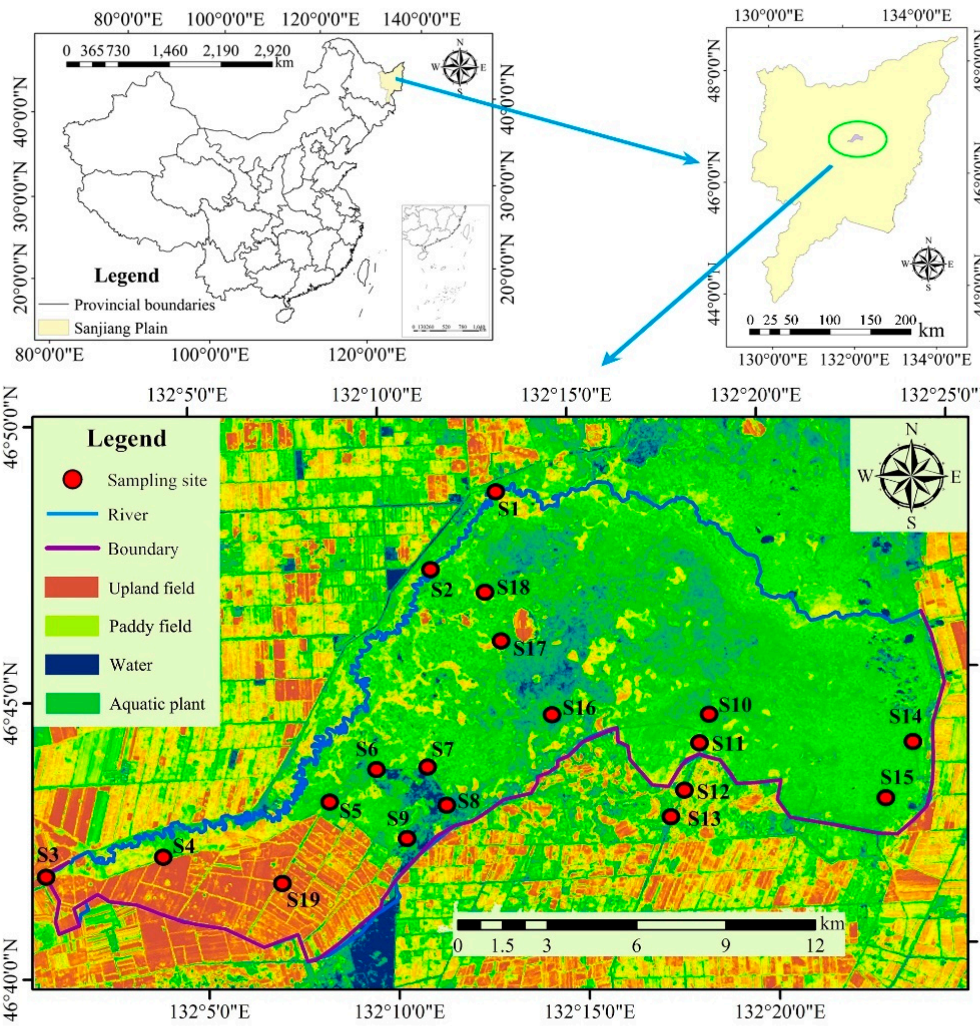

Figure 1. Locations of sampling sites in Qixing River wetland.

2.4. Pollution Assessment Methods

2.4.1. Comprehensive Water Pollution Index

The comprehensive water pollution index (*WPI*) can be used to assess the magnitude of comprehensive pollution attributed to multiple heavy metals in the aquatic environment. It can also highlight the most important indicator among the target metals by evaluating the relative contribution of a single pollutant to the overall pollution. The comprehensive water pollution index (*WPI*) is calculated as:

$$WPI = \frac{1}{n}\sum_{i=1}^{n} P_i = \frac{1}{n}\sum_{i=1}^{n}\frac{C_i}{S_i} \tag{1}$$

where P_i is the pollution index for single metal; C_i is the measured concentration of the *i*th heavy metal (μg·L^{-1}); and S_i is the corresponding limit value for the situation/purpose of interest (μg·L^{-1}). Here we chose the I standard value of the National Environmental Quality Standards for surface water (GB 3838-2002), proposed by the state environmental protection administration of China as the values of S_i. Classifications of *WPI* and P_i are presented in Table S1 in Supplementary Information.

2.4.2. Estimation of Heavy Metal Inventories

To estimate heavy metal inventories in snow cover, the following inventory (I) can be calculated [9,26]:

$$I = \frac{C_i d A \rho_s}{\rho_w k} \tag{2}$$

where I is the heavy metal inventory (μg·m^{-2}); C_i is identical to that mentioned above; d is the thickness of the snow cover (m); ρ_s is the snow cover density (kg·m^{-3}), and ρ_w is the corresponding density of the snowmelt water (1 kg·L^{-1}); A is the unit area (m^2); and k is a unit conversion factor (m^2). The depth and density of the snow cover in the sampling sites from the Qixing River wetland are presented in Table S2.

2.4.3. Exposure Risk Assessment Model

Risk modeling provides a quantifiable and nondestructive means for assessing the potential harm to wetland birds from heavy metals exposure, whilst avoiding direct human contact with potentially endangered and rare species [10,21]. The promulgation of toxicological benchmarks for wildlife by Sample et al. [26] provides a basis for developing an exposure risk assessment model [23]. Generally, the wildlife might be exposed to the pollutants in environmental mediums via food and water ingestion. Given the focus of the present study on cold winter conditions, we considered all water drinking to be via snow consumption. The exposure risk of heavy metals to winter resident birds from heavy metals in environmental media can be calculated as follows [21,27,28]:

$$I_{df} = 0.648BW^{0.651} \tag{3}$$

where I_{df} is the food consumption rate (g·day^{-1}, dry weight), which can be estimated by allometric regression models [29]. BW is the average body weight of the target winter resident birds (g).

$$I_w = 59BW^{0.67} \tag{4}$$

where I_w is water consumption rate (replaced by snow) (mL·day^{-1}), which can be estimated by allometric regression models [30]. Here the unit of BW is kg.

The oral exposure dose of heavy metal can be calculated by Equation (5) [10,28]:

$$E_i = (I_w \times C_i)/BW \tag{5}$$

where E_i is the oral exposure dose of the ith heavy metal (mg·kg^{-1} day^{-1}); I_w is the absorptivity of the snowmelt (mL·d^{-1}); and C_i is the concentration of the ith heavy metal in the snowmelt (mg·L^{-1}). Here the unit of BW is kg.

Potential exposure risk to species can be derived by comparing the heavy metal daily intake dose to the corresponding tolerable daily intake (TDI). The tolerable daily intake (TDI) is calculated by Equation (6) [31]:

$$TDI_i = \frac{(LOAEL_i \times NOAEL_i)^{0.5}}{UF} \tag{6}$$

where TDI_i is the tolerable daily intake of the ith heavy metal (mg kg^{-1} day^{-1}); $LOAEL_i$ is the lowest observed adverse effect level of ith heavy metal (mg·kg^{-1} day^{-1}), and $NOAEL_i$ is no observed adverse effect level of the ith heavy metal (mg·kg^{-1} day^{-1}) [27]; and UF is uncertainty factor, which was used to account for the uncertainty of the assessment model differences in sensitivity among species. The selection value of UF may not be less than 10 for extrapolating to a long-term exposure content without an effect. In the present study, UF = 10 was chosen to evaluate a conservative TDI [31]. The values of $LOAEL$, $NOAEL$, and TDI for each heavy metal are presented in Table S3.

Following a similar methodological approach as the U.S. Environmental Protection Agency (US EPA) human health risk assessment model, a hazard quotient (*HQ*) was employed to estimate each heavy metal exposure risk to the winter resident birds [22].

$$HQ_i = \frac{E_i}{TDI_i} \tag{7}$$

where HQ_i is the hazard quotient of the *i*th heavy metal, the classification of *HQ* is presented in Table S4.

2.5. Statistical Analysis

The sampling sites and heavy metal inventories map were plotted with ArcGIS 10.2 (Environmental Systems Research Institute, Redlands, CA, USA), and statistical analysis of the data was performed by IBM SPSS 20.0 (International Business Machines Corporation, Armonk, NY, USA). Before the statistical work, the K-S test was employed for a normality test. Then, the one-sample and independent-samples *t*-tests were used to determine the intergroup difference for the normality data, while nonparametric tests were employed for non-normal distribution data. Pearson correlation analysis was then applied to analyze the strength of association among the detected data, which was considered to be significant if $p < 0.05$.

3. Results and Discussion

3.1. Levels

Concentrations of Cu, Ni, Cr, Cd, Pb, and Zn were detectable at all sampling sites (Figure 2), and the average levels followed the decreasing trend of Zn (103.46 ± 39.16) > Pb (13.08 ± 4.99) > Cr (11.97 ± 2.82) > Ni (9.55 ± 4.96) > Cu (6.19 ± 1.79) > Cd (0.55 ± 0.25) $\mu g \cdot L^{-1}$; of which the concentration of Zn was the highest in the range of 53.81~203.29 $\mu g \cdot L^{-1}$, and the concentration of Cd was the lowest in the range of 0.09~0.92 $\mu g \cdot L^{-1}$. Compared to our previous study on heavy metals in Qixing River wetland, the concentrations of heavy metals in snow cover were significantly higher than those in water ($p < 0.05$). It should be noted that the concentration of Pb in snow cover was higher than that of other heavy metals, except Zn, which was different from the relative ranking of Pb in water and sediment from the Qixing River wetland [10]. This difference may highlight the relative importance of snow cover, as the results from Peng et al. [32] and Xia et al. [33] have showed that approximately 92.5% of Pb in cultivated soils in China was from atmospheric deposition; thus, the concentration of pollutants in snow cover can not only directly reflect the pollution level of the regional atmospheric environment, but also build an environmental monitoring network system through the snow medium [9,34].

The measured concentrations of heavy metals were compared with those in other studies (Table 1). To some degree, the results of the comparison could at least reflect the pollution levels of heavy metals in snow cover, although the sampling time, methods, and analytical processes among these studies are different. The concentrations of heavy metals in snow cover were significantly higher than those in the snow mountain in Qinghai-Tibet Plateau [35], except for Zn ($p < 0.01$), indicating that the ambient atmospheric environment of the Qixing River wetland was affected by human activities, to a certain extent. On the other hand, the concentrations of Cu and Cr in snow cover of Qixing River wetland were significantly lower than those in Harbin ($p < 0.01$), which reflects the higher density of urbanization. This result was accordant with our previous study, where concentrations of Cu and Cr were shown to gradually decrease with increasing distance from the city [9]. A similar phenomenon has also been described in the studies on heavy metals in fresh snow in Northeast China [5,36]. This shows that the primary fractionation and urban fractionation of heavy metals that exist in the atmosphere are also reflected in fresh snow. The content of Pb in snow cover in Qixing River wetland was not significantly different from that in suburban areas of Harbin, but it was clearly lower than that in rural areas. Some studies have indicated that the main source of Pb in atmospheric particles was related to the burning of crop straw, which are usually used for heating in rural areas of northern China, leading to the increase in Pb content in snow cover [37,38]. Therefore, the fractionation effect on heavy metals may not be a simple function of distance, but the local emission sources will be an important factor [39,40]. It should be noted that the content of Zn in snow cover of Qixing River wetland was significantly higher than that in Urumqi [8], and even higher than that in the urban area of Harbin (Table 1), indicating that the concentration of Zn in snow cover of Qixing River wetland is mainly affected by the local emission sources. In addition, the content of Cr in snow cover of Qixing River wetland was significantly higher than that in the fresh snow of Urumqi, but lower than that in the snow cover ($p < 0.01$). Snow cover, as an environmental medium in frequent contact with the atmosphere, is likely to receive secondary pollution from the surrounding environment. Compared with fresh snow, there are certain differences in the composition, source, and distribution of pollutants. The research on heavy metals in fresh snow and snow cover in Urumqi City also confirmed that measured snow cover can effectively reflect the regional atmospheric environment quality.

3.2. Pollution Assessment

Pollutants accumulating in snow cover will be released and migrate to the atmosphere, water, and soil during the snowmelt period, resulting in adverse effects on environmental quality [9,34]. To further analyze the influence of heavy metals in the snow cover of Qixing River wetland on the surface water environment, they were compared with the surface water environmental quality standard (GB 3838-2002), and the results are presented in Table 2. The concentrations of Cu, Ni, and Cd do not exceed the Class I value of the environmental quality standard for surface water, while the contents of Cr and Zn are between the Class I and Class II standard value, indicating that the atmospheric environment of Qixing River wetland was slightly polluted by the above-mentioned heavy metals. However, the content of Pb in the snow exceeded the class II value of the environmental quality standard for surface water. Whether the elevated value of Pb will affect the growth and reproduction of aquatic animals and plants in the wetland needs further study.

Table 1. Comparison of heavy metals in snow (μg L^{-1}).

Location	Snow Type	Cu	Cr	Zn	Pb	Ni	Cd	References
Qixing River wetland, China	Snow cover	6.19	11.97	103.46	13.08	9.55	0.55	In this study
Qinghai-Tibetan Plateau	Snow cover	BDL-1.23	BDL-0.30	BDL-179.62	BDL-1.48	BDL-1.29	NA	[35]
Harbin (urban area), China	Snow cover	56.86	41.14	62.00	42.74	9.60	1.50	[9]
Harbin (suburban area), China	Snow cover	36.50	27.66	35.13	16.55	8.10	0.79	
Harbin (rural area), China	Snow cover	20.33	18.00	51.67	23.67	4.13	0.57	
Northeastern China (distant from the city)	Fresh snow	0.8–16.7	0.6–1.6	14–110	1.3–10.5	1.3–3.9	0.04–0.57	[5]
Northeastern China (near the city)	Fresh snow	161.39	51.12	88.59	1428.4	51.73	0.66	[36]
Urumqi, China	Fresh snow	16.38	9.88	61.73	53.24	36.89	3.28	[8]
	Snow cover	17.81	17.71	76.64	67.63	60.44	9.33	

Note: BDL means below the detection limit; NA means no value.

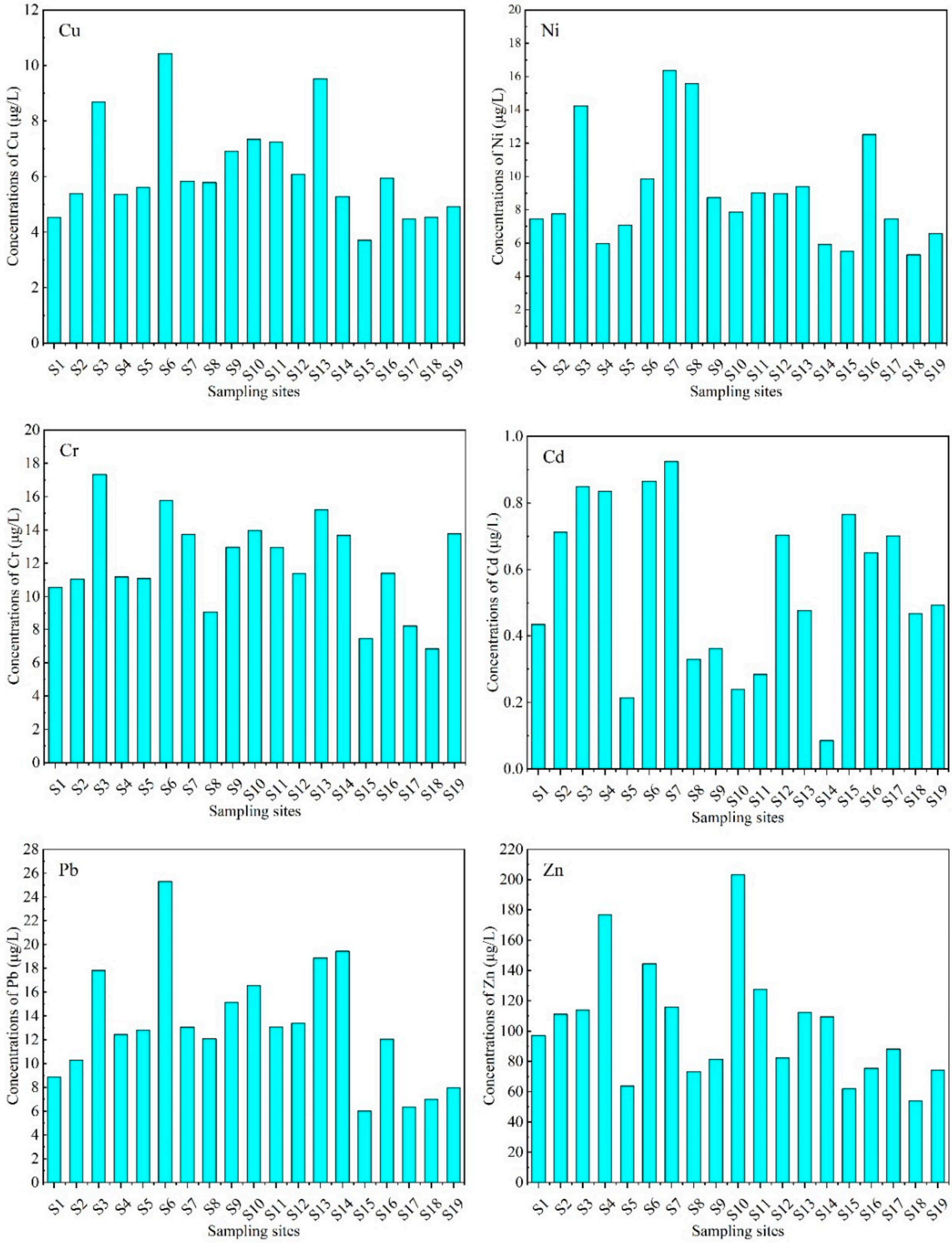

Figure 2. Concentrations of heavy metals in snow cover of Qixing River wetland.

Table 2. Comparison between concentrations of heavy metals in snow cover from Qixing River wetland and environmental quality standards for surface water (μg L^{-1}).

Heavy Metals	National Environmental Quality Standards for Surface Water					Mean ± SD
	Class I	Class II	Class III	Class IV	Class V	
Cu	10	1000	1000	1000	1000	6.19 ± 1.79
Cr	10	50	50	50	100	11.97 ± 2.82
Zn	50	1000	1000	2000	2000	103.46 ± 39.16
Pb	10	10	50	50	100	13.08 ± 4.99
Ni	20	20	20	20	20	9.55 ± 4.96
Cd	1	5	5	5	10	0.55 ± 0.25

The calculated value of the comprehensive pollution index (*WPI*) for snow cover ranged from 0.61 to 1.57 (Figure 3), of which 61% of sampling sites were in "clean" status, and the rest were in "low pollution" levels (as defined in Table S1), suggesting that snow cover in Qixing River wetland was slightly polluted by heavy metals. However, the *WPI* value of snow cover was significantly higher than that in water ($p < 0.05$) [10], which indicated that atmospheric deposition was the major input source of heavy metals in Qixing River wetland. The contributions of the target metals to the *WPI* were: Zn (33.28%) > Pb (21.03%) > Cr (19.26) > Cu (9.95) > Cd (8.80%) > Ni (7.68%) (Figure S1). Compared to water [10], the contribution of Pb to *WPI* in snow cover was 1.2 times higher, which confirmed again that the atmospheric deposition was the main source of Pb in Qixing River wetland. In fact, the input of Pb in cultivated soils has been verified [32].

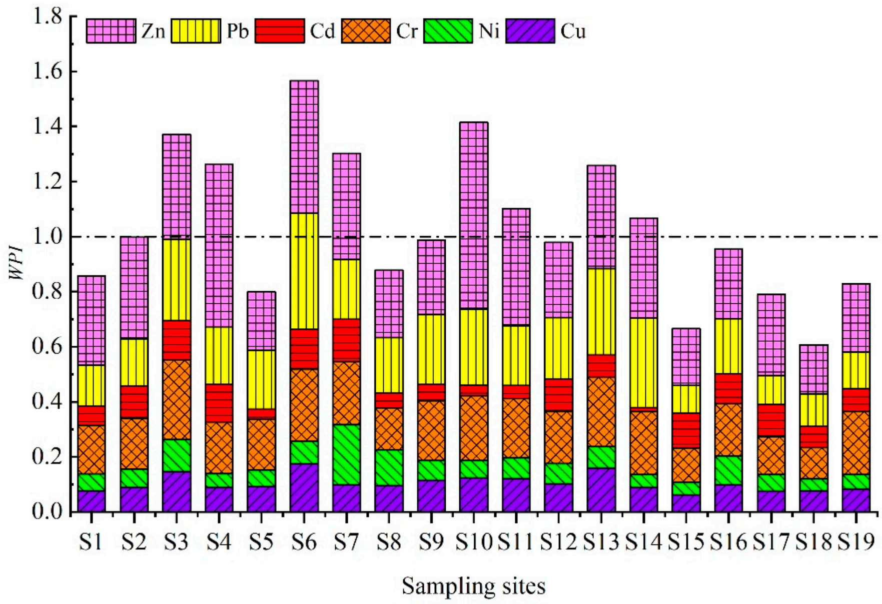

Figure 3. The comprehensive water pollution index of snow cover at each sampling site.

The single-factor pollution index showed that the value of Zn (P_i = 2.07) reached the level of "moderate pollution", and the sampling sites S4 (P_i = 3.54) and S10 (P_i = 4.07) were at the "high pollution" level (Figure 4). Although Zn is an essential trace element for plant growth, its high pollution level should be paid more attention. In addition, Cr and Pb in more than 70% of sampling sites were at the "low pollution" level, except Pb at S6, which was at the level of "moderate pollution". There was a significant correlation among Zn, Cr, and Pb in snow cover (Table S5), indicating that they had similar pollution sources. The single-factor pollution indexes of the other three heavy metal elements were less than one, which indicated that the atmospheric environment of the Qixing River wetland was not greatly affected by Cu, Ni, and Cd.

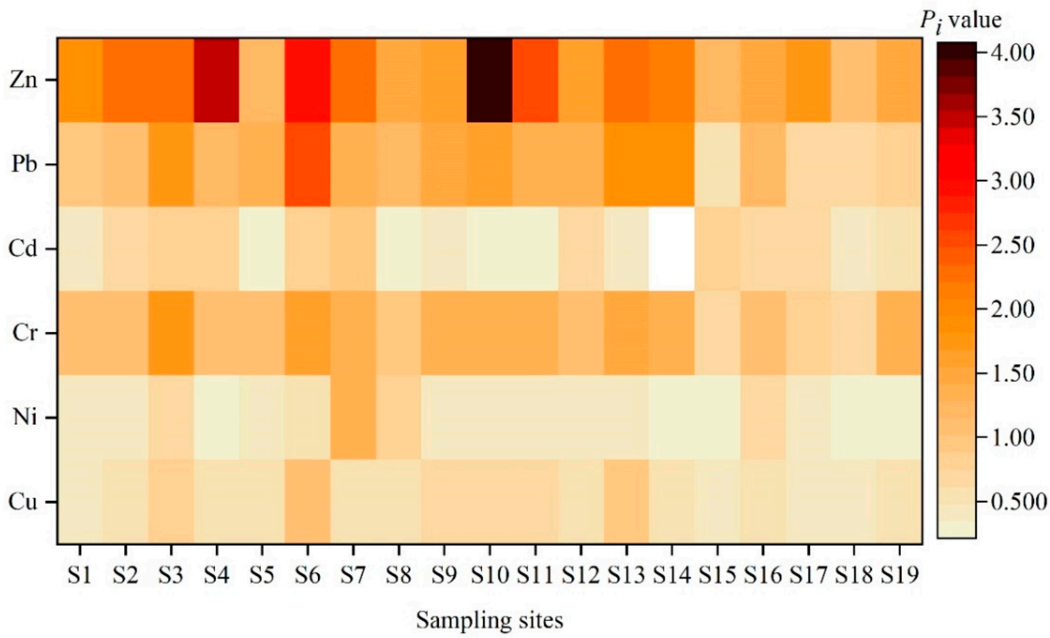

Figure 4. Heat map of Cu, Cr, Pb, Ni, Cd, and Zn in snow cover by single-element pollution index (P_i, Equation (1)).

3.3. Residue Inventory

In general, snow not only participates in the process of the regional water cycle, but also may directly affect the quality of the ecological environment [8]. Thus, the estimation of residual pollutants in snow cover is necessary because it can reflect the input of pollution at a local or regional scale. The residues of heavy metals in snow cover of the Qixing River wetland were evaluated by using Equation (2), and the order was: Zn (2313.57 $\pm$ 1194.67) > Pb (275.35 $\pm$ 111.91) > Cr (266.56 $\pm$ 109.02) > Ni (216.69 $\pm$ 139.24) > Cu (134.41 $\pm$ 52.68) > Cd (13.91 $\pm$ 10.45) $\mu g \cdot m^{-2}$. The coefficients of variation of heavy metal residues were 0.52 (Zn), 0.41 (Pb), 0.41 (Cr), 0.64 (Ni), 0.39 (Cu), and 0.75 (Cd), which were significantly higher than the heavy metal contents in snow cover ($p < 0.05$), as the heavy metal residues were not only affected by pollution sources, but also related to the depth and density of the snow cover. Heavy metal residues in snow cover were significantly correlated with snow depth (Table S6), which is usually related to solar radiation, latent heat, convective energy, and other factors [9], and is also affected by vegetation coverage (density). For example, the air resistance afforded by denser vegetation coverage reduces lateral transportation of snow [41]. This observation was evident in our sampling sites, with those with significant vegetation density (S15–S18) in the wetland buffer zone having significantly greater snow depth than the more exposed sampling sites ($p < 0.05$, Table S2), which also resulted in significantly higher heavy metal residues than other areas ($p < 0.05$, Figure 5).

Due to the long-term land reclamation and associated competition for water, the wetland water supply has been diminishing, a situation that is exacerbated by climate change [42]. As the snowfall amount in Sanjiang Plain is about 40–80 mm, the effective use of snowmelt water has the potential to improve the diminishing wetland water supplies [13]. However, the potential risk of pollutants in snow cover also needs to be considered. According to the depth and density of snow cover at each sampling site of Qixing River wetland (Table S2), it is estimated that snowfall can provide 4.73 $\pm$ 0.45 million m^3 of water quantity inside the wetland. However, the input of Cu, Cr, Ni, Pb, Cd, and Zn would also increase by 26.88 $\pm$ 10.54 kg, 53.31 $\pm$ 21.80 kg, 43.34 $\pm$ 27.85 kg, 55.07 $\pm$ 22.38 kg, 2.78 $\pm$ 09 kg, and 462.71 $\pm$ 238.93 kg, respectively. The contents of Cr, Pb, and Zn in snow samples were significantly correlated (Table S5), indicating that they have similar sources. Zn and Pb have been shown to be dominant in the emission of heavy metals from domestic coal combustion [43]. The concentrations of Cr, Cu, Pb, and Zn particles in snow cover were well correlated (Table S5). The results revealed that large dust, containing Pb and Zn, are produced with the development of coal mining because the Qixing River wetland is located in the downstream of large coal-mines. Therefore, the sources of Cr, Pb, and Zn in the snow cover of Qixing River wetland were probably related to the heating by coal combustion and the mining of coal in winter. However, there was no significant correlation between the content of Cd and the particles in snow cover (Table S5), which indicated that Cd in snow cover may exist mainly in a dissolved state. Bohdálková and co-workers also found that approximately 94% of Cd exists in the dissolved state, and thus it is inferred that the Cd might come from cross-border transport from surrounding areas, through the influence of industrial and traffic emissions [44].

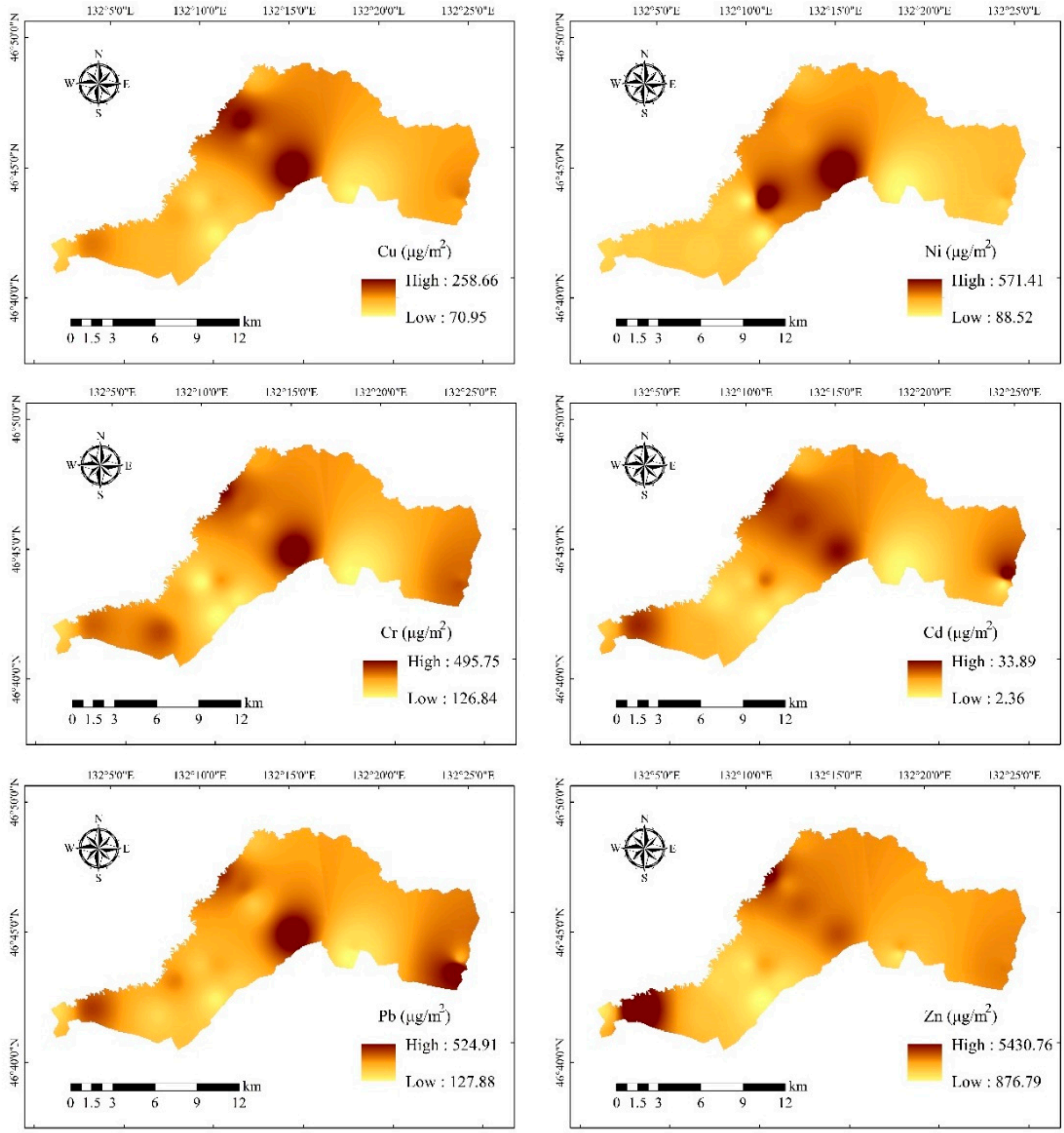

Figure 5. Spatial distributions of Cu, Ni, Cr, Cd, Pb, and Zn residues in snow cover from Qixing River wetland.

3.4. Heavy Metal Exposure Risk to Winter Resident Birds

Qixing River wetland is located in a cold region, northeast China, and the water freezes from the surface downwards and even forms a "frozen bottom" in winter. The snow inside the wetland becomes the main source of drinking water for the winter resident birds, thus two representative winter resident birds, the ring-necked pheasant (*Phasianus colchicus*) and short-eared owl (*Asio flammeus*), were selected as the target species for exposure risk assessment. A body weight of 1464 g and 887 g was chosen for the male and female ring-necked pheasant, and 289 g and 318 g for the male and female short-eared owl, respectively, derived from the wildlife resources investigation results of Qixing River wetland by Tian et al. [45]. Exposure doses of Cu, Ni, Cr, Cd, Pb, and Zn per unit body weight to these two resident birds (calculated using Equation (5)) are presented in Figure S2. Selected toxicity parameters (*NOAEL* and *LOAEL*) and calculated tolerable daily intake doses (*TDI*; Equation (6)) are shown in Table S3. The exposure doses of all the heavy metals involved in the present study were below the corresponding *TDI*, indicating no deleterious effect on the population. The corresponding *HQ* values of heavy metal exposure to ring-necked pheasant and short-eared owl are presented in Figure 6, with the risk (defined as exposure dose > *TDI*) following trend of Cr > Pb > Zn > Cu > Cd > Ni. Exposure risk from snow ingestion in winter can therefore be considered insignificant, given the evidence that *HQ* values were three to five orders of magnitude lower than the risk threshold (*HQ* = 1). The species with a lower body weight will be estimated to have a higher exposure risk, as defined by Equations 3–5. In this case, the short-eared owl had a significantly elevated risk compared to the ring-necked pheasant ($p < 0.05$). This result was generally consistent with that of the Eurasian spoonbills (*Platalea leucorodia*) from the Qixing River wetland in different developmental stages in our previous study [10]. The species with a lighter body weight tends to have higher consumption rates per unit body weight, due to their relatively higher metabolism and growth rates [21], thus the estimated risk was elevated for the lighter bird relative to the larger ones.

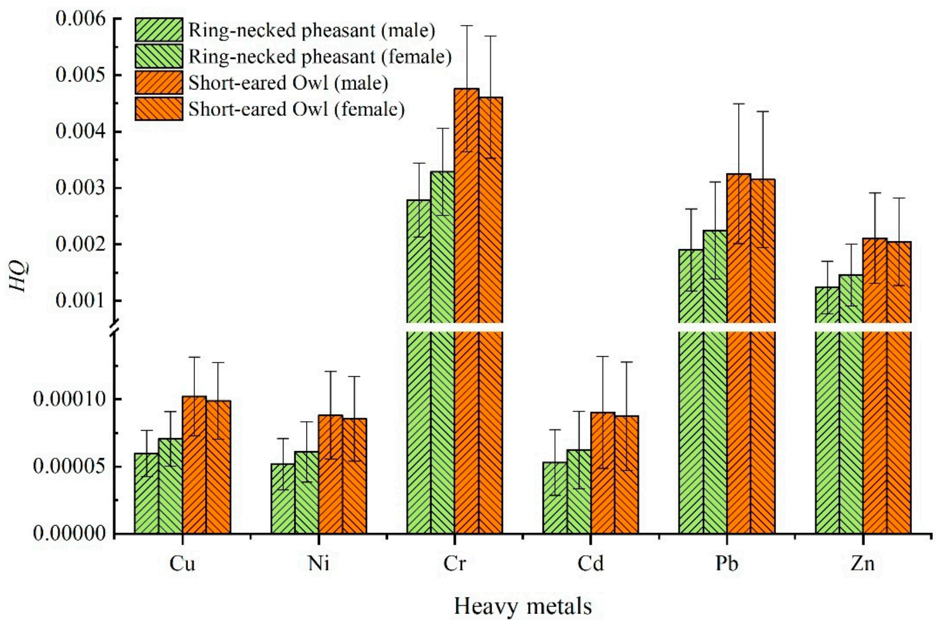

Figure 6. Average hazard quotient for ring-necked pheasant and short-eared owl.

4. Conclusions

The contamination levels and inventories of heavy metals in snow cover were investigated and estimated from Qixing River wetland, a typical natural freshwater wetland in the cold region in northeast China. The heavy metal exposure risk to winter resident birds via snow consumption was quantitatively analyzed. The comprehensive water pollution index (*WPI*) indicated a lower magnitude of contamination in Qixing River wetland ("clean" or "low pollution"), of which Zn, Pb, and Cr made the greatest contributions. Significant correlations among Zn, Pb, Cr, and Cu were observed, demonstrating that the snow cover in Qixing River wetland could be receiving pollution from similar sources, or at least spatially similar sources, such as biomass combustion, as well as the using, production, and transportation of coal resources. The exposure risk assessment indicated there was no deleterious effect on winter resident birds via snow ingestion, but monitoring efforts should be focused on species with a lighter body weight, due to their relatively higher consumption rates of pollutants per unit body weight. Additionally, despite the potential of snowmelt water to compensate for declining water resources, caution should be exercised given the calculated inputs of Cu, Cr, Ni, Pb, Cd, and Zn estimated by this study. However, there is potential to use snow cover as an essential tool for monitoring the pollution characteristics and environmental behavior of heavy metals, as well as for supporting its subsequent management and mitigation in cold regions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/w13162161/s1, Table S1: Classifications of heavy metal pollution degree, Table S2: The depth and density of snow cover in the Qixing River wetland, Table S3: Selected toxicity parameters and calculated *TDIs* in the study (mg·kg^{-1} day^{-1}), Table S4: Classifications of heavy metal exposure risk, Table S5: Pearson correlation matrix for heavy metals and particle contents in snow cover of the Qixing River wetland, Table S6: Pearson correlation matrix for heavy metals residues and snow cover depth in the Qixing River wetland, Figure S1: Contributions of the target heavy metals to the water quality index (*WPI*) in snow cover from the Qixing River wetland, Figure S2: Exposure doses of heavy metals to Eurasian Spoonbills in the Qixing River wetland.

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