Risk Assessment of Heavy Metals In Suspended Particulate Matter In A Typical Urban River of Northern China

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Abstract

Suspended particulate matter (SPM) is a major contamination source in urban rivers. In this work, the Beiyun River, northern China, was used as a case study to determine the characteristics of heavy metal spatial distribution in SPM, and to evaluate the potential ecological risks and identify heavy metal sources. The concentration of seven heavy metals and associated indicators (TC, TN, TP, and OM) were measured at 12 sites and analyzed by Pearson correlation (PC) and principal component analyses (PCA). The average concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb were 70.72, 27.88, 31.35, 115.70, 27.77, 0.23, and 29.62 mg/kg, respectively, and significant spatial differences occurred between some elements. Igeo values indicated the ranking of heavy metal pollution in SPM as As > Cd > Zn > Cu > Pb > Cr > Ni. The $E_i^r$ analysis demonstrated that the order of potential ecological risk of the seven metals was Cd > As > Cu > Pb > Ni > Cr > Zn. RI (potential ecological risk index) results confirmed high potential ecological risk in objective area. Of the measured heavy metals, Cd represented the highest pollution risk. Significant positive correlations were found between TC, TN, TP, and Cu. Three element pairs, Zn-Cd, Cr-Cu, and Cr-Ni, had strong correlations. Zn, Cu, and Ni were mainly introduced by human activities, and Cr was mainly from natural processes. This information on the concentration, risk, and sources of SPM in Beiyun River provides an important reference for reducing heavy metal pollution in SPM of a typical river in the Haihe River Basin.

Highlights

· Cd had a much higher pollution level than other metals.
· The Beiyun River system had a strong potential ecological risk.
· Human activities are the main source of suspended particulate matter in urban rivers.

Introduction

With the rapid development of urbanization, agriculture, and industrialization, urban rivers receive wastewater from residential areas, agricultural cultivation, and industrial production (Yahaya et al. 2019). Numerous sluice dams along rivers cause surface sediment to move into overlying water, introducing new contaminants as suspended particulate matter (SPM). SPM is a major polluter of aquatic environments, and is the main factor in pollutant migration and transformation in rivers (Li et al. 2019). In stationary water, SPM is a component in ecosystem construction and aquatic zone construction (Vercruysse et al. 2017; Wang et al. 2018). Furthermore, SPM plays an important role in controlling the reaction rate of water and sediments, the food chain cycle, and the metabolic rate of biota (Al-Saadi et al. 2002; Turner and Millward 2002). SPM mainly comes from agricultural activities and weathered soil and rock from surface erosion or riverbed erosion, while a small proportion comes from organic matter (OM) and minerals formed in rivers. SPM can combine with pollutants and deposits on the bottom of the river, and has an average particle size of 0.45–63 μm (Lamba et al. 2015; Zheng et al. 2008). In river systems, the physical
and chemical properties of SPM are extremely complex (Droppo et al. 1997). Many processes such as motion, sedimentation, suspension, and resuspension cause the absorption of pollutants on the surface of SPM, which are then transported downstream, significantly reducing water quality. The amount (concentration), quality (surface activity), and composition of SPM are the most critical factors affecting the migration of chemicals in water (Horowitz 2008). Of these, SPM composition affects the absorption of contaminants from environment, and the behavior of pollutants. This is a complex response, with changes in turbidity of water and sediment composition, the photosynthesis of plankton, and changes in the flux of sediment downstream (Paterson and Black 1999).

SPM is generally composed of inorganic mineral particles, organic components, biological communities, and pores. Inorganic mineral particles are particles made by clay and silt or chemical precipitates in sediments, and are the main components of SPM (Droppo 2001; Qafoku et al. 2004). Organic components mostly come from extracellular polymers and cell debris from microbial activities. Biological communities affect pollutant transport and transformation through physical and chemical processes. Pores are gaps or channels for exchanges and reactions between SPM and outer boundary materials, with water retained or passed through them (Qafoku et al. 2004). An increase in pore volume will amplify the surface area of SPM and reduce its density. Organic components in SPM act as the organic coating layer of inorganic particles, which dominate the interaction between SPM and the surrounding aquatic environment (Baoqing et al. 2011). SPM is a crucial carrier of contaminants; the surface of SPM is covered by a bio-organic membrane composed of microorganisms and plankton, on which carbon and hydroxyl functional groups adsorb heavy metals (Marcell and Michael 1997). The functional groups then participate in the migration and transformation of pollutants and particles in river systems. SPM could release OM and relevant metals into the overlying water (He et al. 2016). In addition, SPM is an important adsorbent of harmful heavy metals that have properties of toxicity, persistence, and aggregation (Arnason and Fletcher 2003; Laurent et al. 2009; Yang et al. 2020; Yao et al. 2016). Heavy metals carried by SPM, such as Cd and Pb, not only cannot be eliminated by biodegradation, but can even enter the food chain through phytoplankton, which increases the toxicity to aquatic animals and threatens human health (Yang et al. 2015). The negative effects of SPM on the environmental behavior of heavy metals in aquatic ecosystems should not be overlooked (Hu et al. 2019), and the relationship with toxicity in humans can be determined by researching SPM and the relevant contaminants (Li et al. 2019). Therefore, it is of great significance to study the characteristics of SPM heavy metals and relevant contaminants to improve the migration and transformation of heavy metals in river ecosystems, and to manage sediment-related pollution issues.

In Beijing-Tianjin-Hebei (BTH) regions, growing population density and the rapid development of industry and agriculture has led to the accumulation of heavy metals in rivers, which increases the risk of ecosystem damage, and endangers human health. Numerous studies (Birch et al. 2001; Gu et al. 2012; Niu et al. 2019; Zahra et al. 2014; Zhang et al. 2017a) have reviewed the distribution and transformation of heavy metals in sediments, but the effect of SPM on pollutant transport, adsorption, and the link between them requires further investigation. SPM are one of the critical internal sources of aquatic environments, and comprehensive understanding of SPM is still missing. Currently, pollutant emission is
the main source of urban rivers, which are characterized by numerous inputs, various pollutants, diverse dams along the way, and active movement of SPM, Beiyun River is a typical river that demonstrates all of the above characteristics. In this study, the north section of Beijing-Hangzhou Grand Canal-Beiyun River is used as an example, to demonstrate the accumulation of heavy metals on SPM in rapidly-developing cities. The concentration and pollution characteristics of seven metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) and associated indicators (TC, TN, TP, and OM) of SPM were measured and evaluated in the main stream of Beiyun River. The main objectives of this study are: (1) to measure the concentration and distribution of heavy metals in SPM in selected rivers; (2) to evaluate the pollution level and ecological risk caused by heavy metals; (3) to determine the relationship between heavy metal pollution, environmental factors, and human activities; (4) to analyze the characteristics of SPM pollution in Beiyun River, and the relationship between SPM and sediments.

Materials And Methods

2.1 Study area

The Beiyun River is a major tributary of the Haihe River System (Chen et al. 2015b), which is involved in flood discharge, sewage discharge, and landscape construction, and has irreplaceable study value. Located between the Chaobai and Yongding Rivers, the river is the northern section of the Beijing-Hangzhou Grand Canal. It originates in Changping District, Beijing, and flows through Beijing, Tianjin, and Hebei, finally joining the Haihe River at Dahongqiao in Tianjin (Shan et al. 2011). Tianjin is the main river basin, with many tributaries including the Ziya River, Duliujian River, and Machangjian River. The upper reaches of the region are mainly farmland. As it is an ecological agricultural demonstration zone, Beijing has developed planting and soil fertilizer technology. However, the serious agricultural pollution in Beiyun River still cannot be ignored. In the lower reaches, there are many energy-related and petroleum and metallurgy industries. The area of Beijing-Tianjin-Hebei (BTH) is densely inhabited; therefore, the large quantity of sewage is another factor contributing to the river pollution. The Beiyun River has a number of dams, with a slow flow velocity, and numerous sediment and pollutants deposited in the riverbed. It is one of the main sewage rivers in Beijing City, thus the water quality of this river is below class V (Xiaowei et al. 2009). Approximately 4.4 t of phosphorus is discharged into the river in sewage from Beijing every day, which flows into the Haihe River Basin (Pernet-Coudrier et al. 2012). Industrial wastewater, domestic sewage, agricultural run-off, and other harmful substances in the Beijing urban area and surrounding counties are directly or indirectly discharged into the river without treatment. Due to the effects of long-term erosion, the river incorporates the silt, which is dominated by SPM. The silt accumulates and settles on both sides of the river, resulting in heavy metal pollution in the accumulated SPM. Therefore, SPM has become one of the main sources of pollution in the Beiyun River (Bao et al. 2016).

2.2 Sample collection

In this study, almost all sampling points were distributed along the flow direction of Beiyun River. When selecting the sampling points, it was necessary to avoid static water, backwater, and sewage outlets, to
ensure the points were in the straight river section, with smooth flow and a wide river channel. Twelve samples were collected from the main stream of the Beiyun River in April 2019. The detailed locations of these sampling sites are shown in Fig. 1. To avoid disturbance, a column was used to collect the sediment samples from a depth of 2 cm, and then samples were left to stand for several minutes. SPM combines with pollutants in the aquatic environment, and is deposited on the top layer of sediment; thus the surface layer was selected as the source of SPM. The upper sample can be separated when there is no floating suspended particle in the overlying water. During the sample collection, three surface sediment sub-samples (approximately 5 cm from the top) were collected from each site to obtain representative samples (the distance of three parallel samples was not less than 500 m). Samples (~1 kg weight) from the same site were immediately mixed and homogenized and put into No.7 self-sealed bags and transported back to the laboratory.

The collected samples were spread out in the laboratory with enamel plate and then dried at 25°C. Particles of <63 µm were obtained by sieving through a 250 mesh, after removing rotten branches, leaves, and plant stems. These particles have high geochemical activity and the closest properties to SPM and can, therefore, be utilized as the SPM sample (Pan et al. 2013; Zheng et al. 2008). Finally, a quarter of the sample was removed and stored in sealed plastic bags at room temperature (25°C) until analysis.

### 2.3 Sample analysis

In this study, the contents of heavy metals, OM, TN, TC, and TP in SPM were analyzed. HCl, HNO₃, and HF were mixed, to a final volume of 8 ml (9:3:4, v/v/v), then 0.1 g SPM sample was digested with a MARS Xpress instrument (CEM, Matthews, USA). After the acid was heated to 150°C for at least 2 h, 1–2 drops of HClO₄ were added to the digestion tube (Tang et al. 2010). The extracted liquid was diluted to 50 ml with ultrapure water, then filtered with a 0.45 µm membrane, and stored at 4°C for analysis. Contents of Cr, Ni, Cu, Zn, As, Cd, and Pb were determined by inductively coupled plasma mass spectrometry (ICP-MS, Diane 7700x, USA). All plastic and glass tubes were cleaned by soaking in 10% HNO₃ for at least 48 hours, then washing and rinsing them with ultrapure water. Ultrapure water and Guaranteed Reagent were used during the whole experiment. Blank samples, standard samples, and parallel samples were used in each experiment, and the content of all heavy metals in each sample was the average value of three replicates. The recoveries of all determination results were 85.71–113.67%, and the relative standard deviation between the measured value and the standard value was within 10%.

To measure the OM, the SPM sample was dried in an oven at 105°C for 12 h, and the mass M1 was recorded. Then, samples were heated in a muffle furnace at 550°C for 5 h, and the mass M2 was recorded. The OM content was determined by loss on ignition after heating. To determine TC and TN, 20–30 mg SPM sample was weighed and put into the element analyzer (Vario El III; Elementair, Germany) and the content was analyzed directly. TP was determined by the SMT method (Ruban et al. 2001). Briefly, 0.2 g SPM sample was ashed at 450°C for 3 h, and 20 ml 3.5 mol/L HCl was added into the ash residue. Then, the extract solution above was obtained by shaking for 16 h in a thermostat. After extraction, the
solid-liquid phase was separated by centrifugation for 15 min, and then the content of TP in the extracts was measured by molybdate colorimetry.

2.4 Evaluation method

Due to differences in soil structure, composition, and development, the indices of pollution level, toxicity, and potential risk of soil could not be assessed from the numerical value directly. Therefore, it was necessary to evaluate them by referring to the geochemical background values of corresponding elements in the study area. There are three coefficients that can be used to comprehensively study the degree of heavy metal pollution, including the geoaccumulation index (Igeo) (Muller 1969), the potential ecological risk index (Hakanson 1980), and the average possible effect concentration entropy (MacDonald et al. 2000). These coefficients are widely used because of their universality and accuracy.

Igeo is used to evaluate the pollution level of heavy metals. It can be calculated by following formula:

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right)$$

C_n is the mass of heavy metals (mg/kg) and B_n refers to the geochemical background value contents about different metals (mg/kg). The pollution grade and degree of heavy metals calculated by the Igeo are shown in Table 2.

| Index                     | Cr    | Ni   | Cu    | Zn    | As    | Cd   | Pb    |
|---------------------------|-------|------|-------|-------|-------|------|-------|
| Concentration range       | 62.93–82.54 | 21.22–39.85 | 17.97–58.16 | 51.18–258.34 | 11.16–64.56 | 0.13–0.39 | 22.81–49.37 |
| Samples’ mean value       | 70.72 | 27.88 | 31.35 | 115.70 | 27.77 | 0.23 | 29.62 |
| Chinese mean value        | 76.58 | 36.69 | 90.98 | 194.09 | 14.00 | 2.97 | 90.47 |
| Global mean value         | 51.51 | 127.59 | 191.11 | 388.69 | 9.06 | 0.94 | 137.30 |
| SD                        | 7.35  | 6.21 | 15.07 | 69.78 | 27.22 | 0.13 | 12.56 |
| CV (%)                    | 10.39 | 22.29 | 48.08 | 60.31 | 98.00 | 58.57 | 42.40 |

Note: CV = SD/mean value×100%, is a coefficient that represents variation of heavy metals, 10% < CV < 100% indicates moderate variability.

The potential ecological risk index method is used to evaluate the ecological risk of heavy metals. It can be calculated by following formula:

$$RI_r = \sum T_i \times f_i = \sum [T_i \times (C_i/B_i)]$$
where $E^j_r$ is the potential ecological risk index of corresponding heavy metal, which reflects the toxicity level of the heavy metal to a certain extent; $T_i$ and $f_i$ are the toxicity response parameters and pollution coefficient of the pollutant, respectively; and $C_i/B_i$ is the ratio of the measured content (mg/kg) and background value (mg/kg).

MacDonald (2000) proposed consistent sediment quality criteria (SQGs), threshold effect concentration (TEC), and possible effect concentration (PEC). If the concentration of heavy metal is higher than PEC, heavy metals will have adverse effects on benthos, while negative effects will not occur when the concentrations are lower than TEC. Since SPM pollution comes from residential pollution, as well as agriculture and industry, the pollution from several heavy metals should be taken into account. The mean probable effect concentration quotient ($Q_{m-PEC}$) is used to evaluate the combined pollution caused by the collective action of several heavy metals:

$$Q_{m-PEC} = \sum\frac{C_n}{PEC_n}$$

where $C_n$ is the measured value of heavy metal elements.

### 2.5 Data analysis

Multivariate statistical methods, including principal component analysis (PCA) and correlation analysis (CA), were used to analyze the sources of heavy metal pollution (Buttafuoco et al. 2010; Guagliardi et al. 2012, 2013). Data were analyzed using SPSS20.0 and R3.5.0, and Origin 8.0 software was used for drawing.

### Results And Discussion

To further explore pollution characteristics, based on the measured concentrations, and to compare with other river basins with similar conditions, this research focused on the relationship between the concentration of absorbed heavy metals and the structure of SPM. The Igeo, RI, and $Q_{m-PEC}$ indices were used to determine the degree of pollution, and the pollution sources were inferred from the CA and PCA. The effects from the river system and external factors to SPM were analyzed, and then the effective limit strategies were provided.

### 3.1 SPM heavy metal concentrations

The concentrations of heavy metals are shown in Fig. 2, and corresponding background values are shown in Table 2. Concentrations in SPM from Beiyun River were compared with other typical urban rivers. The average Cr concentration from 12 SPM samples was 70.72 mg/kg, which is higher than concentrations from Luan River (107.17 mg/kg) and lower than that of Bortala (51.55 mg/kg) (Wang et al. 2014; Zhang et al. 2016b). The average concentration of Ni was 27.88 mg/kg, lower than that of Huai River (32.79 mg/kg) and Haihe Basin (41.38 mg/kg), and the same as that of Yellow River sediment (29.4
mg/kg) (Kong et al. 2018; Li et al. 2014; Wang et al. 2015b). The average concentration of Cu was 31.55 mg/kg, which is similar to Bortala Basin (30.09 mg/kg), but higher than that of Luan River (14.92 mg/kg) (Wang et al. 2014; Zhang et al. 2016b). The average concentration of Zn was 115.70 mg/kg, which is lower than that of Xiaobai River sediment (0.16 mg/kg), and higher than that of Yellow River (81.8 mg/kg) (Li et al. 2014). The average concentration of As was 27.77 mg/kg, higher than that of Bortala (9.67 mg/kg) and Haihe Basin (7.56 mg/kg) (Kong et al. 2018; Zhang et al. 2016b). The average concentration of Cd was 0.23 mg/kg, lower than that of Xiaobai River (0.37 mg/kg), and similar to that of Haihe Basin (0.2 mg/kg) (Kong et al. 2018; Li et al. 2014). The average Pb concentration was 29.62 mg/kg, slightly higher than that of Luan River (24.13 mg/kg), but much lower than that of Huai River (53.43 mg/kg) (Wang et al. 2015b; Wang et al. 2014). Of the seven tested metals, Cu, Zn, As, Cd, and Pb were 1.44, 1.48, 2.81, 2.51, and 1.38 times greater than background values, respectively. In terms of concentration distribution, the lower reaches had significantly higher concentrations, which increased with the river flow direction. In summary, the concentrations of Ni, Cu, Zn, and Pb in SPM in this study area were all below the average values of rivers and lakes in China mentioned above. However, the concentrations of As and Cd are much higher than concentrations of these metals in rivers and lakes of China. The concentration of Cr is between the average value from China and rivers across the globe (Fu et al. 2014). Compared with previous studies, the concentrations of Cr, Ni, Cd, Zn, and other elements in the sediments of Beiyun River are slightly different from those of SPM, indicating that SPM is the main component of sediments, especially the top sediment layer (Baoqing et al. 2011; Walling 2005; Weixiao et al. 2013). The results of this study are consistent with those of Atkinson et al. (2007) and Bracken (2010).

### 3.2 Heavy metal concentration and SPM properties

SPM is an essential source of heavy metals in rivers. Cr, Ni, Cu, Zn, Cd, and Pb concentrations in SPM of Beiyun River show an increasing trend, from upstream to downstream, accumulating and migrating downstream, continuously induced by flow (Feng et al. 2017). SPM microstructure changes due to resuspension: more pollutants such as heavy metals and phosphorus, are adsorbed on the surface of SPM and transported downstream, resulting in the accumulation of heavy metals in rivers (Stephens et al. 2001). Heavy metals and SPM can adsorb together as they are affected by van der Waals force. The double-electron-layer structure and large surface area of SPM means that more heavy metals can be adsorbed on the surface (Jin et al. 2018). In addition, the chemical bonds of SPM means they can irreversibly adsorb heavy metals and other pollutants (Chanudet and Filella 2007). Metal oxides in SPM can combine with heavy metals spontaneously, such as Fe and Mn oxides combining with Pb on the inorganic layer, and Mn oxides combining with Zn on the organic layer (Zhang et al. 2019). The shear stress of overlying water means that heavy metals on particles are more stable if they are absorbed by a chemical process, and will exist in the river for a long time.

### 3.3 Risk assessment

Pollution level, risk level and toxicity are all derived from Table 1. In terms of sample distribution, that sites B1, B3, B4, B7, B12, B13, and B15 have moderate-strong pollution, while B5, B6, B8, B9, and B14 have moderate pollution. In terms of element type, the SPM of Beiyun River is moderately polluted with Ni,
moderate-strongly polluted with Cr, Cu, Zn, and Pb, and strongly polluted with As and Cd (Fig. 3b). The comprehensive potential ecological hazard index (RI) and mean potential effective concentration quotient ($Q_{m-PEC}$) of Beiyun River are shown in Fig. 3c and d. From the perspective of different heavy metal elements, the mean $E_r^i$ values decreased in the order Cd > As > Cu > Pb > Ni > Cr > Zn. Among these, Cd pollution is the most serious, and belongs to extremely high risk level. The contribution of Cd to the RI of the study area was up to 60.03%, demonstrating that Cd is the most critical ecological risk factor in SPM of Beiyun River. Moreover, agricultural non-point source pollution has a significant impact on the regional pollution, and Cd should be listed in the priority pollutants list in this study area (Ke et al. 2017). Additionally, Cd has been listed as one of the priority limit pollutants by the United States Environmental Protection Agency (US EPA) (Chen et al. 2015a). In terms of spatial distribution, the concentration of Cr and Zn in the Beijing section was higher, which is consistent with the results of Huo (Huo et al. 2011). In the Tianjin section, the RI value of B6 ~ B9 was low, belonging to slight risk level, which indicates that desilting in Tianjin has played a positive role in controlling heavy metals in recent years. B12, B13, and B15 belong to moderate risk levels, because shipping and petrochemical industry near the estuary seriously affects the quality of river SPM. There is a significant difference between the middle and lower reaches, in terms of Cu, Zn, and Cd. The high RI value of the three metals above is due to frequent human activities downstream (Guo et al. 2010). Among all metals, RI is > 600, demonstrating that the whole river is at high risk level, mainly because it is a sewage river. There are 341 sewage outlets along the river, including 42 large-scale outlets, with 209.28 million tons of industrial and residential sewage discharged into the river every year (Zhang et al. 2015). Figure 3d shows that the $Q_{m-PEC}$ of Cr, Ni, and As is > 0.5, indicating the toxicity of SPM. In addition to SPM properties, many factors such as water flow velocity, physical and chemical properties of sediments, salinity, pH, and dissolved oxygen (DO), all affect the release of metals, resulting in differences in heavy metal concentrations in the basin (Atkinson et al. 2007; Huang et al. 2012).
Table 1
The index categories and evaluation criteria of heavy metals

| Geoaccumulation index ($I_{geo}$) | Potential ecological risk index (E$RI$) | Mean probable effect concentration quotient ($Q_{m-PEC}$) |
|----------------------------------|----------------------------------------|---------------------------------------------------------|
| Grade | Level | E  | RI | Risk level | $Q_{m-PEC}$ | Sediment toxicity |
| ≤ 0 | None | ≤ 40 | ≤ 150 | slight | <0.5 | basically non-toxic |
| 0–1 | None–moderate | 40–80 | 150–300 | moderate | >0.5 | Toxicity |
| 1–2 | Almost moderate | 80–160 | 300–600 | Considerable | |
| 2–3 | Moderate | 160–320 | >600 | High | |
| 3–4 | Moderate–strong | >320 | | Extremely high | |
| 4–5 | Strong | | | | |
| >5 | Seriously strong | | | | |

### 3.4 Source analysis of SPM heavy metals

SPM adsorbed heavy metals in rivers, and combined with sediment by flocculation and sedimentation. The source and migration of these elements can be inferred from correlation among heavy metals (Wang et al. 2012). The correlation coefficient matrix of Cr, Ni, Cu, Zn, As, Cd, Pb, OM, TC, TN, and TP in SPM was obtained by CA (Fig. 4). PCA showed that chemical properties of SPM samples were significantly correlated with heavy metal concentrations. Significant positive correlations were found between TC, TN, TP, and Cu concentrations. Moreover, OM was significantly positively correlated with Ni, Cu, and Zn, indicating that TC, TN, TP, and OM have common sources, and are affected by chemical parameters combined with heavy metals (Zhang et al. 2017b). Among these seven heavy metals, Zn has extremely strong correlation with Cu and Pb. In addition, some metals have strong correlation with each other, such as Zn and Cd, Cr and Cu, and Cr and Ni. This indicates similar pathways and mechanisms of SPM absorbing and transforming these heavy metals from the environment. Cr and Cu in this area are mainly from the electroplating industry (John et al. 2016). The Beiyun River basin is also a typical intensive agricultural area. Zn and Cd are added to chemical fertilizers, pesticides, and feed additives, then accumulate in farmland, livestock, and poultry manure (like cattle dung), and are finally discharged into the river through sewage (Franco-Uria et al. 2009; Wang et al. 2015a). There was a negative correlation between As and Cu, As and Zn, and Cd and Pb, which suggests that As was different from other heavy metals in enrichment and transformation pathways.
In the PCA, the cumulative variance contribution rate of three principal components was 88.12%, which reflected total pollution. The first principal component (PC1) with high variance was Zn, Cu, Pb, and Ni, which explain 57.77% of the variance. The second principal component (PC2) was As, Cr, and Ni, that explains 21.56% of total variance. For the third principal component (PC3), the special element explained 8.79% of the variance. Cr had a higher load in PC2 and PC3, and the second one is higher than the third one. However, Ni had a higher load in PC1 and PC2, and the second one is higher than the first one, which indicates that Cr and Ni may have different sources and are controlled by two different factors. Combined with the results of background value and PCA, PC1 was strongly correlated with Zn, Cu, Pb, and Ni, which suggested that PC1 was made by anthropogenic activities. Anthropogenic sources are generally considered the main reason for the higher environmental concentrations of heavy metals, compared with background concentrations (Franco-Uria et al. 2009; Zhang et al. 2016a). Most Zn and Ni comes from urban industrial sewage (such as metallurgy and electroplating industry), agricultural drainage, and landfill in the BTH region. Incineration also affects Zn and Ni concentrations (Huo et al. 2011). In Northern China, nitrogen fertilizer, phosphate fertilizer, and coal combustion may release Zn, Cu, and Pb, which are important sources of heavy metal pollution in the Beiyun River Basin (Zhang et al. 2016a). PC2 has strong correlation with As, Cr, and Ni, which can be inferred as the joint action of anthropogenic and natural sources. PC3 has strong correlation with Cr and can be inferred as natural sources, mainly from mineral weathering and atmospheric precipitation (Wang et al. 2015a). CA, Zn, Cu, and Ni have, not only strong correlation, but also positive correlation, and these three elements had a higher load in PC1, with concentrations exceeding the background value, implying that human activities have significant influence.

3.5 SPM impacting factors from the environment

With increasing heavy metal contamination, understanding of aquatic elements cycle needs to be explored so a management system to control pollution can be determined (Ma et al. 2019). Serious pollution is the interaction of multiple factors, and is affected by the interactions among land use, rainfall patterns, soil moisture, and hydrology (Atkinson et al. 2007). It is simultaneously affected by numerous internal factors such as overlying water, sediment, aquatic organisms, and human activities in the river system (Fig. 5). The metabolites of organisms enter aquatic ecosystems, and substances in water are transformed into SPM by adsorption, sedimentation, and flocculation processes. The nutrients in SPM are transformed by organisms to maintain their physiological needs via biological assimilation. Organisms continuously metabolize and excrete metabolites, which then enter into SPM again. After subsiding, SPM enters into sediments, and the sediment suspended in organism after disturbed. This is a reciprocating cycle (Turner and Millward 2002). Pollutants in surface water and sediment affect the concentration of SPM through numerous processes, such as sedimentation, migration, and transformation; thus, soil and heavy metal pollution caused by human activities can accumulate in SPM (Feng et al. 2017). The pollutants in SPM affect environment by different processes like suspension, erosion and deposition (Marttila et al. 2013). Thus, SPM plays a crucial role in the interaction between overlying water and sediment. More importantly, there are intermittent and periodic interplay dynamic turnover processes between SPM and sediment (Ciszewski and Grygar 2016; Glaser et al. 2020;
Schwientek et al. 2017). The exchange and transformation of materials in several different media is accompanied by sudden changes in salinity, pH, redox conditions, and dissolved OM concentration, which changes chemical and particulate reactivity (Turner and Millward 2002). Some uncontrollable factors, such as wind-induced resuspension also affect the concentrations and properties of SPM (Shinohara and Isobe 2010). Furthermore, due to the influence of river hydraulic movement, downstream topography, and industrial structure, scour included, the concentrations of heavy metals at the beginning of the river are far lower than in the Bohai Sea estuary. Scour and hydraulic movement lead to sediment deposition, but excessive sediment deposition may cause more serious accumulation of SPM, even heavy metals in downstream areas (Turner et al. 2002). In addition, human intervention along rivers, such as dam construction, soil and water conservation technology, will affect the sediment supply and transport of the river (Chen et al. 2016). There are many gates and dams along Beiyun River, such as Yangwa gate, Yulinzhuang gate, Beiguan gate, etc. A large amount of industrial wastewater and domestic sewage emerged upstream due to the construction of gates and dams. The interception of these gate and dam causes a reduction in the velocity, runoff, and the self-purification capacity of rivers. The increased water pollution further accelerates the accumulation of heavy metals. When the dam is suddenly opened, sewage will discharge at the same time, and the pollutants carried by sewage will induce water pollution events, which is also one of the main factors for heavy metal pollution in the Beiyun River.

Industry, agriculture, and traffic emissions are all significant factors of SPM concentration (Atafar et al. 2010; Harrison et al. 2003; Park and Dam 2010) (Fig. 6). During industrial production, heavy metal concentrations, such as As, Cd, Cu, and Zn increase in the surrounding areas (Park and Dam 2010). Polluted gas is directly released into the air, then forms a dust, combining with other particles (Route  in Fig. 6). Part of the dust deposits on the road, field, etc., while some enters the river by atmospheric precipitation or rainfall (Route  in Fig. 6), then participate in the SPM cycle in the fluvial ecosystem. Apart from the industrial waste, polluted sewage from industrial production is discharged directly into the river through the outlets, which aggravates river SPM pollution (Route  in Fig. 6). In addition, vehicle exhaust emissions is also a fundamental source for the accumulation of SPM. The way of automobile exhaust emission (Route  in Fig. 6) is similar to that of industrial gas (Route  in Fig. 6). High-concentration heavy metals, Cu, Zn, and Pb, are linked to urban transportation (Harrison et al. 2003): traffic-related exhaust emissions account for 34.47% of heavy metals in road dust of Beijing (Men et al. 2018). In agriculture, the use of pesticides and chemical fertilizers increases the accumulation of heavy metals in the soil (Atafar et al. 2010). Irrigation causes pesticide and fertilizer residues to form runoff, which discharges into rivers and aggravates river SPM pollution (Route  in Fig. 6). Moreover, flooding alters SPM transport and overbank deposition (Benedetti 2003). Therefore, the air (dust), farmland, and river form a collective cycle, which affects the concentration of SPM. In this study, heavy metal content is high after the Beiyun River confluence with Ziya River. In terms of spatial distribution, the pollution in the downstream area is higher than that of the upper and middle reaches. Gross domestic product (GDP) is a critical indicator to interpret the impact of human production activities on the environment. Specifically, agricultural and industrial activities represent the primary and secondary industries, respectively. The Beiyun River is located in the BTH region, an area in which the economy is rapidly developing and near to
the capital, which is highly sensitive to GDP. GDP is a critical indicator to evaluate the impact of human activities on river pollution (Zhang et al. 2017b). The concentration of Cu and Pb are closely related to agricultural and industrial activities. In SPM from Beiyun River, the pollution level of Cu and Pb is $3 < I_{\text{geo}} < 4$ and $80 < E < 160$, and the potential ecological hazard index takes in strong risk level. Therefore, agricultural and industrial activities have a great impact on heavy metal pollution in Beiyun River.

### 3.6 Pollution characteristics on SPM and control strategies

Rivers are crucial to agriculture, industry, tourism, transportation, and even flood protection; a balanced river ecology is of great significance to development (Li et al. 2020). Efficient measures must be implemented to manage and monitor pollution from SPM. There are many gates and dams along the Beiyun River, which has a discontinuous flow and a dense population. Furthermore, it contains numerous industrial and domestic sewages from nearby regions. The continuous input of pollution leads to relatively high concentration of heavy metals in rivers, and seriously affects the SPM quality (Huo et al. 2011). Dams accumulate pollutants, while increasing the risk of water and sediment pollution events. For example, heavy metal concentrations from Yulinzhuang sluice and Beiguan sluice to lower point B4 increases significantly. Serious pollution of heavy metals in the lower reaches is extremely high, especially for Zn, As, Cd, and Pb. Of these metals, severe pollution of Cd and Pb is closely related to the production of chemical raw materials in the industrial zone downstream. In addition, Cd and Pb exceeded the standard value in the whole river; therefore, they must be listed in prevention and control objects. The concentration of Cr was between the TEC (43.4 mg/kg) and PEC values (111 mg/kg), thus biological toxicity rarely occurred or even did not occur. Zn is one of the most polluted elements, in the 12 research points, three study points are three times of the background value. Zn pollution is from smelting processing, mechanical manufacturing, galvanizing, organic synthesis, and industrial wastewater discharge. The As concentration exceeded the effective threshold value at some points after leaving the Tianjin urban area, which had adverse effects on benthos by physical digestion in the digestive tract. The significant increase of heavy metal concentration in the estuarine zone may be related to the effects of coastal soil texture and seawater intrusion (Shan et al. 2016).

SPM is a typical heavy metal adsorbent, which makes it an effective way to reduce heavy metal pollution by controlling the concentration (Laurent et al. 2009). In view of the excessive heavy metals in SPM of Beiyun River, the management of external pollution should be increased, and the sources of heavy metal pollution must be reduced. Intercepting installations in all drainage outlets could control the pollution from SPM in this area (Jeong et al. 2020). In the upper reaches, the focus should be on reducing soil erosion by cultivating forests that could increase soil and water conservation, strengthening the protection of existing forest species to reduce soil and water loss and wind sand erosion, and preventing the increase of SPM caused by soil erosion along the Beiyun River (Vercruysse et al. 2017). Soil and water conservation can effectively reduce sediment mixing, and sediment quality can be reversed through forests (Turner and Millward 2002). As for river systems, desilting is a direct method to remove heavy metal pollution (Liu et al. 2016). Machines like silt cleaners and dredgers have been widely used, and desilting is an important method for effectively removing internal pollution, avoiding resuspension, and
reducing the threat to ecosystem balance, which can effectively reduce the concentration of heavy metals. In terms of heavy metal limiting, reducing industrial pollution emissions, such as petrochemical and metallurgical industries, in surrounding areas will be an significant strategy.

Conclusion

In this study, seven heavy metals, and four associated indicators in SPM of Beiyun River are reported. Their concentrations, pollution level, potential risk, and relationship with surrounding factors have been studied for the first time. The risk of heavy metal pollution was evaluated by Igeo, EF, and Q_m−PEC indices, and the source was determined by principal component analysis (PCA).

(1) Concentration and distribution of heavy metals in SPM

The average concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb were 70.72, 27.88, 31.35, 115.70, 27.77, 0.23, and 29.62 mg/kg, respectively. Among these metals, the average concentration of As exceeded the background value by 2.81 times. The concentrations of Cu, Zn, and Cd in the upper, middle, and lower reaches of Tianjin were significantly different, most metals in lower reaches reached the maximum value and those in the middle reaches, near the Tianjin urban area were significantly lower. Thus, the prevention and control policy of urban river pollution is highly efficient.

(2) Risk and order of heavy metals in SPM

The Igeo results showed that the order of heavy metal pollution degree in SPM was As > Cd > Zn > Cu > Pb > Cr > Ni. Zn, Cu, Pb, and Cr were in a state of partial severe pollution. The potential ecological hazard index of single factor heavy metals, $E_{r}^{i}$, showed that the rank of potential ecological risk about heavy metals was Cd > As > Cu > Pb > Ni > Cr > Zn. Cd presented a very strong ecological risk and Ni was a medium ecological risk. The RI method showed that the Beiyun River system had a strong potential ecological risk. Among them, the risk of Cd is much higher than that of other metals.

(3) Sources of heavy metals in SPM

The Beiyun River is located in a typical agricultural area. The heavy metal pollution of SPM is mainly affected by chemical fertilizers, pesticides, feed additives, industrial activities, and landfill. Human pollution is the main reason for the higher concentration of Zn, Cu, Pb, and Ni in SPM than background concentration. In river systems, heavy metals accumulate continuously, and severe pollution will eventually harm human health through food chains.

(4) Counter-measures

In theory, the concentration of SPM should be controlled first. The sediment pollution in upper reaches should be reduced by ameliorating soil erosion. The river itself should be regularly dredged to avoid resuspension and reduce contaminants. In addition, industrial emissions should also be lessened. Waste
incineration, metallurgy, electroplating, and coal combustion all produce numerous pollutants. Controlling industrial pollution emissions can indirectly prevent contamination accumulation in the Beiyun River basin.

Declarations

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CRediT authorship contribution statement

LI Wenye: Experimentalize, Writing - original draft preparation. ZHANG Wenqiang: Guidance, Methodology, Data analysis. SHAN Baoqing: Methodology, Validation, Formal analysis, Review. SUN Baoping: Conceptualization, Editing. GUO Xiaoping: Supervision. LI Zhenhan: Methodology, Revision

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Ethical Approval

I certify that this manuscript is original and has not been published and will not be submitted elsewhere for publication while being considered by Environmental Science and Pollution Research. And the study is not split up into several parts to increase the quantity of submissions and submitted to various journals or to one journal over time. No data have been fabricated or manipulated (including images) to support your conclusions. No data, text, or theories by others are presented as if they were our own.

Consent to Participate

The submission has been received explicitly from all co-authors. And authors whose names appear on the submission have contributed sufficiently to the scientific work and therefore share collective responsibility and accountability for the results.
Consent to Publish

The Author confirms that its publication has been approved by all co-authors, if any and its publication has been approved (tacitly or explicitly) by the responsible authorities at the institution where the work is carried out.

Availability of data and materials

Part of the data generated or analyzed during this study are included in this published article. The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

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Figures
Figure 1

The distribution of sampling points in the Beiyun River, China.
Figure 2

Content of heavy metals in suspended particulate matter (SPM) from Beiyun River, China.
Figure 3

Risk assessments for sites in the Beiyun River, China: (a) Igeo of suspended particulate matter (SPM) samples; (b) Igeo of different metals; (c) RI of SPM samples; (d) Qm-PEC of different metals.
Figure 4

Correlation of heavy metal properties with suspended particulate matter (SPM). Note: Blue means positive correlation, while red infers negative correlation, "*" infers significant correlation at 0.05 level (P < 0.05), "**" infers significant correlation (P < 0.001), and ellipse's eccentricity infers correlation intensity.
Figure 5

Relationship between suspended particulate matter (SPM) and associated factors
Figure 6

Relationship between suspended particulate matter (SPM) and the external environment (Different sources of SPM. Route: ❶Industrial gas emissions; ❷Industrial sewage; ❸Automobile exhaust emission; ❹Agricultural runoff; ❺Atmospheric precipitation or rainfall)

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