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An integrated model for assessing heavy metal exposure risk to migratory birds in wetland ecosystem: A case study in Dongting Lake Wetland, China

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HIGHLIGHTS

- A model was integrated to assess heavy metal exposure to migratory birds in DTW.
- Dunlin showed a higher heavy metal exposure risk than Eurasian Spoonbill.
- Hg, Pb and Cr are likely to have adverse effect on carnivorous migrants.
- Almost all heavy metals were at no risk for Lesser White-fronted Goose.

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ABSTRACT

Heavy metal contamination is present in wetland ecosystem worldwide, and quantitative risk assessment model is significant. In this study, an exposure model was integrated for assessing heavy metal exposure risk to migratory birds in Dongting Lake Wetland (DTW). The concentrations of Cr, Cu, Pb, Cd, Hg and As in water, plant, soil and fish were investigated from 9 migratory bird habitats. The results showed that exposure doses from drinking water pathways were very low. There was a sensitive area that Cd and As exposure doses exceeded the most conservative tolerable daily intake, which is located at the estuary of Xiang River. In general, Dunlin had a greater risk than Eurasian Spoonbill. Hg, Pb and Cr were likely to have adverse effect on carnivorous migrants in DTW, while Cu and Cd were considered to be relatively safe. Almost all heavy metals were at no risk for Lesser White-fronted Goose in DTW.

1. Introduction

Wetland is one of the three major ecosystems in the world, providing irreplaceable ecological functions and economic values (Qu et al., 2011). However, wetland ecosystem has been increasingly affected by heavy metals. Heavy metals enter wetland ecosystem through natural and anthropogenic ways, including hydrological processes, natural erosion, atmospheric deposition, agricultural non-point source pollution, industrial activities, and so on (Tang et al., 2010; Liang et al., 2015).

Some heavy metals are essential elements for organisms but may be toxic with high level, affecting productive function and behavioral features (Ash and Stone, 2003). Heavy metals can be accumulated and biomagnified through the food chain (Yi et al., 2011). Heavy metals enter organisms via direct inhalation, ingestion and dermal contact absorption, resulting in potential risk to wildlife and even human health (Tang et al., 2013). As and its compounds are carcinogenic to organisms (Li and Ding, 2007). Pb can cause lead poisoning and damage to the nervous system and immune function (Youssef et al., 1996). Cd can reduce reproduction and growth performance of bird (Spahn and Sherry, 1999; Feng et al., 2001). Ingestion of even trace quantities of Cd can affect the physiology and health of wildlife (Larison et al., 2000).

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Methylmercury can be bioaccumulated and biomagnified through the food chain, and chronic dietary exposure to small concentrations can impair reproduction of bird (Liu et al., 2008; Frederick and Jayasena, 2010). Moreover, feces can accumulate heavy metals at higher concentrations than diet items (Morrissey et al., 2005). As a result, pollution may transfer to another place through feces of migrants (Liang et al., 2015). Heavy metal exposure risk to birds in wetland ecosystem is an international issue (Cui et al., 2011; Salamat et al., 2014). Although great efforts have been undertaken to show the severity of heavy metal contamination and analyze potential ecological risk in wetlands, few studies have quantitatively evaluated exposure risk to wetland birds.

Morrissey et al. (2005) assessed heavy metal exposure to American Dipper through food ingestion, while exposure from water and soil ingestion was ignored. For the first time, we systematically integrated a comprehensive risk model to evaluate heavy metal exposure to migrants in wetland ecosystem, considering food, water and soil exposure pathways. Furthermore, an uncertainty factor was employed to account for the uncertainty of risk model and differences in sensitivity among species (CCME, 1998). Although the model already exists, it is seldom employed for exposure risk assessment. Moreover, the existing model has been optimized for better application in this study. This study provides a nondestructive and quantifiable means for evaluating and monitoring heavy metal exposure risk to wetland birds instead of causing harm to species by collecting eggs, feathers and even organisms.

Dongting Lake Wetland (DTW) in China has been taken for a case study, which is an important international wintering habitat for East Asian migratory birds. Previous studies have shown a serious heavy metal contamination in DTW (Li et al., 2013, 2014; Liang et al., 2015). However, information on heavy metal exposure risk to migrants in this area is scarce. In this paper, quantitative investigation and prediction of heavy metal exposure risk to migratory birds in DTW were conducted. Three representative carnivorous and herbivorous migrants, Eurasian Spoonbill (*Platalea leucorodia*), Dunlin (*Calidris alpina*) and Lesser White-fronted Goose (*Anser erythropus*), were chosen for study.

2. Materials and methods

2.1. Study area

Dongting Lake, the second largest freshwater lake in China, covers about 2820 km^2 (approximately 28°30′–29°38′N, 112°18′–113°15′E) in the northern part of Hunan Province on the middle and lower reaches of Yangtze River (Wu et al., 2013). The lake lies in the subtropical monsoon climate zone with abundant precipitation and longtime sunshine. Annual precipitation is approximately 1100–1400 mm, mainly between April and September. The mean depth is 6–7 m, and the hydrology cycle is about 18 d. It is recorded that the average annual temperature is 16.4–17.0 °C and the frost-free period is 259–277 d. Wet season lasts from May to October, and dry season runs from November to March. The Three Gorges Dam impounds during wet season and then supplies water for the lake during dry season (Wu et al., 2015). Dongting Lake has both storage and release function with the characteristic of water carrying. During wet season, the water level rises with big volume of water body, drawing water from four tributaries (Yuan River, Xiang River, Zi River and Li River) and overwhelming the marshlands. The water area shrinks to just 18% in the dry season (Fig. 1), and tracts of grassy marshlands appear as the water level falls, supporting a wide variety of flora and fauna and providing abundant food for migratory birds.

Due to the special geographical position and unique climate conditions, DTW provides an ideal habitat for migratory birds to migrate, inhabit and wintering. It plays an important role in Northeast Asia crane migration network, East Asia goose and duck migration network and East Asia–Australia wader migration network. The lake includes three important nature reserves: East Dongting Lake National Nature Reserve, South Dongting Lake Wetland and Waterfowl Provincial Nature Reserve, and West Dongting Lake National Nature Reserve. East Dongting Lake Nature Reserve was registered in the List of Wetland of International Importance through the Ramsar Convention in 1992 and the other two in 2002. Refer to the data from East

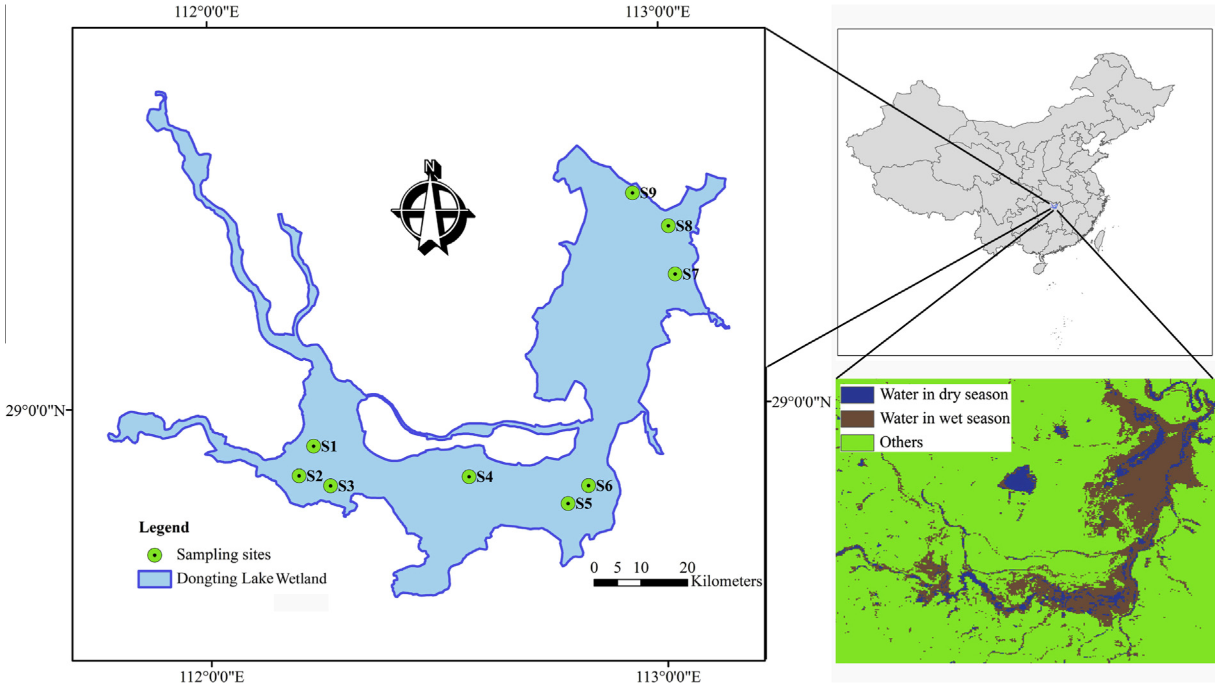

Fig. 1. Sampling sites in DTW, mid-south China. S1, S2 and S3 are located at West DTW. S4, S5 and S6 are located at South DTW. S7, S8 and S9 are located at East DTW.

Dongting Lake National Nature Reserve Authority, 131 species of aquatic plants, 117 species of freshwater fish and 340 species of waterfowls with 39 species listing in the international Redbook have been recorded in East DTW. Moreover, there are about 130 000 migratory birds and more than 70% of Lesser White-fronted Goose (*Anser erythropus*) in the world wintering in East DTW each year (Yuan et al., 2014).

2.2. Sample collection and treatment

In January 2014, water, fish, plant and soil samples were collected from 9 main migratory bird habitats in the study area, where migratory birds are widely distributed (Fig. 1).

Water samples were collected by the lake in 500 mL acid-washed polyethylene bottles, acidified with 1 mL HNO_3 and stored at 4 °C. Twenty small fish (with a length of about 10 cm) were collected at each sampling site. Samples were kept in an ice foam box, took back to the laboratory and subsequently washed with ultrapure water. Four samples of newly grown plant and the top soil (5 cm in thickness) were collected from each sampling site, refrigerated with polyethylene bags. Fish and soil samples were stored at −20 °C for measuring. All water, fish, plant and soil samples were collected in a 50 m^2 area from each site.

2.3. Analytical methods and quality control

5 mL HNO_3 and 7 mL mixed acid (HNO_3:$HClO_4$ = 5:2) were added in acidified water samples for digestion. Fish, plant and soil samples were dried in an oven at 90 °C until constant weight. Fish samples were homogenized with a porcelain mortar. 1.000 g preprocessed fish samples were accurately weighed and then transferred to 50 mL conical flasks. Samples were added with 10 mL mixed acid (HNO_3:$HClO_4$ = 9:1) and soaked overnight for digestion. The digested samples were diluted to a final volume of 50 mL with ultrapure water and then filtrated through a 0.45-μm organic membrane. Plant samples were powdered with a high-speed grinder. 0.500 g preprocessed samples were accurately weighed and then transferred to airtight Teflon vessels, added with 12 mL mixed acids (HNO_3:$HClO_4$ = 3:1) for digestion using the intelligent graphite digestion (SISP DS-360, China). Soil samples were ground gently, sieved with 100 mesh sieve for homogenization. Precise 0.500 g preprocessed samples were weighted and transferred to airtight Teflon vessels, added with 10 mL HCl and then 13 mL mixed acid (HNO_3:HF:$HClO_4$ = 5:5:3) for digestion using the intelligent graphite digestion.

The Atom Absorption Spectrophotometer (AAS, PE AAnalyst 700, USA) was used to analyze Cr, Cu, Pb and Cd. Hg and As were measured by the Atomic Fluorescence Spectrophotometer (AFS, AFS-9700, China). Sample duplicates, method blanks and standard reference materials were used to validate the results of each batch of samples. The analytical precision was conducted with repetitive rate of 10%. The recoveries of standard samples in digestion process ranged from 95% to 105%.

2.4. Integrated exposure risk assessment model

2.4.1. Exposure assessment

The exposure model has been systematically integrated in an effort to quantify the risk of species exposure to chemicals in the surrounding environment. As dermal contact and inhalation routes of wildlife exposure are usually ignored, we consider contaminant exposure through oral ingestion of environmental medium (Suter, 2011). Besides, food composition and daily movement of migratory birds were not considered in the model. Therefore, an external measurement based exposure model for quantifying heavy metal risk to migratory birds can be calculated as follows.

$$I_{df} = 0.648BW^{0.651} \tag{1}$$

where I_{df} is food consumption rate (dry weight) (g d^{-1}); *BW* is body-weight of selected birds (g). Food consumption rates are estimated from allometric regression models (Nagy, 1987). *BW* (average body weight) of 2000 g was chosen for Eurasian Spoonbill or Lesser White-fronted Goose, and 60 g for Dunlin.

$$I_W = 59BW^{0.67} \tag{2}$$

where I_w is water consumption rate (mL d^{-1}), and the unit of *BW* is kg. Water consumption rates are also estimated from allometric regression models (Calder and Braun, 1983).

$$I_s = P \times I_{df} \tag{3}$$

where I_s is soil consumption rate (g d^{-1}) and *P* is the proportion of soil accounted food. In this study, *P* (18%) of Western Sandpipers (*Calidris mauri*) was chosen for Eurasian Spoonbill and Dunlin. 8.2% of Canada Goose (*Branta canadensis*) was chosen for Lesser White-fronted Goose (Beyer et al., 1994).

$$E_j = \sum_{i=1}^{m} (I_i \times C_{ij})/BW \tag{4}$$

where E_j is oral exposure dose of heavy metal (*j*) (mg kg^{-1} d^{-1}); *m* is the number of absorbing medium (for example: food, water or soil); I_i is the absorptivity of medium (*i*) (g d^{-1} or mL d^{-1}); and C_{ij} is concentration of metal (*j*) in medium (*i*) (mg kg^{-1} or mg L^{-1}).

2.4.2. Risk characterization

Potential exposure risk to species is evaluated by comparing the estimated elemental intake dose to tolerable daily intake (*TDI*). *TDI* is an estimate of a substance that is not anticipated to result in adverse effect.

$$TDI_j = (LOAEL_j \times NOAEL_j)^{0.5}/UF \tag{5}$$

where TDI_j is tolerable daily intake of heavy metal (*j*) (mg kg^{-1} d^{-1}); $LOAEL_j$ is the lowest observed adverse effect level of heavy metal (*j*) (mg kg^{-1} d^{-1}); $NOAEL_j$ is no observed adverse effect level (mg kg^{-1} d^{-1}). *LOAEL* and *NOAEL* for avian toxicity tests were taken from toxicological benchmarks for wildlife (Sample et al., 1996). *UF* is uncertainty factor. The selection of *UF* value may not be less than 10 for extrapolating to a long-term exposure concentration without an effect, and may be higher than 10 depending on the substance, type, amount and quality of data available (CCME, 1998). In the presented study, *UF* = 10 was chosen as the most conservative *TDI* (mc*TDI*). The most dangerous *TDI* (md*TDI*) is gained when the value of *UF* is 100.

Refer to human health risk assessment model, hazard quotient (*HQ*) has been employed to estimate the exposure risk to birds (USEPA, 2001; MEPPRC, 2014).

$$HQ_j = E_j/TDI_j \tag{6}$$

where HQ_j is the hazard quotient of heavy metal (*j*). If $HQ < 1$, it is considered that the exposed population is unlikely to experience adverse effect, whereas if $HQ > 1$, negative effect on population may occur. Refer to grades of geo-accumulation index for assessing heavy metal contamination in sediments (Müller, 1969), heavy metal exposure risk to birds was divided into four levels: no risk ($HQ < 1$), low risk ($1 < HQ < 2$), moderate risk ($2 < HQ < 3$) and high risk ($HQ > 3$), respectively.

3. Results and discussion

3.1. Statistics of heavy metal concentrations

The concentrations of six heavy metals in water, fish, plant and soil from DTW are shown in Table 1. The contents of heavy metals in water were all lower than class I of Chinese environmental quality standards for surface water. However, most of the concentrations in soils exceeded the background values of DTW except for Cr. This was consistent with previous studies (Li et al., 2014; Liang et al., 2015). This phenomenon of low concentration in water but high contamination in soil was primarily due to sedimentation and ingestion by aquatic flora and fauna. The result was accordant with previous work (Fu et al., 2014). Besides, heavy metals have low solubility in water. Heavy metals in water bodies can be adsorbed by surface sediment (Olivares-Rieumont et al., 2005).

3.2. Heavy metal exposure doses to migratory birds

The values of mc*TDI* and md*TDI* are calculated according to Eq. (6) and showed in Table 2. Exposure doses of Cr, Cu, Pb, Cd, Hg and As to Eurasian Spoonbill, Dunlin and Lesser White-fronted Goose are presented in Fig. 2. Drinking water exposure pathway has been ignored in this study because of low concentration. In general, two carnivorous migrants presented similar results. Dunlin showed relatively higher exposure dose than Eurasian Spoonbill, demonstrating birds with lighter weight mostly have higher exposure risk. Large animals have more food and water consumption but lower metabolic rate than small animals. Therefore, unit weight of small animals has higher oral exposure (Suter, 2011). Fig. 2 also shows that heavy metal concentrations in soil and soil consumption rate had a great influence on migrants in DTW. Only consider food exposure is incomplete. Both food and soil exposure should be taken into account when evaluating birds exposure risk.

For Eurasian Spoonbill and Dunlin, Cr exposure doses all exceeded md*TDI*. Fish exposure doses were both lower than mc*TDI* while total exposure doses were over mc*TDI* due to relatively higher soil exposure doses of Cr. Cu exposure doses were almost under mc*TDI*. Fish exposure of Cu to Eurasian Spoonbill was under md*TDI*, demonstrating Cu exposure by fish intake was relatively safe. Pb exposure doses all exceeded md*TDI*. Total exposure doses were all over mc*TDI*. Soil exposure doses were in a large range, implying that the distribution of Pb was uneven in DTW, and Pb probably had various sources such as chemical industries and smelting plants (Liang et al., 2015).

Cd exposure doses were all lower than mc*TDI*. Both food and soil exposure doses to Eurasian Spoonbill and Lesser White-fronted Goose were even less than md*TDI*. An outlier (S5) was found within soil exposure doses. It is located at Hengling Lake, the estuary of Xiang River which is the most serious contamination area of DTW (Liang et al., 2015). As the total exposure dose of Cd was higher than mc*TDI* for Dunlin in this region, negative effect on migratory birds living here may occur. Almost all Hg exposure doses to Eurasian Spoonbill and Dunlin exceeded mc*TDI*. Just fish exposure pathway could cause a significant impact on carnivorous migrants in DTW. Wiener and Spry (1996) showed that freshwater fish could accumulate methylmercury with high assimilation. Hg exposure doses of fish varied widely, perhaps because different species of fish have different bioaccumulation capacities of Hg. Exposure doses of Hg to Lesser White-fronted Goose were lower than mc*TDI*. Concentrations of Hg in plant samples were not detected, and the exposure pathway was mainly from soil. Feature of As exposure to carnivorous migrants was special. Fish exposure pathway of As was very safe. There was also an outlier, which exceeded mc*TDI*. It is located at Hengling Lake (S5) as well as Cd. Therefore, this region is demonstrated to be at risk as one of waterfowl habitats. Attentions should be taken and strategies should be designed to control the effects of heavy metal pollution on waterfowls and the ecosystem in this area.

Table 1
Average concentrations of heavy metals in fish, water and sediment from DLW.

	Water (mg L^{-1})		Fish (mg kg^{-1}, dw[c])	Plant (mg kg^{-1}, dw[c])	Sediment (mg kg^{-1}, dw[c])	
	CV[a]	St[b]			CV[a]	BV[d]
Cr	0.004	0.01	2.82 ± 1.02	1.84 ± 1.73	70.62 ± 7.70	83.92
Cu	0.01	0.01	1.47 ± 0.30	16.18 ± 2.92	40.13 ± 13.58	25.00
Pb	0.003	0.01	2.95 ± 2.00	8.73 ± 1.83	57.41 ± 30.47	27.75
Cd	0.0001	0.001	0.63 ± 0.55	0.50 ± 0.31	4.06 ± 5.90	0.23
Hg	0.00002	0.00005	0.06 ± 0.04	–	0.22 ± 0.15	0.07
As	0.0042	0.05	0.16 ± 0.19	1.02 ± 1.03	24.30 ± 22.45	13.41

[a] CV: concentration value.
[b] St: Chinese environmental quality standards for surface water, class I.
[c] dw: dry weight.
[d] BV: the background values of heavy metals in sediments from DTW (Liang et al., 2015).

Table 2
Toxicity parameters of *NOAEL* and *LOAEL*, most conservative tolerable daily intake (mc*TDI*) and most dangerous tolerable daily intake (md*TDI*) of heavy metals (mg kg^{-1} d^{-1}).

	Cr	Cu	Pb	Cd	Hg	As
NOAEL	3.28	11.7	1.13	1.45	0.0064	2.46
LOAEL	13.14	15.4	11.3	20	0.064	7.38
mcTDI	0.66	1.34	0.36	0.54	0.002	0.43
mdTDI	0.066	0.134	0.036	0.054	0.0002	0.043

3.3. Heavy metal exposure risk to migratory birds

*HQ*s of the three studied birds from DTW are presented in Fig. 3. For Eurasian Spoonbill and Dunlin, risk of six heavy metals was decreased in the following sequence: Hg > Pb > Cr > As > Cu > Cd. The result was generally consistent with that of sediment from DTW in previous studies because of the high soil consumption rate (Liang et al., 2015). However, Cd was shown the highest risk in soil but the lowest risk to migrants, probably due to its higher *TDI* for migrants.

Dunlin had a greater risk than Eurasian Spoonbill. High risk of Hg, Pb and Cr was presented to Dunlin with 7.92, 5.74 and 3.66 of *HQ*, respectively. Moderate risk of Hg was presented to Eurasian Spoonbill. Low risk of Cr and Pb was presented to Eurasian Spoonbill as well as Cu and As to Dunlin. No risk of Cu, Cd and As was presented to Eurasian Spoonbill as well as Cd to Dunlin. Only Cd was shown no risk to both Eurasian Spoonbill and Dunlin. On the whole, Hg, Pb and Cr were most likely to have adverse effect on carnivorous migratory birds perched in DTW. Cu and Cd were considered to be relatively safe. In addition, benthic invertebrates, such as shrimp and screw, are also diet composition and prey for waterfowls. The overall risk of carnivorous migrants may be higher when considering benthic invertebrates, which may accumulate more heavy metals (Morrissey et al., 2005).

For Lesser White-fronted Goose, heavy metal exposure risk was decreased in the following sequence: Pb > Cu > Cr > Hg > As > Cd. All elements were at no risk except Pb. It was due to its higher concentration in plants of DTW, and Pb exposure dose to Lesser White-fronted Goose exceeded mc*TDI*. In addition, compared with Eurasian Spoonbill, Lesser White-fronted Goose had higher plant ingestion exposure dose of Pb. However, the total exposure dose was almost the same due to different soil consumption rates, which were 18% for Eurasian Spoonbill and 8.2% for Lesser White-fronted Goose, respectively. Thus, the parameter selection

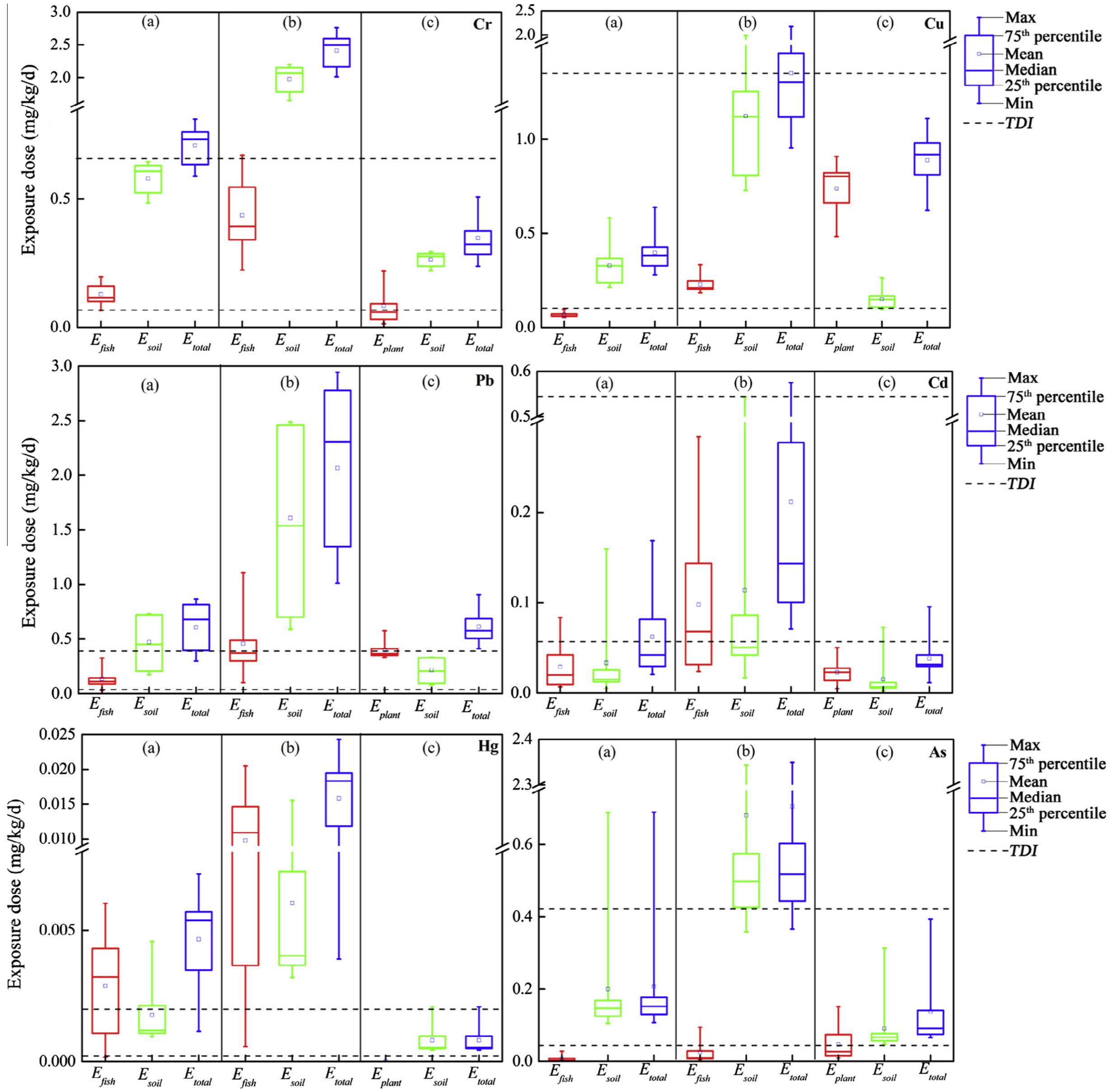

Fig. 2. Fish, plant, soil and total exposure doses of heavy metals to migratory birds in DTW: (a) for Eurasian Spoonbill, (b) for Dunlin and (c) for Lesser White-fronted Goose. E_{fish}: exposure dose via fish-eating pathway; E_{plant}: exposure dose via plant-eating pathway; E_{soil}: exposure dose via soil pathway; E_{total}: exposure dose via both food and soil pathways.

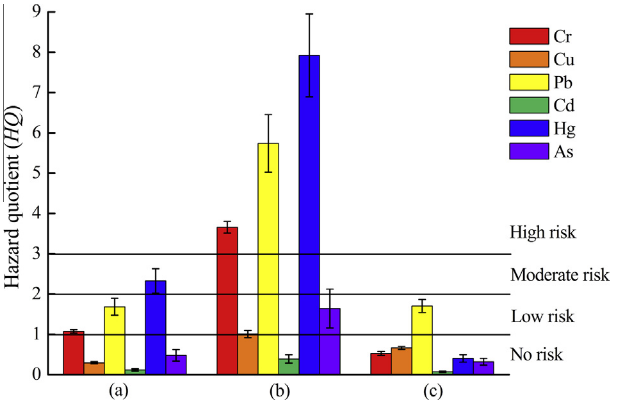

Fig. 3. Average hazard quotient (*HQ*) of six heavy metals in each habitat for Eurasian Spoonbill, Dunlin and Lesser White-fronted Goose in DTW. (a) For Eurasian Spoonbill, (b) for Dunlin and (c) for Lesser White-fronted Goose. Error bars represent the standard errors.

of soil consumption rate influences the model evidently. In general, heavy metal exposure risk to herbivorous migratory birds was relatively safer than carnivorous ones in DTW.

4. Conclusion

An exposure risk assessment model for evaluating heavy metal exposure risk to migratory birds in wetland ecosystem had been integrated and applied. Water, fish, plant and soil samples were collected to quantitatively analyze heavy metal exposure risk to three representative migratory birds. Dunlin showed a relatively higher exposure dose and risk than Eurasian Spoonbill. Water exposure doses were very low while soil environment quality, and soil consumption rate had a great influence on migrants in DLW. The estuary of Xiang River was the most serious contamination area where Cd and As exceeded mc*TDI*. Negative effect on waterfowl may occur in this region that should take special attention. Risk to migratory birds in DTW was decreased in following sequence: Hg > Pb > Cr > As > Cu > Cd for carnivorous migratory birds and Pb > Cu > Cr > Hg > As > Cd for herbivorous ones, respectively. In general, Hg, Pb and Cr were likely to have adverse effect on carnivorous migrants in DTW, while Cu and Cd were considered to be relatively safe. Heavy metal exposure risk to herbivorous migrants was safer than carnivorous ones with almost all *HQ* of selected heavy metals were below 1 in each habitat in DTW.

The model employed is demonstrated to be effective for exposure risk assessment, and the results are considered to be useful in developing migratory birds conservation strategies in DTW ecosystem. However, this study does not consider the diet composition of carnivorous migrants, and the real risk might be higher when considering benthic invertebrates.

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