Acta Geochim (2018) 37(4):526–536
https://doi.org/10.1007/s11631-017-0242-7

ORIGINAL ARTICLE

Enrichment characteristics and risk assessment of Hg in bird feathers from Caohai wetland in Guizhou Province, China

Fengcheng Peng[1] · Tianrong He[1] · Zhenji Li[2] · Mengyu Chen[3] · Xiaoli Qian[3] · Lingxia Zeng[1] · Yiyuan Xu[1,2,3]

Received: 7 June 2017 / Revised: 25 August 2017 / Accepted: 27 September 2017 / Published online: 19 October 2017

Abstract Based on the analysis of the enrichment characteristics of Hg and MeHg in bird feathers from Caohai National Nature Reserve in Guizhou, the risks of Hg pollution to the birds from Caohai wetland have been evaluated. The total Hg content of bird feathers ranges from 40 to 5058 ng/g with an average of 924 ng/g. The content of MeHg is significantly correlated with total Hg (r = 0.68, $p < 0.01$), and the content are among 0.75 and 113 ng/g. The total Hg content in the birds feathers is significantly dependent on their feeding habits, which is mainly in accordance with the following rule: carnivorous birds > omnivorous birds that are mainly carnivorous > omnivorous birds that are mainly herbivorous. There are also differences in the Hg enrichment ability in the different parts of bird feathers, and the total Hg and MeHg content in the wing feathers are significantly higher than that in the other parts of feathers. The bioaccumulation coefficients of aqueous Hg and MeHg by bird feathers are 0.9×10^4–112.13×10^4 (mean value is 20.47×10^4) and 0.47×10^4–70.4×10^4 (mean value is 9.52×10^4), respectively. Although the whole Hg level in Caohai bird feathers is not too high, the Hg content in some carnivorous birds exceeds over or approaches the abnormal threshold when birds are breeding (5 μg/g), which indicates that the birds in Caohai wetland are faced with some risks of ecological Hg pollution.

Keywords Caohai wetland · Total Hg · Methyl Hg · Bird feathers

✉ Tianrong He
hetianrong@139.com

Fengcheng Peng
1099600869@qq.com

Lingxia Zeng
1215241292@qq.com

Yiyuan Xu
2513086435@qq.com

1 Key Laboratory of Karst Environment and Geohazard Prevention, Guizhou University, Guiyang 550003, China

2 Area Management Bureau of Guizhou, Caohai National Nature Reserve, Bijie 553100, China

3 The School of Resources and Environment Engineering, Guizhou University, Guiyang 550003, China

1 Introduction

Hg, especially MeHg, can accumulate in the environment and organism for a long time, which causes irreversible damage of organism (Clarkson 2015). Hg enters the body mainly through ways like digestive tract and respiratory tract and subsequently, binds plasma protein. It can also enter the central nervous systems through the blood–brain barrier, which cause its damage and also the language and memory dysfunction of these poisoning people. At the same time, it can as well cause damage to the kidneys, which leads to the kidney failure, even life-threatening.

Many studies have found that wetlands are the source of methyl Hg (Allan and Heyes 1998; Hall et al. 2008). Abundant organic matter and the anaerobic environment in wetlands favored the formation of MeHg (Barkay et al. 1997; MacMillan et al. 2015). Hg methylation in wetlands is thought to be carried by anaerobic bacteria, mainly sulfate reducing bacteria (SRB) (King et al. 2001), methanogens (Hamelin et al. 2011; Gilmour et al. 2013) and iron reducing bacteria (Fleming et al. 2006; Kerin et al. 2006). The MeHg produced in wetlands was easy to accumulate and be biomagnified through the food chain, and caused high concentrations of MeHg in fish and wading bird (Beyer et al. 1997; Fitzgerald et al. 1998).

Birds are an important part of wetland ecosystem, which is one of the highest trophic levels in a wetland ecosystem. Birds have a strong metabolic mechanism due to their adaptation to flight, and consequently, have a very high rate in the biotransformation of exogenous compounds (Lin 2007). These features make them particularly vulnerable to environmental pollutants. Therefore, many scholars at home and abroad regard birds as the indicator organism for environmental pollution (Zhu et al. 2014; Adams and Frederick 2008), such as to monitor the environmental Hg pollution. Birds eat the fish rich in MeHg, which is the main route of the MeHg exposure of birds in the wetland (Bouton et al. 1999; Albers et al. 2007). Hg pollution can change both the foraging efficiency (Ackerman et al. 2008) and behavior (Custer et al. 2010) of birds, reduce the hatching success rate (Meng 2006) of birds and the survival rate of nestling birds (Broo and Odsjö 1981), ultimately change the population structure of birds (Furness and Camphuysen 1997). Therefore, studying the enrichment characteristics of Hg in the birds of wetland ecosystem is significantly important for the evaluation of the ecological risk of wetland ecosystems.

The distribution of Hg in birds was highly selective, and they are mainly accumulated in liver and kidney. However, bird feather sample is usually collected for the evaluation of Hg pollution in the birds because other tissue samples, like blood, liver, and kidney can't easily be collected. Furthermore, some studies have found that above 70% of the Hg burden in the whole body was in the feathers (Honda et al. 1986; Braune and Gaskin 1987). The body feathers were proved to provide the most representative sample for estimating whole-bird Hg content and many studies used the feathers to monitor Hg levels of birds in marine, freshwater and terrestrial ecosystems (Furness et al. 1986; Mallory et al. 2015).

Caohai National Nature Reserve is located in the southwest of Weining County in Guizhou Province (Fig. 1), that is, in the east longitude of 104°10′–104°25′, the north latitude of 26°45′–27°00′ and at an altitude of 2172–2234 m. Its depth of water is 1–3 m, and vegetation area keeps above 30 km^2. Caohai wetland is famous for its lush plants with a core area of about 2162 km^2. Bird resources are rich in Caohai wetland, which is known as the "bird kingdom". Therefore, it becomes the most important wintering place for rare birds like black necked cranes. Every year, more than 100 thousand migratory birds rest or winter in Caohai wetland. Caohai wetland has become to be one of main wintering places of black necked cranes that are under the first-class protection in China, and the number of grey crane wintering here are about 1500 every year. Caohai wetland is also the important wintering place for other birds, such as Hooded Cranes, black storks, geese and ducks, and waders.

The pollution of Caohai wetland has been reported in many related types of research. Caohai wetland has been subjected to a large amount of wastewater from daily life and the pollution from surrounding lead–zinc smelting (Li 2003; Zhang and Lei 2010; Zhang et al. 2013), therefore, ecosystem security was faced with a potential threat. Recent studies have shown that the content of heavy metals like Pb and Cd in part fish from Caohai wetland has exceeded the national food safety standard (Bi 2007). Qian (2007) have studied the Hg and MeHg distribution characteristics in the water and sediment in Caohai wetland, but they have not studied the enrichment characteristics of Hg in Caohai food chains. Hg in the Caohai environment may be enriched and enlarged in the relatively long food chains, which leads to the ecological security threats to birds. In this paper, the distribution of Hg of bird feathers in Caohai wetland is studied, and the ecological risk of birds is also evaluated.

2 Experimental section

2.1 Sample collection

The samples of bird feathers in Caohai wetland mainly came from two parts: one part of samples from dead birds collected by Caohai administration, during the collection, their body length, and body weight were recorded; another portion of samples from the natural shedding feather of birds in Caohai wetland, which were classified and numbered according to their categories. In this study, 18 kinds of feather samples (total 59 samples) were collected, which belonged to 6 orders or 7 families. The basic information of bird feathers is listed in Table 1. It can be seen from Table 2 that the samples collected in this study mainly belonged to large and medium-sized birds, and feeding habits of the birds could be divided into four groups: carnivorous bird, omnivorous birds that are mainly carnivorous, omnivorous birds that are mainly herbivorous, herbivorous birds.

After the birds feathers were brought back to the laboratory, they were washed with deionized water, dried in a freeze dryer (FDU -1110, TOKYORIKAKIKAI CO. LTD), and crushed by grinding machine.

In order to gain a better understanding of the enrichment characteristics of Hg and its ecological risks, we also have collected the plant, benthic animal and fish samples from Caohai.

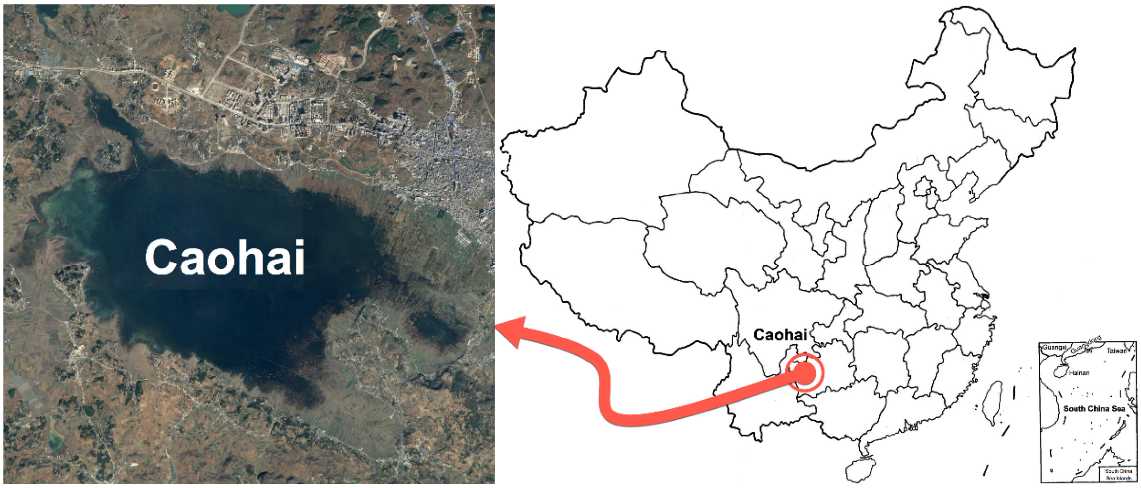


Fig. 1 Location map of Caohai wetland

2.2 Sample determination

Hg species in the samples of a bird feather, animal samples, and plant were measured using the methods that are based on purging, trapping and cold vapor atomic fluorescence detection (Brooks Rand Model III).

The total Hg (THg) of bird feathers and animal samples are determined by di-acid digestion, followed by gold trapping and cold atomic fluorescence spectrometry (Yan et al. 2005): (1) accurately weigh feather sample 0.1000 g and add them into 25 mL colorimetric tube, followed by 10 mL GR H_2SO_4 and HNO_3 mixtures (v:v = 3:7). The colorimetric tube is sealed with plastic wrap and subsequently heated in a water bath to 95–140 °C for about 2–3 h, then a little double-deionized water is added after cooling. (2) Add 0.5 mL BrCl, and volume is close to the scale line (25 mL) by double-deionized water. After sealing by Parafilm, it keeps more than 24 h for the full oxidation of Hg in various states to Hg^{2+}. (3) After oxidation, $NH_2OH{\cdot}HCl$ is added to destroy the free halogens before adding stannous chloride ($SnCl_2$) to convert Hg(II) to volatile Hg(0). (5) The resulting sample is then purged with Hg-free N_2 and Hg(0) is absorbed onto a gold trap (6) The CVAFS analyzer is used to analysis and determination of Hg(0) released from the gold trap.

THg content in plant samples: (1) accurately weigh 0.1–0.2 g sample (accurate to 0.0001 g) into 25 mL colorimetric tube, and add 5 mL ultra pure HNO_3; (2) cover tube by preservative film, and heat it in water bath under 95 °C for 3 h; (3) add a little double-deionized water and 0.5 mL BrCl into the tube, and shape it. (4) The volume is close to the scale by double-deionized water r and place it for more than 24 h for the full oxidation of Hg in various states by BrCl to Hg^{2+}. Then the sample was treated and analyzed following the procedure described previously.

MeHg content in bird feathers is determined by alkaline digestion coupled with GC–CVAFS method (Yan et al. 2005): (1) accurately weigh 0.1000 g feather samples and add them to a 50 mL centrifuge tube, then 5 mL 200 g/L KOH solution is added. After its digestion for 3 h in a water bath at 75 ± 3 °C, it is volume to 25 mL by 60 °C double-deionized water and then shook equably. (2) 50 µL sample is added to a 200-mL bubbler with 80 mL double-deionized water. The resulting sample is then adjusted to pH 4.9 with an acetate buffer and the Hg in the sample was methylated in the closed bubbler by the addition of sodium tetraethyl borate. (3) The ethyl analog of CH_3Hg, CH_3-CH_2CH_2Hg, was separated from the solution by purging with N_2 onto a Tenax trap. (4) The trapped $CH_3CH_2CH_2Hg$ was then thermally desorbed, separated from other Hg species by an isothermal gas chromatography (GC) column, decomposed to Hg(0) in a pyrolytic decomposition column (700 °C) and then carried into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection.

MeHg in the plant: (1) accurately weigh 0.1–0.2 g plant sample (dry weight) and add them into a 50 mL centrifuge tube,then 5 mL 250 g/L KOH solution was added. The sample in the tube is fully digested in water bath or oven at 75–80 °C for 3 h. After cooling down the tube to room temperature, 3 mL concentrated HCl is slowly added to mediate the solution to be acidic (pH = 1–2). (2) 10 mL of CH_2Cl_2 was added into the tube, then it was closed and shaken for 30 min. 10 mL of the CH_2Cl_2 layer was pipetted into another 50-mL centrifuge tube after the tube was centrifuged at 3000 rpm for 30 min. About 40 mL of double-deionized water was added to the tube. The tube was heated at 45 °C in a water bath until no visible solvent was left in the tube and the remaining liquid was then purged with N_2 for 8 min in a water bath at 80 °C to

Table 1 Bird sample information of Caohai wetland

Name	Latin	Order	Families	Class	Phylum	Feeding habits		Migration habit
Bar-headed goose	Anserindicus	Anseriformes	Anatidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
Green winged duck	Anascrecca	Anseriformes	Anatidae	Aves	Chordate	Omnivorous	Omnivorous party al feeding	Migratory birds
Anas poecilorhyncha	Anaspoecilorhyncha	Anseriformes	Anatidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
Pochard	Aythyaferina	Anseriformes	Anatidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
Mallard duck	Anas platyrhynchos	Anseriformes	Anatidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
Ruddy shelduck	Tadornaferruginea	Anseriformes	Anatidae	Aves	Chordate	Omnivorous	Omnivorous partial meat feeding.	Migratory birds
Black necked crane	Grusnigricollis	Gruiformes	Cariamidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
Grey crane	Grusgrus	Gruiformes	Cariamidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
White crane	Grus leucogeranus	Gruiformes	Cariamidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
Bone top wing	Fulicaatra	Gruiformes	Rallidae	Aves	Chordate	Omnivorous	Omnivorous partial meat feeding	Part of the migration, part of the resident birds
Moorhen	Gallinulachloropus	Gruiformes	Rallidae	Aves	Chordate	Omnivorous	Omnivorous partial feeding	Migratory birds
Pheasant	Phasianuscolchicus	Galliformes	Phasianidae	Aves	Chordate	Omnivorous	Herbivorous	Stay bird
Great bittern	Botaurusstellaris	Ciconiiformes	Ardeid	Aves	Chordate	Carnivorous	Carnivore	Stay bird
Heron	Ardeacinerea	Ciconiiformes	Ardeid	Aves	Chordate	Carnivorous	Carnivore	There are migratory birds in the south, and migratory birds migrating from the north in winter
Little grebe	Tachybaptusruficollis	Podicipedidae	Podicedidae	Aves	Chordate	Carnivorous	Carnivore	Stay bird
Blake kite	Aquila	Falconiformes	Accipitridae	Aves	Chordate	Carnivorous	Carnivore	Migratory birds

Table 2 Hg content in bird feathers of Caohai wetland (ng/g)

Name	Body length (cm)	Body weight (kg)	Number	Total Hg content (ng/g)	Hg Mean value (ng/g)	MeHg content (ng/g)	MeHg Mean value (ng/g)
Bar-headed goose	62–85	2–3	14	41–1294	389	1.49–39.9	9.43
Green winged duck	30–50	0.2–0.5	1	447	447	6.24	6.24
Anas poecilorhyncha	50–64	1	1	193	193	4.37	4.37
pochard	42–49	0.7–1.1	13	152–2760	740	1.06–53.5	11.4
Mallard duck	47–62	0.9–1.3	2	880–894	886.6	4.49–24.1	14.3
Ruddy shelduck	51–68	0.9–1.7	2	671–2692	1681.6	14.0–17.1	15.5
Black necked crane	110–120	4–6	4	285–880.3	643.7	5.01–14.5	58.8
Grey crane	100–10	3–6	3	73.8–3096	1096.1	1.66–46.4	16.9
White crane	130–140	4.9–7.4	3	1622–4130	3141	12.6–43.5	23.7
Bone top wing	350–430	0.4–0.8	6	129–435	280.6	0.99–9.38	4.57
Little egret	52–68	0.3–0.6	3	995–2445	2559	27.7–57.7	41.7
Great bittern	59–77	0.4–1.4	2	409–5058	2733	6.88–91.1	49.0
Heron	75–110	1–2	2	46.8–122	84.2	0.75–2.79	1.77
Little grebe	25–32	<0.3	1	1947	1947	113	113
Blake kite	21–91	0.6–1.0	1	485	485	4.96	4.96
Tufted duck	75–105	3.8–8.75	4	717–2257	1771	0.97–20.4	14.8
Pheasant	73–86.8	1.26–1.65	1	239	239	1.48	1.48

remove solvent residue. (3) The sample was brought to 50 mL with double-deionized water before an appropriate volume (generally 15 mL) of the sample was transferred to a 200-mL bubbler for MeHg analysis following the procedure described previously.

2.3 Quality control

Quality assurance and quality control of the process of analysis were carried out by using duplicates, method blanks, matrix spikes, and certified reference materials (GSB-26, TORT-2). The minimum detection limit is 0.6 pg, the method blank is 9.45 pg. The reference values of total Hg and MeHg were 0.27 ± 0.06 and 0.15 ± 0.01 μg/g, respectively, and the measured values were 0.25 and 0.15 μg/g, respectively. The reference values of total Hg in plant reference materials were 14.6 ± 2.4 μg/g, the measured value was 14.2 μg/g, and the recovery rate of MeHg was 94%.

The measured THg concentration of 0.25 ± 0.03 μg/g ($n = 4$) was obtained from TORT-2 with a certified value of 0.27 ± 0.06 μg/g. The measured MeHg concentration of TORT-2 was 0.154 ± 0.008 μg/g ($n = 4$), which was comparable with the certified value of 0.152 ± 0.013 μg/g. The recovery rates of the reference materials are among 90%–110%, which is 5 ha calculated using (determined value/standard value) $\times$ 100%. The relative deviation of the parallel sample is less than 10%. Therefore, the experimental results are reliable.

2.4 Data manipulation

In this study, the data is analyzed by using Microsoft Excel 2010 and SPSS11.0 statistical software, and the relevant data analysis charts are drawn using Origin 7.5 and Microsoft Excel 2010.

3 Results

3.1 The total Hg content in Caohai birds

Bird resource in Caohai is rich, the number of wintering birds in Caohai wetland annually are over 100 thousand. Studies have shown that birds can discharge up to 90% of Hg from their feathers, so the amount of Hg in the birds feathers can reflect the Hg pollution in their living environment (Burger 1993). In this study, THg and MeHg concentrations in feather samples are shown in Table 2. As is shown in the table, the total Hg contents of the feathers vary in different species of birds. Overall, the THg content in the bird feathers of Caohai wetland range from 40 to 5058 ng/g with a mean value of 1005 ng/g, which are much lower than that of pollution area, as compared with the Hg concentration of 7.1 ± 3.7 μg/g in Japan Shiranui Sea reported by Doi et al. (1984), and much lower than those in some natural waters reported in Europe and North America, for example, THg concentration of 0.24–44 μg/g with an average of 5.60 μg/g in the bird feathers in Canadian Arctic marine reported by Mallory et al. (2015), THg concentration of 0.34–45.8 μg/g (mean value is 6.92 ± 7.58 μg/g) in peninsular Florida and the Florida Keys reported by Rumbold et al. (2017). However, compared with the total Hg content (2.00 ± 2.05 μg/g) in the Heron feathers of Sanjiang plain reported by Zhilong et al. (2017), THg content in feather of Caohai birds is relatively higher.

3.2 MeHg content in the birds feathers of Caohai wetland

Overall, MeHg content in the bird feathers in Caohai wetland ranges from 0.75 to 113 ng/g with a mean value of 15.0 ng/g, and the ratio of MeHg content accounts for 0.31%–5.96% with a mean value of 1.87% in the THg content, which is significantly lower than that in bird feathers of Canadian Arctic marine reported by Mallory et al. (2015) (mean value is 4.42 μg/g) and that in the fish-eating birds reported by Wang et al. (2011) (553 ng/g). These studies show that in the adult birds if MeHg content is 15 μg/g (wet weight) in the body tissues like brain, it will lead to MeHg toxicity and death. If MeHg is 3 μg/g (wet weight) in the brain, bird embryo mortality will increase (Wiener et al. 2003). For ordinary birds, the diet containing 0.3 μg/g (wet weight) of MeHg will seriously reduce the reproductive success rate (Barr 1986). In this study, MeHg content in the food sources of birds in the Caohai wetland is as follows: aquatic plants, 0.004–0.16 ng/g with a mean value of 0.023 ng/g; fish, 0.10–36.5 ng/g with a mean value of 3.04 ng/g; snails, 0.05–15.2 ng/g with a mean value of 2.33 ng/g, which are significantly lower than 0.30 μg/g, and also significantly lower than that of the reported content in corresponding aqueous products of other wetland ecosystems. At the same time, the MeHg ratio in the total Hg content is also significantly lower than that in other wetland ecosystems. For example, the MeHg content in the aquatic plants of Caohai wetland is significantly lower than that in the mangrove wetland plants in China (0.22–1.76 ng/g, MeHg ratio is 1.36) (Ding et al. 2010) and also that in experimental lakes area in Canada (10.2 ± 6.8 ng/g, MeHg ratio is 0.12) (Moore et al. 1995). Both the MeHg content and ratio in fish of Caohai wetland are lower than those in the fish of Hongfeng Lake (mean value is 12 ng/g, MeHg ratio is 37.5%) (He et al. 2010) and in the fish of Dongfeng reservoir (mean value is 10.2 ng/g, methylation rate is 21.3%) (Jiang 2005) under the same background area. The low MeHg level in the bird food sources of Caohai wetland may lead to the low MeHg content and ratio in the birds feathers. Of course, the transfer of the absorbed MeHg in birds to inorganic Hg cannot be ruled out.

4 Results analysis and discussion

4.1 The effects of bird feeding habits on THg and MeHg content in bird feathers

Many studies show that the THg content in bird feathers is affected by many factors, such as life habit, food source, age and so on (Jin and Xu 1997). Hg in the environment can not only enter the body of the bird through the food chain but also be attached to its wings by atmospheric aerosols. It can be enriched directly through water and dust, but mainly through the food chain (Lin 2007). In this study, carnivorous (Animals are food) birds include great bittern, eagle. The omnivorous birds that are mainly carnivorous (The main foods are animals, as well as a little plant) include white crane, little egret, little red, and any provision of herons. The omnivorous birds that are mainly herbivorous (The main foods are plants, as well as a little animal) include crane, mallard, pochard, black necked crane, green winged duck, geese, Morillon, pheasant, coot, and poecilorhyncha. As can be seen in Fig. 2, except for eagle and heron, THg content for the rest birds follows the order: carnivorous birds > omnivorous birds that are mainly carnivorous > omnivorous birds that are mainly herbivorous, which indicates that the THg content in the birds feathers has a relationship with their food sources. THg content in aquatic plants, benthic animal and fish of Caohai are 0.04–3.78 ng/g with an average of 1.07 ng/g (wet weight), 0.51–6.6 ng/g with an average of 7.82 ng/g (wet weight), and 1.10–68.2 ng/g with an average of 8.47 ng/g (wet weight), respectively. Obviously, THg content in an animal of Caohai wetland is significantly higher than that in plants. Therefore, THg content in carnivorous birds is higher than that in omnivorous birds. This content in eagle and the heron may not meet this rule due to the small sample size. In addition, many factors like age structure and air Hg content in the living environment may be related to THg content in the birds feathers, which is gradually enriched with the increase of age. But in this study, we have found that THg content in the birds feathers is not significantly correlated with the weight and length of birds.

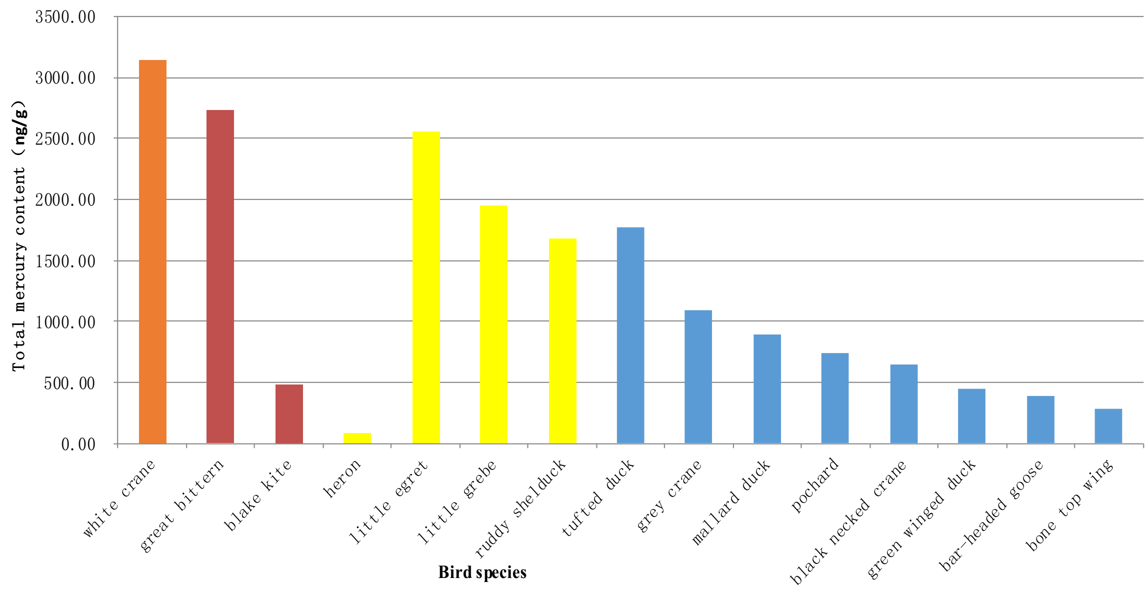
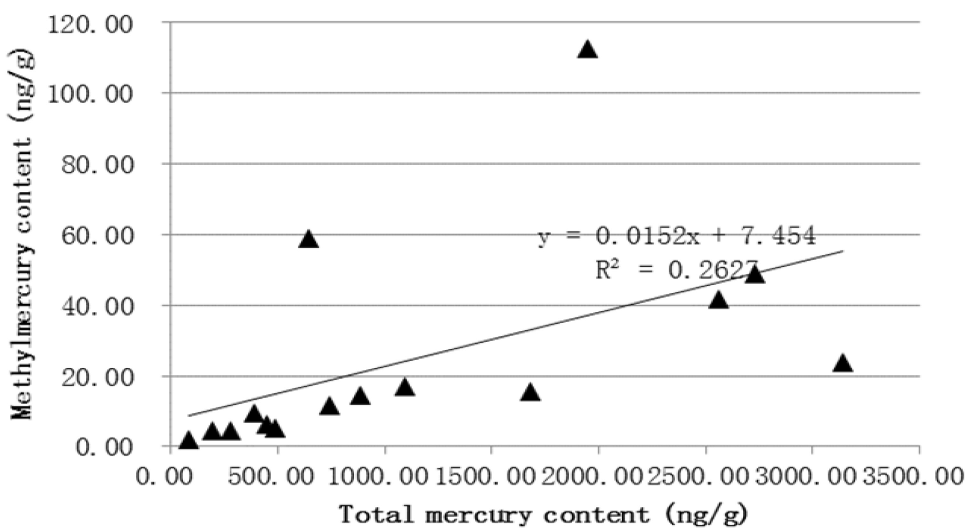


Fig. 2 Total mercury content in birds with different feeding habits (ng/g)

Fig. 3 The correlation between THg and MeHg content in bird feathers of Caohai wetland



Correlation analysis shows that MeHg content in bird feathers of Caohai wetland are significantly correlated to THg content ($r = 0.68$, $p < 0.01$) (Fig. 3), which indicates that the MeHg content in the birds feathers is greatly influenced by THg content. Based on the analysis of the MeHg content (Fig. 4), MeHg content in the bird feathers of Caohai wetland does not satisfy the following rule: carnivorous birds > omnivorous birds that are mainly carnivorous > omnivorous birds that are mainly herbivorous, which are probably attributed to the fact that only parts of MeHg come from food sources, or the transformation of enriched MeHg in vivo. Relevant problems need further researches.

4.2 The differences in the distribution of THg and MeHg in the different feathers of birds

To study the distribution of Hg in the feathers from the different body part of the bird, feather samples from the different body part of bar-headed goose, Pochards, and Fulicaatra are classified and THg and MeHg content are determined. The relevant results are shown in Figs. 5 and 6.

THg content of goose feathers follows the order of tail feathers > wing feathers > abdomen feathers; THg content of common pochard feathers follows the order of wing feathers > abdomen feathers > tail feathers > back feathers; THg content of Fulica atra feathers follows the order of wing feathers > abdomen feathers > back feathers.

Fig. 4 The distribution of MeHg content in bird feathers of Caohai wetland with different feeding habit

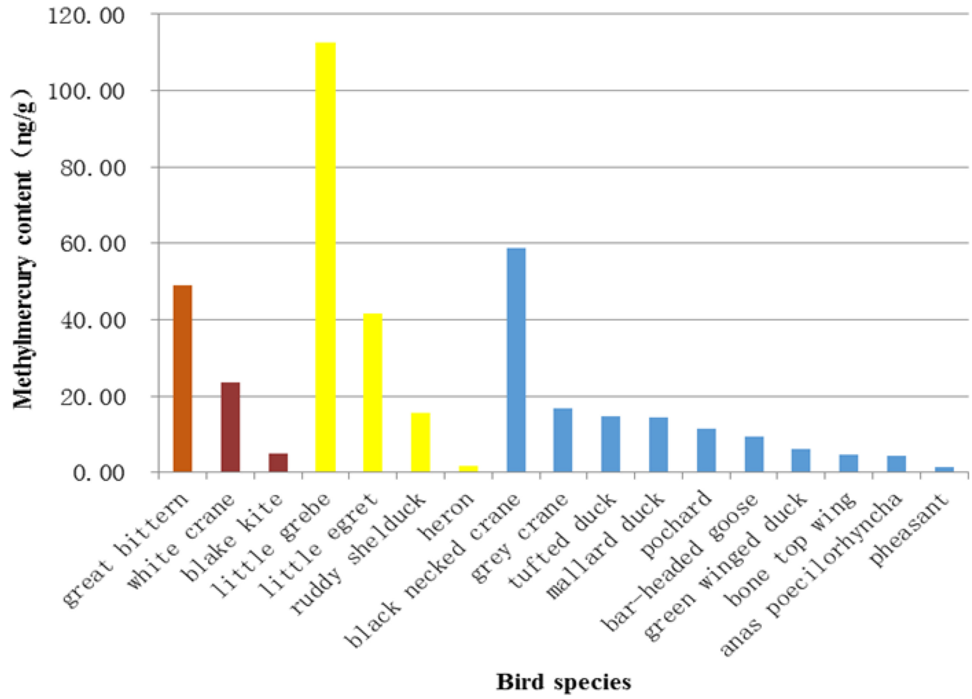
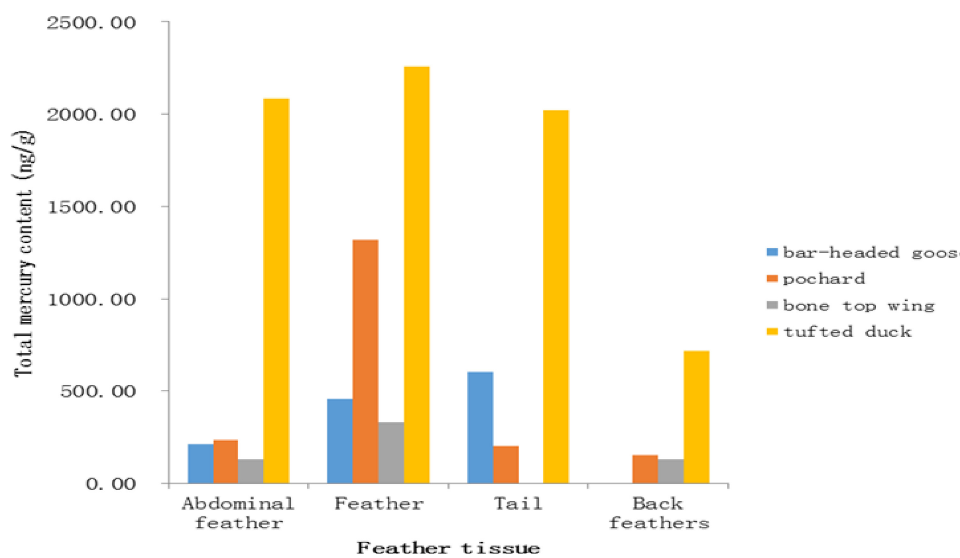


Fig. 5 Total Hg content in the birds feathers of Caohai wetland



Therefore, although THg distributes differently in the feathers of a different bird, THg concentration is relatively high in wing feathers. This primary rule is similar to the cases reported by Guo et al. (2001) on the brown eared pheasant and kittiwakes. The differences in the Hg distribution in different parts of bird feathers may be related to their own tissue properties, the order of molting and the length of exposure time. When the Hg is absorbed into the bird body, it can be oxidized to Hg^{2+}. The unique chemical properties of Hg^{2+} that are very easy to bind with the feathers rich in sulfhydryl groups (Guo et al. 2001) and the content of sulfhydryl groups is different in the feathers from the different body part of the bird. These characters are the important reasons for the selective accumulation of Hg. In addition to the characteristics of their own tissues, the Hg content in the birds feathers is related to the exposure time of feathers in the air. There are some differences in the order of molting for different birds, therefore, the distribution of Hg in the feathers of different birds is different. In this study, THg and MeHg in the wing feathers are relatively high, which may be related to the long molting time, long exposure time to air for the accumulation of Hg.

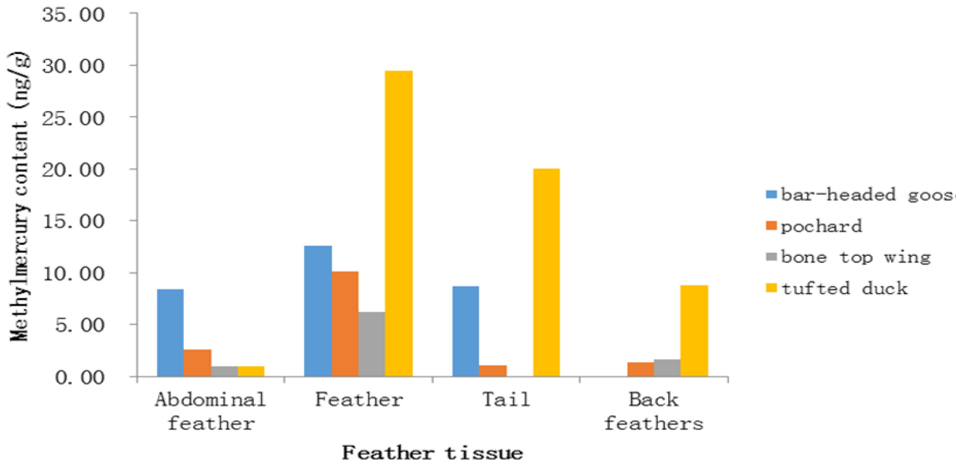


Fig. 6 Total MeHg content in the birds feathers of Caohai wetland

4.3 The risk assessment of Hg pollution in the birds of Caohai wetland

In the ecological system, Hg content increases gradually along the food chains, and the enrichment coefficient can reach a higher level in each trophic level. In this study, the bioaccumulation coefficient (BCF) of aqueous Hg is calculated using the following equation:

$$BCF = C_p/C_w$$

where, BCF—bioconcentration factor, C_p—Hg concentration in bird feather (ng/g), C_w—dissolved Hg concentration in water (ng/mL) (Ordiano-Flores et al. 2011).

According to the findings of Caohai during the same period, the mean dissolved THg content in water of Caohai wetland is 4.51 ng/L, and the dissolved MeHg is 0.16 ng/L (Gao 2016). The bioaccumulation coefficients of aqueous THg and MeHg in Caohai by bird feathers are 0.9×10^4–112×10^4 (mean value is $20.47 \times 10^{4)}$and 0.47×10^4–70.4×10^4 (mean value is 9.52×10^4), respectively. The BCF of THg in bird feathers is higher than that of gull feathers in Bohai Bay sea, whose mean value is 1.23×10^5. However, the opposite trends are observed for the MeHg content, where the mean value for latter is 1.5×10^6. The BCF of MeHg in the bird feathers of Caohai wetland is lower than that of THg, which is different from the conclusions of previous studies. This is related to the lower MeHg and the lower percentage of MeHg in the THg content in the food chain of Caohai wetland.

Some research showed that when the Hg content in the feather is as high as 5 ppm, birds would be abnormal, which results in the abnormal hatching rate and survival rate (Eisler 1987). In this study, THg content reaches 5 ppm only in a feather sample (great bittern), and some of the birds such as a crane, crane, and egrets also have high levels over 3 ppm, which indicate that birds in Caohai wetland face high ecological risk of Hg pollution. The scope of activities of birds in this study is wide, and most of the birds are migratory birds. They come to Caohai wetland every winter and move back to their life places every spring, therefore, the Hg content cannot be fully representative of the Hg pollution in this area. Some birds live in Caohai wetland for a long time, their Hg content can reflect the situation of Hg pollution in Caohai wetland to some extent. To more accurate assessment of Hg pollution in Caohai wetland birds, three resident birds, namely, the great bittern (its highest value is 5057 ng/g and mean value is 2733 ng/g), any provision (1947 ng/g) and spot billed Duck (197 ng/g), are selected from the bird samples for further analysis. It can be found that the bioaccumulation coefficient of resident carnivorous birds is very high. These results indicate that although the Hg content levels in aquatic plants, benthic animal, and fish in Caohai wetland are low, due to bioaccumulation and biomagnification of Hg in the food chain, Hg content is high in the birds at the top of the food chain, especially for the carnivorous birds whose nutrient level is close to mankind. They are facing the ecological risk of Hg.

5 Conclusion

Birds are particularly susceptible to environmental pollutants, consequently are often used as indicators of environmental pollution. Guizhou Caohai National Nature Reserve is the wintering place for many rare birds. Because the Caohai wetland has suffered from the pollution from wastewater and a variety of indigenous zinc smelting, therefore, the birds are faced with a large ecological security risk. In this study, a total of 18 types of feathers with a total of 59 bird samples are collected, and their accumulation characteristics of THg and MeHg are analyzed. The main conclusions are listed below:

1. THg content in bird feathers of Caohai wetland ranges from 40.4 to 5058 ng/g with an average of 1005 ng/g. The content of MeHg is significantly correlated with THg (r = 0.68, $p < 0.01$), and the content are among 0.75 and 112.6 ng/g with an average of 15.0 ng/g. Compared with that of the other ecosystems that is not contaminated by Hg, Hg level in bird feathers of Caohai wetland is in a pretty or higher level, but the content and proportion of MeHg is significantly lower than that in other ecosystems, which may be related to the lower MeHg content in food sources of Caohai bird.
2. The difference in THg content in the feathers of different birds is significant, which generally follows the order: carnivorous birds > omnivorous birds that are mainly carnivorous > omnivorous birds that are mainly herbivorous, which means that Hg content is mainly related to the food source for birds. There are also differences in the Hg distribution in different parts of bird feathers, which is affected by the factors like the order of molting and exposure time in the air.
3. Although the whole Hg level in the Caohai bird feathers is not high, the Hg content in some carnivorous birds exceeds over or approaches the abnormal threshold when birds are breeding (5 μg/g), which indicates that the birds in Caohai wetland are faced with ecological risks of Hg pollution.

Acknowledgements This study was supported by the National Natural Science Foundation of China (No. 41363007).

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