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Assessing heavy metal pollution of the largest nature reserve in Tianjin City, China

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Abstract Beidagang Wetland (BW) Nature Reserve is centrally situated in Tianjin City, experiencing an extreme industrial development. This study uses index characteristic analysis systems for assessing the individual and combined heavy metal pollution loading in the water during the spring and autumn seasons. By combining the pollution level of single pollutant, a more comprehensive evaluation of water quality in BW was achieved. Water quality was worst during autumn due to high level of Cd and Pb, which indicate the type of anthropogenic activities have a serious effect on heavy metal pollution in BW. In addition, high exchangeable amounts of Cd (>40%) were found in the sediments of BW, indicating Cd pollution has emerged. There is a need for appropriate abatement actions curbing heavy metal loading and improving water quality of the BW Nature Reserve, thereby ensuring a sustainable management of its ecosystem services.

Keywords: Assessment; Water quality; Sediment; Wetland

Along with economic development and population growth, the problem of water pollution has increased (Tang et al. 2022). Most of the pollutants, such as nutrients and heavy metals, discharged into water bodies eventually end up and accumulate in the sediments (Hwang et al. 2019; Fang et al. 2019), making especially wetlands a sink of these pollutants. Subsequently, wetlands may also act as a source of these pollutants, by releasing their pool of pollutants back into the overlying water (Huo et al. 2013), sustaining the level of these contaminants in the water body. The level of contaminants in the sediments is thus a good measure for the current state of the wetland environment.

Development of the Bohai sea economic zone is a major national strategy in order to promote the economy of the hinterland. The aim for the coordinated plan of the Beijing-Tianjin-Hebei region is to achieve perfect urban layout and form. However, along with the rapid economic development in this region, there has been a rapid increase in local industrial activities producing lead-containing batteries, non-metallic minerals, metal surface treatment, chemical raw materials and other chemical products. Their emissions of wastewater to the local environment poses a great threat to the BW ecosystem (Li et al. 2021).

Previous studies have focused on nutrients in Beidagang Wetland (BW), but lack of attention to heavy metals (Perez and Anderson 2009; Garnier et al. 2015). This lack of a knowledge poses a main restriction for achieving sustainable management of the valuable BW (Li et al. 2021). In this study, water quality is assessed based on the levels of seven heavy metals. These parameters were selected for assessment based on their current level of contamination of the BW water environment, as well as their ecological effect. From the sediments, heavy metals were extracted using the three-step Community Bureau of Reference (BCR) sequential extraction procedure. The combined levels of these contaminants were assessed using comprehensive pollution index (Larner et al. 2006; Rauret et al. 1999; Pueyo et al. 2008). Knowledge gained from this study is a prerequisite for selecting optimal abatement and conservation strategies ensuring a sustainable water management and water security.

Materials and Methods

The BW Nature Reserve (Fig.1), covering a total area of 44,240 hectares, was established in 2001 (Li et al. 2021). The wetland area is an important ecological barrier between the industrial area and the new Binhai residential area in the north. BW is divided into eight areas: I.e., S1 - the main Beidagang (BDG_w) Reservoir area, situated in the west; S2 - along the lower reaches of DuliuJian River, including WanMu (WM) fish farming pond; S3 - an additional part of the Beidagang (BDG_e) reservoir area on the east side; S4 - east ShaZiJing (SJZ) Reservoir; S5 - QianQuan (QQ) reservoir furthest to the west; S6 - LiErWan (LEW); S7 - lower part of LiErWan reservoir (LEW_s); and S8 - MaPengKou (MPK) along the coast. The BDG reservoir is the main part of the BW Nature Reserve, centrally located in terms of neighboring the Dagang oilfield to the southeast. It plays a central role in the Dagang entire ecosystems by mediating the filtration of the industrial pollution and by generating a local microclimate.

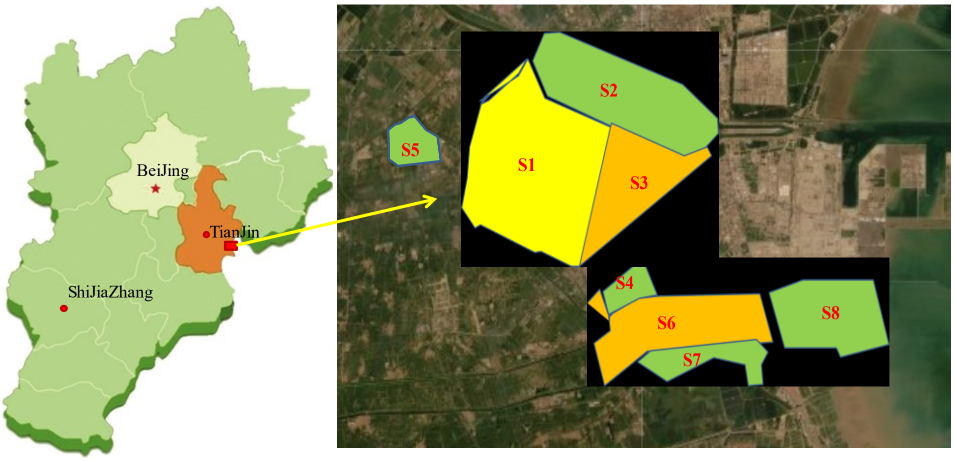

Fig.1 Map of the study area and sampling sites (S1 - BDG$_w$; S2 - WM; S3 - BDG$_e$; S4 - SJZ; S5 - QQ; S6 - LEW; S7 –LEW$_s$; and S8 - MPK).

Water samples were collected in the spring and autumn of 2020 from between 4 and 14 sites in each area (Table S1 – Table S8). Generally, water samples were collected at 20 cm depth in the reservoirs. Where water depths exceeded 2 m, samples from 20 cm were merged with water collected at 1.5 m below water surface. Samples were collected in triplicate doubles in order to ensure accuracy and precision of the data. Half of the 500 mL water sample was filtrated through 0.45μm membrane filters (Covelli and Fontolan 1997).

Sediment samples were collected in 2020 from the same sites as water samples (Table S1 – Table S8), using a bottom sediment grab sampler. Sediment samples were placed in self-sealing bags and immediately transported to the laboratory for cooling. In the laboratory the samples were freeze-dried using FD-1A-50 freeze drier and passed through 100-mesh screens, prior to storage until analysis (Song et al. 2020). All plastic ware was cleaned by soaking in 10% (v/v) HNO_3 for more than 24 h and then rinsed with Milli-Q water (>18 MΩ cm). Heavy metal fraction is crucial to the level of heavy metal pollution (Rauret et al. 1999), so BCR sequential extraction scheme was used as described in S2 to extract fractions of heavy metals in the sediments. All supernatants were filtered through a 0.45μm cellulose filter prior to storage for analysis (Larner et al. 2006; Rauret et al. 1999).

The Ca, Mg, Na and K analyses were carried out using inductively coupled plasma

(ICP)-optical emission spectrometer (OPTIMA 2000 DV, Perkin Elmer Inc., Waltham, MA). The samples were analyzed for Cd, Cr, Cu, Ni, Pb and Zn using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) according to standard methods. pH in sediment samples was conducted as described in standard method. All chemicals were analytical-reagent-grade or equivalent analytical purity. Relative standard deviation (RSD) of parallel samples were lower than 10% implying good data precision. The accuracy of heavy metal data was assured using standard reference material (GBW-07309).

Water quality was assessed using both the single factor pollution index (P_i) and the comprehensive pollution index method (P). Following the Chinese environmental quality standard for surface waters (GB3838, 2002) P_i relate the measured concentration of contaminants to the Chinese governments limit values, while the P is the average P_i values for each area. P values exceeding 1 indicate high level of pollution, values greater than 2 imply serious pollution (Desaules et al. 2012; Cresswell et al. 2012). These methods are described in detail in the supplementary data (S3-S4). The potential ecological risk (PER), posed by the levels of pollutants in the sediments, was determined as described in S5 (Håkanson 1980; Abrahim and Parker 2008; Cappuyns 2008). The PER method provides index values (E^i_r) for each heavy metal (i) based on its concentration relative to background values and a toxicity factor (Guo et al. 2010). The comprehensive PER index (RI) is the sum of the PER indexes. Statistical assessment of the data was performed using SPSS 16.0. Visualization of sample sites distribution was achieved using Google Earth. Origin Pro 8.5 software was used to plot the data.

Results and Discussion

Physical and chemical characteristics of sediments are presented in Table 1. The mean value of pH was 7.4, indicating the sediments were neutral or slightly alkaline. Moreover, the mean values of K, Na, Ca and Mg were 23.3, 14.1, 36.9 and 16.3 g/kg, respectively. Mean P_i values of the studied heavy metals in spring and autumn water from the eight areas (S1-8 in Supporting data) of the BW are shown in Table 2. Mean level of Cd exceeded the Chinese standard limit at all sites during both seasons, while Pb was above the limit in most of the study areas. It was reported that the pollution of heavy metals in river sediments from Haihe River Systems was ubiquitous because of rapid urbanization and agricultural intensification in this region (Tang et al. 2013). The results of this study has indicated heavy metal pollution of the BW, implying that urgent abatement actions are required to curb the pollution from the neighboring industries. In addition, the mean P_i of Cr, Cu, Zn, and Zn meet their standard, implying no pollution by these contaminants in the BW.

Table 1 Physical and chemical properties of sediments from the BW (SD, standard deviation).

	Item	**Range**	**Mean**	**SD**
Sediment	pH	7.0~8.4	7.4	0.32
	K (g/kg)	18.9~34.1	23.3	2.6
	Na (g/kg)	13.3~15.1	14.1	0.40
	Ca (g/kg)	29.3~48.5	36.9	4.1
	Mg (g/kg)	10.7~28.2	16.3	3.4

Table 2 Single factor pollution index (P_i) of overlying water from the BW (Yellow: exceeds the standard; Orange: serious pollution degree).

Spring	Cd	Cr	Cu	Ni	Pb	Zn
BDGw	1.9	<1	<1	<1	<1	<1
LEW	10	<1	<1	<1	4.3	<1
MPK	18	<1	<1	<1	9.0	<1
WM	10	<1	<1	<1	4.3	<1
BDGe	6.3	<1	<1	<1	1.1	<1
SJZ	14	<1	<1	<1	5.7	<1
QQ	9.6	<1	<1	<1	2.4	<1
LEWs	16	<1	<1	<1	6.9	<1
Autumn	Cd	<1	<1	<1	Pb	<1
BDGw	5.0	<1	<1	<1	<1	<1
LEW	15	<1	<1	<1	8.9	<1
MPK	15	<1	<1	<1	11	<1
WM	8.0	<1	<1	<1	4.6	<1
BDGe	5.0	<1	<1	<1	<1	<1
SJZ	11	<1	<1	<1	6.9	<1

QQ	5.0	<1	<1	<1	<1	<1
LEWs	17	<1	<1	<1	10	<1

A main aim when assessing the state of an environment is to identify risk areas that require specific attention. The comprehensive pollution indexes (P) for each of the eight areas of BW are shown in Fig. 2. It is clear from the figure that all sites, with the exception of BDG$_{w}$, have high pollution level in the spring. The conditions are slightly better in the autumn, were BDG$_{w}$, BDG$_{e}$ and QQ fall slightly below the high pollution classification. Areas with P values greater than 2, having serious pollution, are at especially high ecological risk. These were MPK, WM, SJZ, QQ and LEW$_{S}$ in the spring, and LEW, MPK, SJZ and LEW$_{S}$ in the autumn. Overall, the results show that LEW, MPK, SJZ and LEW$_{S}$ are the areas with higher water pollution by heavy metals, though there are concerns regarding pollution levels in different seasons at LEW and QQ.

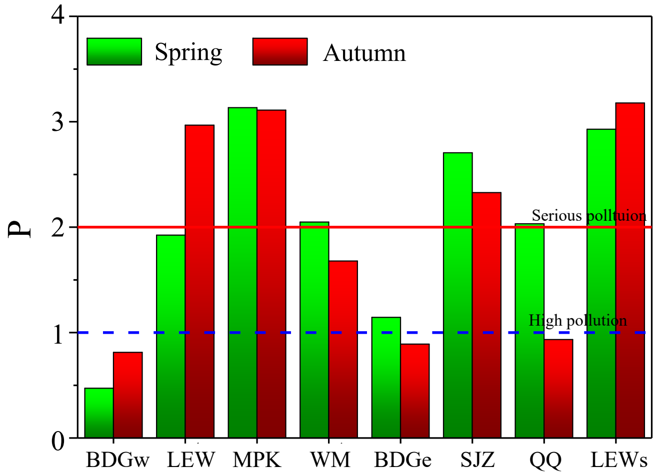

Fig.2 The comprehensive pollution indexes (P) of water from the BW.

In this study, all sediment samples had levels of Cd, Ni and Zn above the Chinese soil environmental quality standard (Fig. 3). For Cu and Pb, the levels were below the limit value in only two samples, respectively. However, in regards to Cr only 20% of the samples were above the limit value. Therefore, Cd, Ni, Pb, Cu and Zn could be regarded as pollutants in BW sediments, and the sediment samples were mainly contaminated by high Cd and Zn contents. Some previous studies indicated that the residual fractions of heavy metals have lithogenic sources but that non-residual fractions are mainly related to anthropogenic inputs (Gao and Chen, 2012; Islam et al., 2015). The relative amounts of exchangeable (B_1), ferro-manganese bond or reducible (B_2), organic matter-bound or oxidisable (B_3), and residual (B_4) heavy metals pools are shown in Fig. 4. Regarding Cd the exchangeable fraction (B_1) was the highest comprising more than 40% of the total Cd content. The mean percentage of organic matter-bound or oxidisable pools (B_3) of Cr, Cu, Ni and Zn accounted for more than 26%. Regarding the ferro-manganese bond or reducible pools (B_2), the Pb comprised more than 65%. These results show that the heavy metals differ widely in the way they are bound to the sediments (Nolan et al. 2005; Filgueiras et al. 2002): The Cd is mainly found in the exchangeable pool (B_1); Pb is mainly found to be adsorbed to iron (B_2); Zn, Ni and Cu are mainly bound to organic matter (B_3); while Cr has the highest residual fraction (B_4). These differences are partly caused by the form in which these heavy metals are emitted to the BW environment, the levels of the contaminants in the environment, and partly governed by their chemical properties, such as the ionic- and covalent index. As shown in Table 2, the high contamination by Cd in the water were likely mainly due to the high exchangeable amounts of Cd in the sediments.

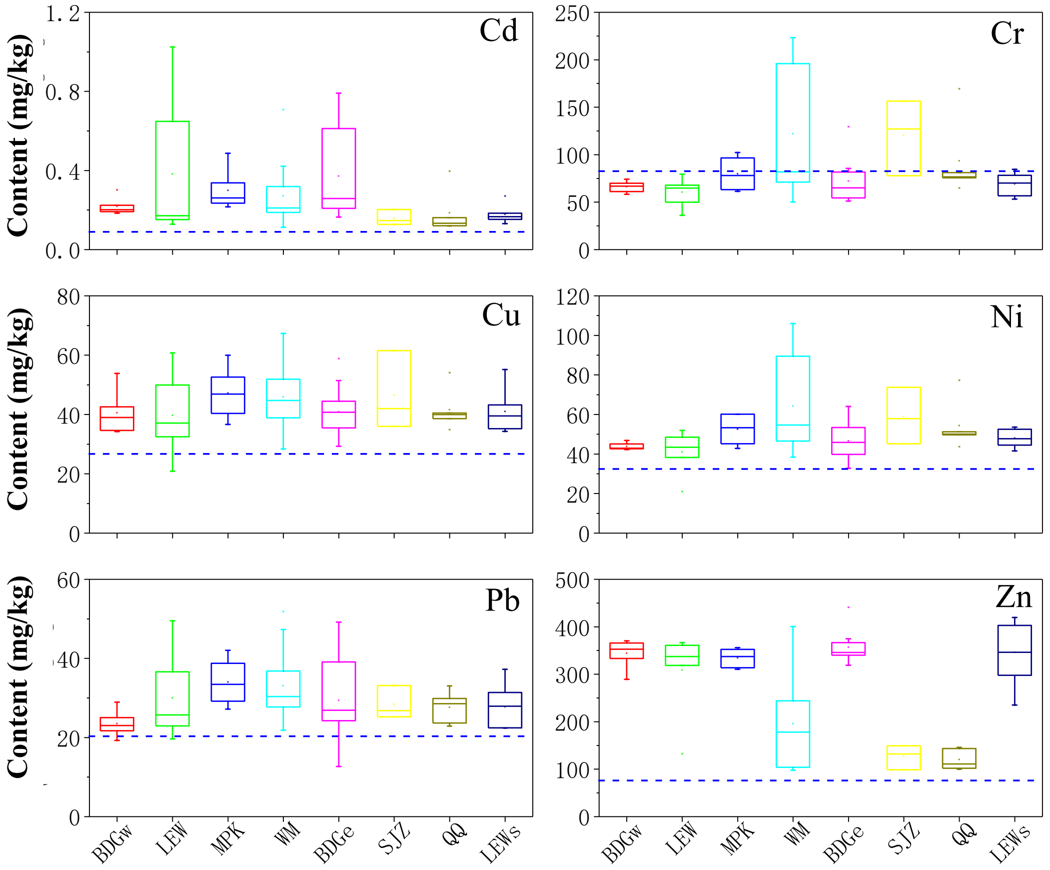

Fig.3 The distribution of heavy metal contents in the sediments from the BW.

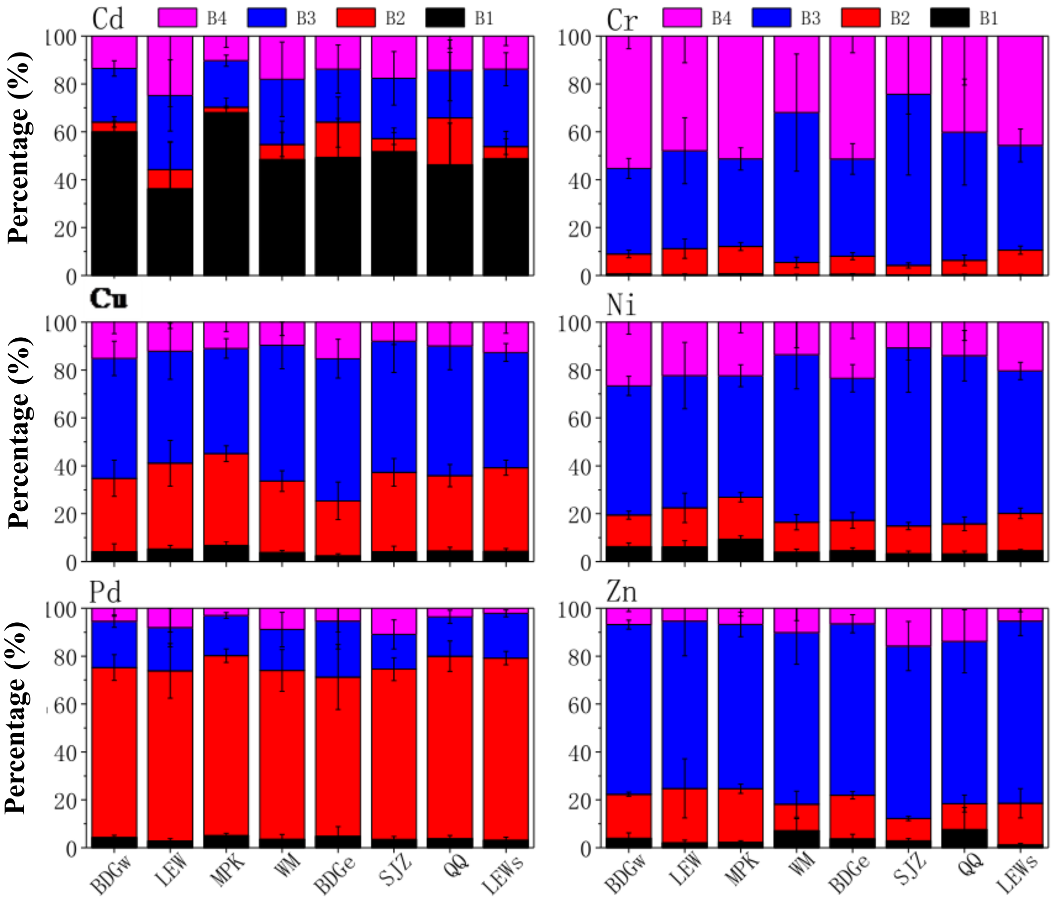

Fig.4 The distribution of fraction percentage of heavy metals in the sediments from the BW.

The toxicities and bioavailabilities of heavy metals are dependent on the chemical speciation and concentrations of the metals (Islam et al., 2015). Especially, the pool of exchangeable (B_1) heavy metals is the fraction of main contemporary ecological concern, as these ions are in rapid equilibrium with the water and thus readily bioavailable. The other fractions are rather stable forms that are not readily available, though may become available over time. The large exchange pool of Cd at LEW and BDG_e are thus of prime ecological concern, while the contamination by Ni, Cr, Pb, Cu, and Zn are expected to have less ecological impact (Jonge MD et al. 2012a, b). The mean PER value for Cd (E^{Cd}_r) at LEW, MPK, WM and BDG_e were higher than 80, implying a considerable degree pollution. Ignoring Cd, the RI adds up to less than 40, implying a low ecological risk in the BW regarding the other heavy metals. Adding Cd (E^{Cd}_r), which had mean values above 50, raised the RI to moderately polluted in LEW and BDG_e (Fig. 5). However, except for at LEW and BDG_e, there is according to the RI low ecological risk in other areas of BW.

Beijing-Tianjin-Hebei is the largest urbanized region in northern China, comprising the economic region surrounding the cities of Beijing, Tianjin, and Hebei, along the coast of the Bohai Sea (Wang et al. 2014). The BW is the largest wetland nature reserve in Tianjin City, which is served as an important habit for the migratory shorebirds in the East Asian-Australasian flyway. It has been listed as an international important wetland because of abundant waterbirds resources. The quality of water and sediments in BW is very important to the migratory shorebirds, especially heavy metal pollution (Chen et al. 2018). Soils in China have been contaminated with heavy metals to varying degrees, and Cd and Hg have been identified as priorities for control due to their higher concentrations in soils and higher public health risks (Zhang et al. 2015). At the same time, these heavy metals also entered in the water environment and posed risk (Pavageau et al. 2002). In the BW, LEW, MPK, SJZ and LEWS were found with high water pollution by Cd and Pb, meanwhile, moderate ecological risk associated with heavy metals was observed in at LEW and BDG$_e$.

In 2021, there are more than 70 species of migratory birds in BW, and the total number is close to 450,000. A bird's choice of habitat during migration must be ecologically safe, and there is plenty of food. If these conditions are not available, they will not settle down and would rather continue to migrate (Xie et al. 2011). The habitat quality of migratory birds in BW has been of particular concern. In addition to polycyclic aromatic hydrocarbons (Wang et al. 2020), heavy metals in the water and sediments of BW also present ecological risks in this study. Toxic metals could pose a serious threat to aquatic ecosystems because of their toxicity, recalcitrant nature and persistence, accumulation and potential to enter the food chain (Nobi et al. 2010, Zhang et al. 2014). Eventually, it will threaten the safety of migratory shorebirds. Therefore, appropriate abatement actions curbing heavy metal loading should be taken to improve water and sediment quality of the BW nature reserve.

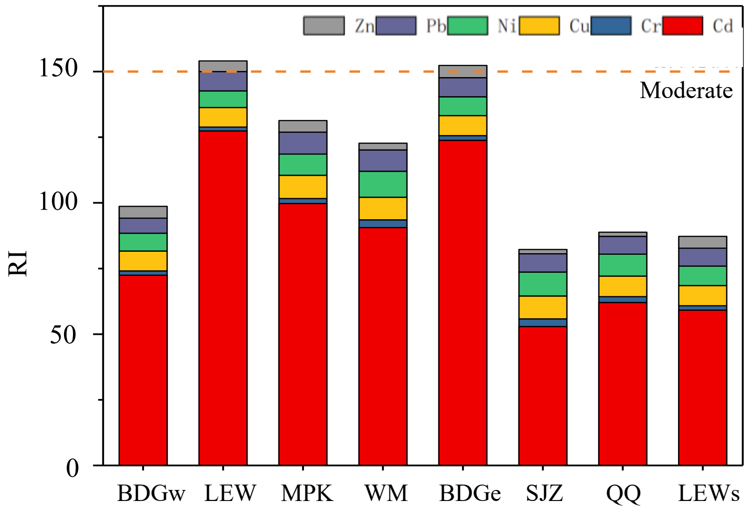

Fig.5 The RI values of heavy metals in sediments from the BW.

This study assessed the levels of heavy metal concentrations in the water, during spring and autumn, and in the sediments of the BW Nature Reserve situated in the heavy industrialized Tianjin City. Levels of Cd in the surface waters, during both spring and autumn, exceeded the Chinese limit values. The levels of Pb in the water posed also a cause for concern. The sediment samples were moderately polluted in regards to their total Cd levels. Moreover, the Cd is mainly found in the exchangeable fraction (B1), which is a fraction that poses contemporary ecological risk. There is therefore an urgent need to determine the source of the Cd pollution and enforce appropriate abatement actions to curb this pollution. Although the sediments generally had a low degree pollution, the water quality was poor. This will eventually cause the environmental conditions of the sediments to also deteriorate. These findings imply that more attention is required regarding the ecological impact of heavy metal pollution in these wetland systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at .

References

Abrahim GMS, Parker RJ (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment* 136:227-238

Chen Y, Song Q, Pan L, Jia M, Li C, Hu B, Wu G (2018) Trace metals, organic carbon and nutrients in the Beidagang Wetland Nature Reserve, northern China. *Plos ONE* 13: e0204812.

Covelli S, Fontolan G (1997) Application of a normalization procedure in determining regional geochemical baselines. *Environmental Geology* 30:34-45

Cresswell T, Smith REW, Nugegoda D, Simpson SL (2013) Challenges with tracing the fate and speciation of mine-derived metals in turbid river systems: implications for bioavailability. *Environmental Science and Pollution Research* 20:7803-7814

Desaules A (2012) Critical evaluation of soil contamination assessment methods for trace metals. *Science of the Total Environment* 426:120-131

Fang T, Yang K, Lu WX, Cui K, Li J, Liang YY, Hou GJ, Zhao XX, Li H (2019) An overview of heavy metal pollution in Chaohu Lake, China: enrichment, distribution, speciation, and associated risk under natural and anthropogenic changes. *Environmental Science and Pollution Research* 26:29585–29596

Filgueiras AV, Lavilla I, Bendicho C (2002) Chemical sequential extraction for metal partitioning in environmental solid samples. *Journal of Environmental Monitoring* 4:823-857

Gao XL, Chen CTA (2012) Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Research* 46:1901-1911

Garnier J-M, Garnier J, Jezequel D, Angeletti B (2015) Using DET and DGT probes (ferrihydrite and titanium dioxide) to investigate arsenic concentrations in soil porewater of an arsenic-contaminated paddy field in Bangladesh. *Science of the Total Environment* 536:306-315

Guo WH, Liu XB, Liu ZG, Li GF (2010) Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. *Procedia Environmental Sciences* 2:729-736

Hakanson L (1980) An Ecological Risk Index for Aquatic Pollution Control – A Sedimentological Approach. *Water Research* 14:975-1001

Huo SL, Xi BD, Yu XJ, Su J, Zan FY, Zhao GC (2013) Application of equilibrium partitioning approach to derive sediment quality criteria for heavy metals in a shallow eutrophic lake, Lake Chaohu, China. *Environmental Earth Sciences* 69:2275-2285

Hwang DW, Kim PJ, Kim SG, Sun CI, Kim TH (2019) Spatial distribution and pollution assessment of metals in intertidal sediments, Korea. *Environmental science and Pollution Research* 26:19379-19338

Islam MS, Ahmed MK, Raknuzzaman M, Habibullah-Al-Mamun M, Islam MK (2015) Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. *Ecological Indicators* 48: 282-291

Larner BL, Seen AJ, Townsend AT (2006) Comparative study of optimised BCR sequential extraction scheme and acid leaching of elements in the certified reference material NIST 2711. *Analytica Chimica Acta* 556:444-449

Li H, Lei P, Li X, Liu HL, Zhou B, Chen C, Xing MN, Li XX, Kong WL (2021). Distribution characteristics and pollution assessment of nitrogen and phosphorus in sediments from Beidagang Wetland in Tianjin City. *Acta Scientiae Circumstantiae*, 41: 4086-4096.

Nobi EP, Dilipan E, Thangaradjou T, Sivakumar K, Kannan L (2010) Geochemical and geo-statistical assessment of heavy metal concentration in the sediments of different coastal ecosystems of Andaman Islands, India. *Estuarine Coastal and Shelf Science* 87:253-264

Jonge MD, Teuchies J, Meire P, Blust R, Bervoets L (2012a) The impact of increased oxygen conditions on metal-contaminated sediments part I: Effects on redox status, sediment geochemistry and metal bioavailability. *Water Research* 46:3387-3397

Jonge MD, Teuchies J, Meire P, Blust R, Bervoets L (2012b) The impact of increased oxygen conditions on metal-contaminated sediments part II: Effects on metal accumulation and toxicity in aquatic invertebrates. *Water Research* 46:2205-2214

Nolan AL, Zhang H, McLaughlin MJ (2005) Prediction of zinc, cadmium, lead, and copper availability to wheat in contaminated soils using chemical speciation, diffusive gradients in thin films, extraction, and isotopic dilution techniques. *Journal of Environmental Quality* 34:496-507

Pavageau MP, Pecheyran C, Krupp EM, Morin A, Donard OFX (2002) Volatile metal species in coal combustion flue gas. *Environmental Science & Technology* 36:1561–1573.

Perez AL, Anderson KA (2009) DGT estimates cadmium accumulation in wheat and potato from phosphate fertilizer applications. *Science of the Total Environment* 407:5096-5103

Pueyo M, Mateu J, Rigol A, Vidal M, Lopez-Sanchez JF, Rauret G (2008) Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environmental Pollution* 152:330-341

Rauret G, Lopez-Sanchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A, Quevauviller Ph (1999) Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring* 1:57-61

Song ZX, Song GF, Tang WZ, Yan DD, Shan BQ (2020) Determining cadmium bioavailability in sediment profiles using diffusive gradients in thin films. *Journal of Environmental Sciences* 91:160-167

Tang WZ, Zhao Y, Wang C, Shan BQ, Cui JG (2013) Heavy metal contamination of overlying waters and bed sediments of Haihe Basin in China. *Ecotoxicology and Environmental Safety* 98:317-323

Tang WZ, Pei YS, Zheng H, Zhao Y, Shu LM, Zhang H (2022) Twenty years of China's water pollution control: Experiences and challenges. *Chemosphere* 295:133875

Wang NL, Wang JM, Li YY, Xing MN, Zhou B, Li X, Li XX, Kong WL, Ding LX, Liu HL (2020) Occurrences, Retention and Risk Assessments of PAHs in Beidagang Wetland in Tianjin, China. *Bulletin of Environmental Contamination and Toxicology* 105:607-612

Wang SJ, Ma HT, Zhao YB (2014) Exploring the relationship between urbanization and the eco-environment-A case study of Beijing-Tianjin-Hebei region. *Ecological Indicators* 45:171-183.

Xie Z, Liu J, Zhu G, Shao Q, Xu X (2011) Evaluating Habitat Change and Boundary Adjustment of a Nature Reserve in Coastal Wetlands: Case Study of Beidagang Nature Reserve, China. *Journal of Coastal Research* 27:966-972.

Zhang X, Zhong T, Liu L, Ouyang X (2015) Impact of soil heavy metal pollution on food safety in China. *PLoS ONE* 10: e0135182

Zhang C, Yu ZG, Zeng GM, Jiang M, Yang ZZ, Cui F, Zhu MY, Shen LQ, Hu L (2014) Effects of sediment geochemical properties on heavy metal bioavailability. *Environment international* 73:270-81

Supplementary data for

Assessing heavy metal pollution of the largest nature reserve in Tianjin City, China

S1.1 Main Beidagang Reservoir (BDGw)

Table S1 Coordinate of sampling sites in BDGw.

No.	Name	Longitude	Latitude
0	BDGw1	117.390557020	38.767444830
1	BDGw2	117.382883830	38.765102480
2	BDGw3	117.344893930	38.780070110
3	BDGw4	117.329913330	38.787721650
4	BDGw5	117.310310320	38.800997130
5	BDGw6	117.281882160	38.786062950
6	BDGw7	117.264735296	38.757758398
7	BDGw8	117.278374730	38.743390110
8	BDGw9	117.299231800	38.734495600
9	BDGw10	117.254118030	38.710676810
10	BDGw11	117.306728430	38.692476460
11	BDGw12	117.346104640	38.683563120
12	BDGw13	117.352355000	38.679533740

S1.2 Lower Reaches of DuliuJian River (WM)

Table S2 Coordinate of sampling sites in WM

No.	Name	Longitude	Latitude
0	WM1	117.452535340	38.790061360
1	WM2	117.445092890	38.792587470
2	WM3	117.431506020	38.796778380
3	WM4	117.400416057	38.800134557
4	WM5	117.373080610	38.802829202

5	WM6	117.350041310	38.806177613
6	WM7	117.375644042	38.790576465
7	WM8	117.390058698	38.785621511
8	WM9	117.428156090	38.780492110
9	WM10	117.466910890	38.785648330
10	WM11	117.473585050	38.781419510
11	WM12	117.456580060	38.790605110
12	WM13	117.445869240	38.775804090
13	WM14	117.443676210	38.772255330
14	WM15	117.445461520	38.768847430

S1.3 Additional Beidagang Reservoir (BDGe)

Table S3 Coordinate of sampling sites in BDGe

No.	Name	Longitude	Latitude
0	BDGe1	117.4009455	38.76279668
1	BDGe2	117.3841357	38.69526438
2	BDGe3	117.3847358	38.69516349
3	BDGe4	117.4198303	38.71431155
4	BDGe5	117.4396821	38.73207277
5	BDGe6	117.4768625	38.74440317
6	BDGe7	117.4767763	38.74507204

S1.4 ShaJingZi Reservoir (SJZ)

Table S4 Coordinate of sampling sites in SJZ

No.	Name	Longitude	Latitude
0	SJZ1	117.42516155	38.67802394
1	SJZ2	117.40292275	38.66675919
2	SJZ3	117.38834166	38.65683151
3	SJZ4	117.39160152	38.64672878

4	SJZ5	117.43211479	38.66391744

S1.5 QianQuan Reservoir (QQ)

Table S5 Coordinate of sampling sites in QQ

No.	Name	Longitude	Latitude
0	QQ1	117.211975970	38.770522166
1	QQ2	117.224171446	38.763291812
2	QQ3	117.221707034	38.747179411
3	QQ4	117.201356285	38.747379612
4	QQ5	117.197446014	38.770691560

S1.6 LiErWan (LEW)

Table S6 Coordinate of sampling sites in LEW

No.	Name	Longitude	Latitude
0	LEW1	117.391132300	38.627460790
1	LEW2	117.407303290	38.639422200
2	LEW3	117.415462670	38.615596400
3	LEW4	117.428670710	38.620635870
4	LEW5	117.443523270	38.622719200
5	LEW6	117.458322820	38.622866920
6	LEW7	117.484371570	38.622667590
7	LEW8	117.494278500	38.623031940
8	LEW9	117.510216890	38.623682830
9	LEW10	117.529167320	38.624406690

S1.7 LiErWan Reservoir (LEWs)

Table S7 Coordinate of sampling sites in LEWs

No.	Name	Longitude	Latitude
0	LEWs1	117.4421054670	38.6180405530

1	LEWs2	117.4259222360	38.6111418290
2	LEWs3	117.4424805250	38.6073800470
3	LEWs4	117.4678236620	38.6113247870
4	LEWs5	117.4883246900	38.6184931530
5	LEWs6	117.5156203840	38.6193927460
6	LEWs7	117.5304424430	38.6125619930

S1.8 MaPengKou (MPK)

Table S8 Coordinate of sampling sites in MPK

No.	Name	Longitude	Latitude
0	MPK1	117.552967101	38.632146149
1	MPK2	117.572620190	38.634076690
2	MPK3	117.581223709	38.641160645
3	MPK4	117.578982480	38.650621213
4	MPK5	117.562907296	38.653141986
5	MPK6	117.546242178	38.651206902

S2. Extraction procedure

First step (Exchangeable and weak acid soluble fraction, B_1): 1 g soil sample was extracted with 40 mL of 0.11 mol L^{-1} acetic acid (Merck Suprapur) solution by shaking in a mechanical, end-over-end shaker at 30 ± 10 rpm at 22 ± 5 ºC for 16 h. The extract was separated by centrifugation at 3000 ×g for 20 min, collected in polyethylene bottles and stored at 4 ºC until analysis. The residue was washed by shaking for 15 min with 20 mL of doubly deionized water and then centrifuged, discarding the supernatant.

Second step (Ferro-manganese bond or reducible fraction, B_2): 40 mL of 0.5 mol L^{-1} hydroxylammonium chloride (Merck pro-analysis) solution was added to the residue from the first step, and the mixture was shaken 30 ± 10 rpm at 22 ±5 ºC for 16 h. The acidification of this reagent is by the addition of a 2.5% (v/v) 2 mol L^{-1} HNO_3 solution (prepared by weighing from a suitable concentrated solution). The extract was separated and the residue was washed as in the first step.

Third step (Organic bound or oxidisable fraction, B_3): 10 mL of 8.8 mol L^{-1} hydrogen peroxide (Merck Suprapur) solution was carefully added to the residue from the second step. The mixture was digested for 1 h at 22 ± 5 ºC and for 1 h at 85 ± 2 ºC, and the volume was reduced to less than 3 mL. A second aliquot of 10 mL of H_2O_2 was added, the mixture was digested for 1 h at 85 ± 2 ºC, and the volume was reduced to about 1 mL. The residue was extracted with 50 mL of 1 mol L^{-1} ammonium acetate (Merck pro-analysis) solution, adjusted to pH 2.0, at 30 ± 10 rpm and 22 ± 5 ºC for 16 h. The extract was separated and the residue was washed as in previous steps.

Residue from the third step (Residual fraction, B_4): the residue from step 3 was digested with aqua regia, following the ISO 11466 (ISO, 1995b). In this case, the amount of acid used to attack 1 g of sample was reduced to keep the same volume/mass ratio: 6.0 mL of HCl (37%) and 2.0 mL of HNO_3 (70%) were added, and then add 2 mL hydrofluoric acid by microwave digestion.

The quality of the analytical data for the sequential extraction procedure was assessed by carrying out analyses of the certified reference materials GBW07438. Three independent replicates were performed for each sample and blanks were measured in parallel for each set of analyses using BCR procedure. The moisture content of each sample was determined by drying a separate 1 g sample in an oven (105±2 ºC) to constant mass.

S3. Single factor pollution index

The single factor pollution index method is the ratio of the measured value of a single water quality index to the evaluation standard value, which is used to evaluate whether the water quality index meets the requirements of the corresponding standard. We here use the Chinese governments Environmental quality standards for surface waters (GB 3838, 2002). The expression is as follows:

$$P_i = C_i/C_o$$

Where P_i is the single factor pollution index; C_i is the actual concentration measurement value of item i; C_0 is the evaluation standard limit of the index i. When $P_i \leq 1$, it indicates that this index meets the standard; When $P_i > 1$, it indicates that the index exceeds the standard. The larger P_i and more serious pollution degree of the index are.

S4. Comprehensive pollution index

The comprehensive pollution index is a statistical analysis on the basis of single factor pollution index, and a comprehensive evaluation of water pollution degree is made according to arithmetic average, weighted average or other mathematical results of selected water quality index P_i. The mean comprehensive pollution index formula is as follows:

$$\mathbf{P} = \frac{1}{n}\sum_{i=1}^{n} P_i$$

Where P is the mean comprehensive pollution index, and Pi is the single factor pollution index. P is the arithmetic mean of the single factor pollution index of n indices. The pollution degree of the mean comprehensive pollution index is divided into: $P \leq 0.20$, good water quality; 0.21~0.40, the water quality is good; 0.41~0.70, light pollution; 0.71~1.00, moderate pollution; 1.01~2.00, high pollution; $P \geq 2.01$, serious pollution (Desaules et al. 2012; Cresswell et al. 2012).

S5. Potential ecological risk

The potential ecological risk (PER) method was developed by Hakanson (Håkanson 1980). The PER index was introduced to assess the degree of contamination of trace metals in the soils. The equations for calculating the PER indexes are as follows:

$$E_r^i = T_r^i \times C_f^i = T_r^i \times (C_s^i / C_n^i),$$

$$RI = \sum_{\mathrm{i=1}}^{n} E_r^i ,$$

where C^i_s is the content of the element in samples, C^i_n is the background value of the element, C^i_f is the single element pollution factor, E^i_r is the PER index of an individual element, and T^i_r is the biological toxicity factor of an individual element, which are defined as Cd=30, Cr=2, Cu=Ni=Pb=5, and Zn=1(Guo et al. 2010). *RI* is the comprehensive PER index, which is the sum of E^i_r.

Table S9 shows the factor standard of different levels.

Potential ecological risk (PER) index			
E_i^r	**PER of individual elements**	***RI***	**Comprehensive PER**
<40	Low	<150	Low
40–80	Moderate	150–300	Moderate
80–160	Considerable	300–600	High
160–320	High	≥600	Serious
≥320	Very high		

References:

Cresswell T, Smith REW, Nugegoda D, Simpson SL (2013) Challenges with tracing the fate and speciation of mine-derived metals in turbid river systems: implications for bioavailability. *Environmental Science and Pollution Research* 20:7803-7814

Desaules A (2012) Critical evaluation of soil contamination assessment methods for trace metals. *Science of the Total Environment* 426:120-131

Guo WH, Liu XB, Liu ZG, Li GF (2010) Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. *Procedia Environmental Sciences* 2:729-736

Håkanson L (1980) An ecological risk index for aquatic pollution control: A sedimentological approach. *Water Research* 14:975-1001