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Aquatic methylmercury is a significant subsidy for terrestrial songbirds: Evidence from the odd mass-independent fractionation of mercury isotopes

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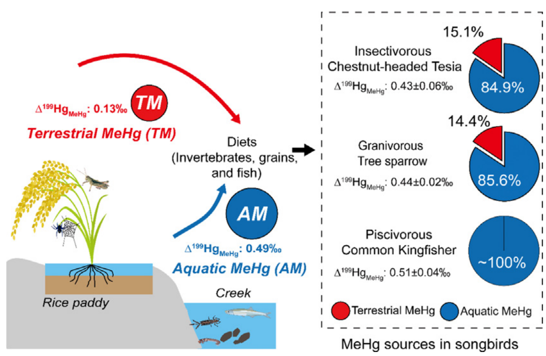
HIGHLIGHTS

- [Hg], [MeHg], and Hg isotopes were measured in food and feathers of songbirds.
- MeHg was the dominant form of Hg in feathers.
- MIF of Hg isotopes does not occur in terrestrial trophic transfers.
- MIF of MeHg isotope signatures in feathers revealed MeHg sources in songbirds.
- MeHg of aquatic origin is a significant subsidy to terrestrial songbirds.

GRAPHICAL ABSTRACT



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ABSTRACT

In contrast to aquatic food chains, knowledge of the origins and transfer of mercury (Hg) and methylmercury (MeHg) in terrestrial food chains is relatively limited, especially in songbirds. We collected soil, rice plants, aquatic and terrestrial invertebrates, small wild fish, and resident songbird feathers from an Hg-contaminated rice paddy ecosystem for an analysis of stable Hg isotopes to clarify the sources of Hg and its transfer in songbirds and their prey. Significant mass-dependent fractionation (MDF, δ^{202}Hg), but no mass-independent fractionation (MIF, Δ^{199}Hg) occurred in the trophic transfers in terrestrial food chains. Piscivorous, granivorous, and frugivorous songbirds and aquatic invertebrates were all characterized by elevated Δ^{199}Hg values. The estimated MeHg isotopic compositions obtained using linear fitting and a binary mixing model explained both the terrestrial and aquatic origins of MeHg in the terrestrial food chains. We found that MeHg from aquatic habitats is an important subsidy for terrestrial songbirds, even those that feed mainly on seeds, fruits, or cereals. The results show that MIF of the MeHg isotope is a reliable tool to reveal MeHg sources in songbirds. Because the MeHg isotopic compositions was calculated with a binary mixing model or directly estimated from the high proportions of MeHg, compound-specific isotope analysis of Hg would be more useful for the interpretation of the Hg sources, and is highly recommended for future studies.

1. Introduction

Mercury (Hg) is a global, nonessential, toxic, and bio-accumulative contaminant. Hg is released from both natural sources (volcanic eruptions, geothermal hot springs, and wildfire; Edwards et al., 2021; Engle et al., 2006;

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Kumar et al., 2018) and anthropogenic sources (artisanal gold mining and coal combustion; Telmer and Veiga, 2009; Wang and Luo, 2017). In the environment, inorganic Hg (IHg) is readily converted to the more toxic form of methylmercury (MeHg) by anaerobic microbial methylation (Gilmour et al., 1992; Stein et al., 1996; Selin, 2009). MeHg is easily accumulated and biomagnified along food chains, especially in high trophic level predators (Baeyens et al., 2003; Hammerschmidt et al., 2013), posing a potential health risk to humans and wildlife (Scheuhammer et al., 2007; Eagles-Smith et al., 2016).

Songbirds (*Passeriformes*) are popular sentinels of the Hg burden or exposure risk and Hg contamination of surrounding environment, because of their wide distribution and large population, diverse diet types, and high trophic levels, and their high susceptibility to anthropogenic contamination (Edmonds et al., 2010; Hartman et al., 2013; Townsend et al., 2013; Jackson et al., 2015; Low et al., 2020). Because the Hg exposure is greater in both contaminated sites and remote areas (Cristol et al., 2008; Rimmer et al., 2010; Jackson et al., 2011a; Luo et al., 2020; Li et al., 2021), the biomagnification of Hg in songbirds has become a subject of increasing concern. Recently, terrestrial songbirds inhabiting Hg-contaminated rice paddies in Hg mining areas have extremely high total Hg (THg) concentrations in their feathers, including the adult chestnut-headed tesia (190 μg/g, fresh weight, f.w.) and russet sparrow nestlings (10.8 μg/g, f.w.) reported by Abeysinghe et al. (2017) and Su et al. (2021), respectively. Both these values exceed the threshold (3 μg/g) in feathers at which songbird reproduction is affected (Jackson et al., 2011b). This elevated Hg (mainly MeHg) provides an opportunity to study the Hg sources in songbird and the Hg biomagnification in terrestrial food chains.

Stable Hg isotopes are emerging as an important tool for identifying the sources and biological processes of Hg in environmental studies (Blum et al., 2014; Tsui et al., 2020; Li et al., 2022). Mass-dependent fractionation (MDF, mainly referring to δ^{202}Hg) and mass-independent fractionation MIF (mainly referring to odd MIF of Δ^{199}Hg and Δ^{201}Hg) are the two major types of Hg isotope fractionation. MDF occurs in many physical, chemical, and biological processes, including microbiological reduction, methylation, demethylation, and photoreduction (Kritee et al., 2009; Zheng et al., 2007; Perrot et al., 2015). In contrast, odd MIF is commonly observed during the photochemical reduction of divalent Hg (Hg^{2+}) and the photodemethylation of MeHg in aquatic ecosystems (Bergquist and Blum, 2007; Kritee et al., 2018). Researchers have reported that the transfer of Hg in aquatic food chains shows no significant MIF or MDF between fish and their prey at low trophic levels (Kwon et al., 2012), whereas an increase in MDF (~2 ‰, δ^{202}Hg) has been observed between fish and human hair, mammals, and waterfowl (Du et al., 2018; Kwon et al., 2014). Based on the unique Hg isotope fractionations (MDF and MIF), an effective tracing tool can be established and used to identify the sources or transfer processes of Hg in predators or human beings.

Currently, most studies of Hg isotopes in avian species have focused on piscivorous, insectivorous, and carnivorous birds, such as waterfowl (Kwon et al., 2014), seabirds (Renedo et al., 2018a, 2018b, 2020, 2021), and plateau raptors (Liu et al., 2020). In recent studies, tissues or organs, including feathers (Renedo et al., 2018a, 2020, 2021; Liu et al., 2020), blood (Kwon et al., 2014; Renedo et al., 2018a, 2018b; Tsui et al., 2018), muscles (Liu et al., 2020; Manceau et al., 2021), liver and kidney (Renedo et al., 2021; Manceau et al., 2021), and eggs (Day et al., 2012) have been used to determine the sources and transfer of Hg in birds. The blood and feathers of songbirds are commonly used as non-invasive indicators of the bird Hg burden, over several weeks with blood and intermoult period (several months) with feathers (Renedo et al., 2018a; Furness et al., 1986; Bearhop et al., 2000). However, a study by Tsui et al. (2018) remains the first and only study reporting the MeHg sources in terrestrial songbirds using Hg isotopic compositions in songbird blood. The application of Hg isotopic compositions in bird feathers to trace Hg sources in birds, especially non-migratory terrestrial songbirds remains limited.

In the present study, feathers and prey items of resident songbirds inhabiting the Wanshan Hg mining area were collected to investigate the transfer and biomagnification processes of Hg in terrestrial food chains. This study used Hg isotopes in songbird feathers to explore the possibility of tracing Hg sources in songbirds over a relatively long period, and provides new insights into the sources and transfers of elevated Hg concentrations to terrestrial songbirds inhabiting Hg-mining areas. The main objectives of this study were: 1) to analyze the Hg concentrations and Hg isotopic compositions in organisms of different trophic levels in the terrestrial ecosystem; 2) to discuss the isotope fractionation of both THg and MeHg in the associated food chains; and 3) to reconstruct the Hg sources in songbirds and the transfer of Hg, particularly MeHg, from their prey or diets to songbirds.

2. Materials and methods

2.1. Sample collection

Samples were collected from the Wanshan mercury mining area (WSMM, 27°24.63′ N, 109°07.38′ E), an abandoned artisanal retorting site near a large abandoned intensive mine (Gouxi), including soils, rice plants, invertebrates, and resident songbird feathers (Fig. S1). The sampling campaign was conducted with the approval of the Institute of Geochemistry, Chinese Academy of Sciences and the permission of the Natural Resources Administration of Wanshan District, Guizhou Province, China.

During the harvest season, as shown in Fig. S2, terrestrial invertebrates including caterpillars, rice green stink bugs (*Nezara viridula*), grasshoppers (*Oxya chinensis*), katydids (*Phaneropteridae*), mantis (*Tenodera sinensis*), spiders including riparian spider (*Tetragnatha nitens*) and upland spider (*Crocothemis servilia*), damselfly, and dragonflies (*Orthetrum melania* and *Crocothemis servilia*) were captured near rice paddies with insect sweep nets (38 cm diameter). Small fish (length 2–6 cm), including sharpbelly and goby fish, and aquatic invertebrates including shrimp (*Atyoidae*), caddisfly larvae (*Trichoptera*), water beetles (*Cybister sugillatus*), and water striders (*Aquarius elongatus*) were collected with sweep nets in the Hg-contaminated creek. Given the limited biomass of invertebrates and fish species, at least 20 individuals of each species were collected, and homogeneously mixed in 1 to 5 samples to meet the determination requirements for quantifying the target contaminants (Table 1).

Adult resident songbirds, including primary insectivorous species (spot-breasted scimitar babbler *Erythrogenys mcclellandi*, n = 5; streak-breasted scimitar babbler *Pomatorhinus ruficollis*, n = 5; hwamei *Garrulax canorus*, n = 5; chestnut-headed tesia *Cettia castaneocoronata*), n = 4; frugivorous species (collared finchbill *Spizixos semitorques*, n = 4; and brown-breasted bulbul *Pycnonotus xanthorrhous*, n = 4), a granivorous specie (tree sparrow *Passer montanus*, n = 6), and a piscivorous specie (common kingfisher *Alcedo atthis,* n = 6) were captured with mist nets between August and September 2019, and their primary feathers were collected. Other samples, including rhizospheric soils (n = 3), leaves (n = 3), and grains (n = 3) of rice plants were collected during the harvest season. To discuss the differences in Hg isotope ratios the home range and foraging territories, we collected the feathers of russet sparrow nestlings (~14 days after hatching) in field nest boxes set up in 2019, which fed mainly on rice-paddy invertebrates based on field observation.

In the laboratory, the feathers were washed ultrasonically with detergent, acetone, and deionized water, air-dried, and cut into pieces of ~0.2 mm with ceramic scissors. The fish and invertebrates were washed carefully with deionized water and ultrapure water, freeze-dried, mixed if the individuals were too small for analysis, and ground with an agate mortar and pestle. Based on field feeding observations of granivorous songbirds, the rice grain hulls were removed, pulverized electrically, and then passed through a 100-mesh sieve. The rice leaves were cleaned thoroughly three times with tap water and deionized water, then freeze-dried, and pulverized in the same way as the rice grains. The soil samples were air-dried, ground with a ceramic mortar and pestle, and then passed through a 200-mesh sieve.

2.2. Hg concentration analysis

2.2.1. Total Hg

Following Luo et al. (2020), 0.05–0.1 g of invertebrates, 0.1 g of fish, and 0.1 g of rice plants were digested in 5 mL of nitric acid (HNO_3), and

Table 1
Concentrations and isotopic compositions of THg and MeHg in paddy soil, rice plants invertebrates, and fish samples around a rice paddy habitat.

Samples	N[a]	THg	MeHg	MeHg%	Δ^{199}Hg (SD)	Δ^{201}Hg (SD)	δ^{202}Hg (SD)	$\Delta^{199}Hg_{MeHg}$	$\delta^{202}Hg_{MeHg}$
		μg/g	μg/g	%	‰	‰	‰	‰	‰
Paddy soil	3	30.6 ± 1.19	2.87 ± 0.01[b]	0.009	0.04 ± 0.02	−0.03 ± 0.03	−1.03 ± 0.08	0.13 ± 0.02[c]	−1.55 ± 0.23[c]
Rice leaves	3	1.08 ± 0.65	6.97 ± 0.26[b]	0.65	−0.05 ± 0.01	−0.08 ± 0.01	−2.99 ± 0.05	0.13 ± 0.04[c]	−1.13 ± 0.54[c]
Rice grains	3	0.089 ± 0.002	37.0 ± 0.70[b]	41.6	−0.06 ± 0.01	−0.11 ± 0.004	−2.05 ± 0.05	0.13[c]	−1.31[c]
Raspberry	3	0.14 ± 0.03	1.06 ± 0.05[b]	0.78	−0.06 ± 0.01	−0.01 ± 0.05	−3.38 ± 0.00		
Rice Green Stink Bugs	3	0.47 ± 0.02	0.45 ± 0.04	95.2	0.12 (0.06)	0.06 (0.08)	−2.23 (0.11)	0.12	−2.23
Katydids	2	0.71	0.11	14.8	0.05 ± 0.06	0.00 ± 0.03	−1.64 ± 0.01		
Grasshoppers	3	0.29 ± 0.01	0.03 ± 0.001	11.0	0.02 ± 0.15	−0.06 ± 0.09	−2.07 ± 0.60		
Caterpillars	3	0.83 ± 0.03	2.88 ± 0.75[b]	0.35 ± 0.10	−0.00 (0.06)	−0.13 (0.08)	−3.72 (0.11)		
Mantis	1	0.552	0.407	73.7	0.02 (0.06)	−0.03 (0.08)	−1.81 (0.11)	0.06	−1.39
Riparian spider	5	1.69 ± 0.27	0.85 ± 0.08	50.2	0.20 ± 0.06	0.14 ± 0.06	−1.48 ± 0.09		
Upland spider	3	1.06 ± 0.002	0.55 ± 0.04	52.0	−0.09 ± 0.003	−0.18 ± 0.02	−1.21 ± 0.004		
Dragonfly-1	2	0.93	0.86	92.8	0.17 (0.06)	0.06 (0.08)	−1.85 (0.11)	0.17	−1.85
Dragonfly-2	2	1.41 ± 0.04	0.79	55.9	0.21 (0.06)	0.16 (0.08)	−1.79 (0.11)		
Damselfly	2	0.99 ± 0.1	0.59 ± 0.06	59.9	0.06 ± 0.06	−0.01 ± 0.005	−2.09 ± 0.49		
Water beetles	2	1.38 ± 0.10	1.28 ± 0.06	92.8	0.54 ± 0.09	0.33 ± 0.03	−0.21 ± 0.11	0.54	−0.21
Caddisfly larvae	3	10.2 ± 3.5	0.13 ± 0.02	1.41 ± 0.5	0.10 ± 0.06	0.03 ± 0.065	−0.96 ± 0.10		
River shrimp	3	6.39 ± 1.70	0.31 ± 0.06	4.90	0.09 ± 0.04	0.03 ± 0.07	−0.79 ± 0.03		
Water striders	2	0.97 ± 0.02	0.66 ± 0.01	68.1	0.34 ± 0.01	−0.26 ± 0.004	−1.45 ± 0.04	0.49	−1.62
Sharpbelly	4	0.60 ± 0.13	0.42 ± 0.07	71.5 ± 10.7	0.30 ± 0.10	0.15 ± 0.07	−1.02 ± 0.08	0.41	−1.00
Goby fish	2	1.57 ± 0.02	0.34 ± 0.01	21.5 ± 0.46	0.10 ± 0.02	−0.05 ± 0.02	−1.28 ± 0.03		

[a] Except for soil and rice plants, N is the number of mixed samples for other taxa samples.
[b] The data displayed in ng/g.
[c] MeHg isotopes in paddy soil, rice leaves, and rice grains were cited from previous studies of Qin et al. (2020) and Li et al. (2017). Dragonfly-1 is *Orthetrum melania,* Dragonfly-2 is *Crocothemis servilia.*

0.1 g soil samples were digested in 5 mL of fresh aqua regia ($HCl:HNO_3$ = 3:1, v/v) at 95 °C for 3 h in a water bath. The THg in the biological samples was measured using a cold-vapor atomic fluorescence spectrometer Brooks Rand Model III (Brooks Rand Company, Seattle, USA) according to Method 1631E (USEPA, 2002). The THg in the soil digests was measured using a cold-vapor atomic absorption spectrometer F-732VJ (Huaguang Company, Shanghai, China), as described previously (Yin et al., 2013).

2.2.2. MeHg

MeHg concentrations were measured as described previously (Liang et al., 1994, 1996; Zhang et al., 2022). In brief, about 0.1 g samples of invertebrates, fish, and rice plant were digested with 5 mL of 25 % KOH methanol solvent for 3 h at 75 °C, and 3.7 mL of hydrochloric acid (HCl) was then added to acidify the samples. About 0.2 g soil samples were extracted using copper sulfate ($CuSO_4$). The digested solutions of plant and soil samples were then extracted with dichloromethane (CH_2Cl_2) and back-extracted into an aqueous phase for analysis. All digests were measured using a gas chromatograph cold vapor atomic fluorescence spectrometer Merx (Brooks Rand Company, Seattle, USA) according to USEPA Method 1630 (USEPA, 1998).

Because the mass of an individual feather is very low (<10 mg), we modified the reported method (Hammerschmidt and Fitzgerald, 2006) to measure MeHg and THg in the feather samples simultaneously. In brief, about 0.005 g feathers was digested using 4 mL of 4 M HNO_3 for 16 h at 55 °C, and 1 mL of the digest was used directly for MeHg determination. 3 mL of HNO_3 was added to ensure complete digestion of the remaining digests, which were then oxidized using BrCl for the THg analysis. The THg content was calculated based on the digestate volume used for MeHg analysis. In this study, the Hg concentrations are given in dry weight (d.w.) for all samples except feathers, which are given in air-dried weight (d.w.) or fresh weight (f.w.) following Abeysinghe et al. (2017) and Evers et al. (2008).

2.2.3. Quality assurance/quality control (QA/QC)

Duplicates, method blanks, and certificated reference materials (CRMs) were used to ensure the quality of the data. Tort-2 (lobster hepatopancreas, Canada) and GBW0910b (human hair, China) were used as CRMs for the biotic samples. ERM CC580 (estuarine sediment, Belgium) and GBW10020 (citrus leaves, China) were used as CRMs for the soil and rice samples, respectively. The recoveries of THg in Tort-2, ERM CC580, GBW0910b, and GBW10020 were 99.7 ± 5.1 %, 102.7 ± 2.7 %, 101.8 ± 17.3 %, and 96.3 ± 7.2 %, respectively, and the recoveries of MeHg in Tort-2 and ERM CC580 were 100.7 ± 9.9 % and 98.4 ± 10.4 %, respectively (Table S1). For the feather samples, yield recoveries of 97.8 ± 10.7 % (THg) and 101.1 ± 13.4 % (MeHg) in Tort-2 confirmed the additional HNO_3 completely digested all the MeHg in feather samples.

2.3. Stable Hg isotope analysis

The stable Hg isotope ratios were determined using a multi-collector inductively coupled plasma mass spectrometer Neptune Plus (MC–ICPMS; Thermo Scientific, USA) at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry Chinese Academy of Sciences. The bird feathers, invertebrates, soils, and rice plants were digested using similar procedures to those used for the THg analysis. The digests were filtered and diluted to 1–2 ng/mL and acid concentrations of <20 % before the Hg isotope analysis, as reported by Yin et al. (2010) and Qin et al. (2020). Isotope values are reported using the delta notation in parts per thousand (‰), and MDF (in the form δ^{xxx}Hg, where xxx refers to 199, 200, 201, or 202) and MIF (in the forms Δ^{199}Hg and Δ^{201}Hg) were calculated using the following equations, as recommended by Bergquist and Blum (2007):

$$\delta^{xxx}\mathrm{Hg} = 1000 \times \left[\left(\delta^{xxx}\mathrm{Hg}/\delta^{198}\mathrm{Hg}\right)_{sample} / \left(\delta^{xxx}\mathrm{Hg}/\delta^{198}\mathrm{Hg}\right)_{NIST\ 3133} - 1\right] \quad (1)$$

$$\Delta^{199}\mathrm{Hg} \approx \delta^{199}\mathrm{Hg} - \left(0.2520 \times \delta^{202}\mathrm{Hg}\right) \quad (2)$$

$$\Delta^{201}\mathrm{Hg} \approx \delta^{201}\mathrm{Hg} - \left(0.7520 \times \delta^{202}\mathrm{Hg}\right) \quad (3)$$

The thallium standard (NIST SRM 997) and sample–standard bracketing were used to correct for instrument bias according to Yin et al. (2016) and Foucher and Hintelmann (2006), and the Hg concentrations in the samples and acid matrices of the bracketing standard (NIST SRM 3133) were systematically matched <10 %. The CRMs of mercuric chloride standard solution NIST SRM 3177 (δ^{202}Hg = −0.53 ± 0.10 ‰, Δ^{199}Hg = 0.00 ± 0.02 ‰, n = 24, SD), lichen ERM BCR 482 (δ^{202}Hg = −1.71 ± 0.11 ‰, Δ^{199}Hg = −0.65 ± 0.03 ‰, n = 5, SD), yellow red soil GSS-5 (δ^{202}Hg = −1.85 ± 0.06 ‰, Δ^{199}Hg = −0.32 ± 0.06 ‰, n = 3, SD), and Tort-2 (δ^{202}Hg = −0.00 ‰, Δ^{199}Hg = 0.71 ‰, n = 1) were close to the data reported by Schneider et al. (2021), Estrade et al. (2010), Huang et al. (2015), and Kwon et al. (2014), as shown in Table S2.

2.4. Estimation of MeHg isotope ratios

Because the proportion of MeHg in THg (MeHg%) in the samples of songbird feathers, water beetles, rice green stink bugs, and dragonflies (*Orthetrum melania*) were > 90 %, the measured THg isotopic values ($\delta^{202}Hg_{measure}$ and $\Delta^{199}Hg_{measure}$) can be regarded as the MeHg isotopic compositions ($\delta^{202}Hg_{MeHg}$ and $\Delta^{199}Hg_{MeHg}$). However, since the THg in foliar samples occurs mainly as IHg, the measured Hg isotope ratios in rice leaves can be roughly regarded as the IHg isotopic compositions ($\delta^{202}Hg_{IHg\text{-}terr.}$ and $\Delta^{199}Hg_{IHg\text{-}terr.}$) in the terrestrial food chain. According to Tsui et al. (2012, 2014), the linear fitting of the THg isotope ratios and MeHg% was used to estimate the average isotopic compositions of IHg ($\delta^{202}Hg_{IHg\text{-}aqua.}$ and $\Delta^{199}Hg_{IHg\text{-}aqua.}$) and MeHg ($\delta^{202}Hg_{MeHg\text{-}aqua.}$ and $\Delta^{199}Hg_{MeHg\text{-}aqua.}$) in the aquatic habitat. This method of estimation resulted in MeHg isotope ratios similar to those determined directly, as verified by Rosera et al. (2022). Therefore, the MeHg isotope ratios in terrestrial and aquatic organisms with relatively higher MeHg% (i.e., > 50 %) were estimated with a binary mixture model (Eqs. (4) and (5)). In brief, based on MeHg% (f_{MeHg}, here ranging from 0 to 1) and the measured THg isotope ratios ($\delta^{202}Hg_{measure}$ and $\Delta^{199}Hg_{measure}$), the MeHg isotope ratios ($\delta^{202}Hg_{MeHg}$ and $\Delta^{199}Hg_{MeHg}$) in the biota were estimated as follows:

$$\delta^{202}Hg_{MeHg} = \left[\delta^{202}Hg_{measure} - \delta^{202}Hg_{IHg} \times \left(1 - f_{MeHg}\right)\right] / f_{MeHg} \quad (4)$$

$$\Delta^{199}Hg_{MeHg} = \left[\Delta^{199}Hg_{measure} - \Delta^{199}Hg_{IHg} \times \left(1 - f_{MeHg}\right)\right] / f_{MeHg} \quad (5)$$

2.5. Statistical analysis

All descriptive statistical analyses and linear fitting were performed using Origin Pro 2020 (Learning edition, Origin Lab, USA), and the significance level for linear fitting was set to $p \leq 0.05$.

3. Results and discussion

3.1. THg and MeHg concentrations

3.1.1. Soil and rice

The THg and MeHg concentrations are listed in Table 1. The rice paddy soil THg was 30.6 ± 1.19 μg/g on average, which exceeded the national soil pollution risk screening value for paddy soil of 1.0 μg/g THg (MEE, 2018), indicating that the rice paddies were significantly Hg-contaminated from Hg mining and retorting activities. As expected, the THg and MeHg in the rice leaves were 1.08 ± 0.65 μg/g and 6.97 ± 0.26 ng/g on average, respectively, whereas the average THg and MeHg in the rice grains were 0.089 ± 0.002 μg/g and 37.0 ± 7.03 ng/g, respectively that exceeded the national safety quality standard in rice of 20 ng/g THg (NHC, 2017). The MeHg% levels in rice paddy soil, rice leaves, and rice grains were 0.009 %, 0.65 %, and 41.6 %, respectively, similar to data reported in previous studies; i.e., 0.02 % in soils, 1.0 % in rice leaves, and 29.9–74 % in rice grains (Qin et al., 2020; Feng et al., 2016; Rothenberg et al., 2017).

3.1.2. Invertebrates and fish

Both the THg and MeHg concentrations in the invertebrate samples showed large variations. Overall, the caddisfly larvae and shrimp had the highest THg concentrations of 10.2 ± 3.51 μg/g and 6.39 ± 1.70 μg/g, respectively. As expected, carnivorous invertebrates showed higher THg concentrations than herbivorous invertebrates. The THg concentrations in riparian spider (*Tetragnatha nitens*, 1.69 ± 0.27 μg/g), dragonflies (*Crocothemis servilia*, 1.41 ± 0.04 μg/g), and water beetles (1.38 ± 0.10 μg/g) were higher than those in grasshoppers (0.29 ± 0.01 μg/g). Water beetles had the highest MeHg concentrations (1.28 ± 0.06 μg/g), followed by riparian spider (0.85 ± 0.08 μg/g) and water striders (0.66 ± 0.01 μg/g), whereas the lowest concentration was observed in caterpillars (2.88 ± 0.75 ng/g). Small fish had elevated THg concentrations of 0.60 ± 0.13 μg/g (sharpbelly) and 1.57 ± 0.02 μg/g (goby fish). Among the invertebrates, rice green stink bugs and water beetles showed the two highest MeHg% at 95.2 % and 92.8 %, respectively that is related to their intake of abundant MeHg in rice and aquatic invertebrates. Higher trophic levels of invertebrates included mantis (73.7 %), water striders (68.1 %), dragonflies (50.2–92.8 %), and two species of spiders (50.2 % and 52.0 ± 3.90 %), all contained higher MeHg% than caterpillars (0.35 ± 0.10 %), katydids (14.8 %), and grasshoppers (11.0 %) Fig. S2 and Table S3). In the aquatic habitat, water beetles (92.8 %), sharpbelly (71.5 ± 10.7 %), and water striders (68.1 %) showed much higher MeHg % than benthic goby fish (21.5 ± 0.46 %), river shrimp (4.90 %) and caddisfly larvae (1.41 ± 0.5 %).

3.1.3. Songbird feathers

THg, MeHg, and MeHg% in feathers are listed in Table 2. Overall, THg was much higher in insectivorous bird feathers than in feathers from frugivorous or granivorous birds. Among these birds, the insectivorous spot-breasted scimitar babbler had the highest average THg of 110 ± 48 μg/g, whereas the herbivorous collared finchbill had the lowest THg of 8.5 ± 1.7 μg/g that was similar to that of the piscivorous common kingfisher (9.9 ± 1.3 μg/g). High THg concentrations were also observed in the insectivorous chestnut-headed tesia (78.1 ± 14.5 μg/g) and hwamei (54.5 ± 13.6 μg/g). A large variation in Hg concentrations was observed for the insectivorous spot-breasted scimitar babbler and streak-breasted scimitar babbler, which may reflect the variability in Hg across sampling sites or prey species. The MeHg% in the feathers of all songbirds, as apex predators, were close to 90 %, supporting the notion that MeHg is the main species of Hg in adult bird feathers (Bond and Diamond, 2009; Renedo et al., 2017).

3.2. Hg isotope ratios and fractionation

3.2.1. MDF

The Hg isotopic compositions of samples from each taxon are listed in Tables 1, 2 and S4. The δ^{202}Hg of rice paddy soil was −1.03 ± 0.08 ‰, which is similar to previously reported values of −0.93 ± 0.33 ‰, −1.30 ± 0.14 ‰, and − 1.17 ± 0.01 ‰ (Feng et al., 2016; Qin et al., 2020; Chang et al., 2021). The rice grains and leaves showed relatively negative δ^{202}Hg values of −2.05 ± 0.05 ‰ and −2.99 ± 0.05 ‰, respectively, similar to previously reported values, which ranged from −2.34 ‰ to −2.16 ± 0.04 ‰ in grains and from −3.43 ± 0.06 ‰ to −3.28 ± 0.07 ‰ in leaves (Yin et al., 2013; Qin et al., 2020; Feng et al., 2016; Chang et al., 2021).

Except for katydids (−1.64 ± 0.01 ‰), the herbivorous invertebrates, including grasshoppers (−2.07 ± 0.60 ‰), rice green stink bugs (−2.23 ‰), and caterpillars (−3.72 ‰), showed lower δ^{202}Hg values, whereas the carnivorous spiders (−1.48 ‰ to −1.21 ‰), mantis (−1.81 ‰), and dragonflies (−1.85 ‰ to −1.79 ‰) showed higher δ^{202}Hg values. In comparison, sharpbelly (−1.02 ± 0.08 ‰) and goby fish (−1.28 ± 0.03 ‰), and aquatic invertebrates such as caddisfly larvae (−0.96 ± 0.10 ‰), water striders (−1.45 ± 0.04 ‰), water beetles (−0.21 ± 0.11 ‰), and river shrimp (−0.79 ± 0.03 ‰) had relatively higher δ^{202}Hg values, but with large variations, which may be related to their dietary type and MeHg%. Except for water beetles, aquatic organisms at much higher trophic levels and with much higher MeHg% will have more-negative δ^{202}Hg values.

Among the songbirds, the piscivorous common kingfisher had the highest δ^{202}Hg value (−0.75 ± 0.11 ‰), followed by the granivorous tree sparrow (−1.12 ± 0.01 ‰), the insectivorous chestnut-headed tesia (−1.18 ± 0.13 ‰) and hwamei (−1.24 ± 0.14 ‰), and the frugivorous collared finchbill (−1.25 ± 0.18 ‰) and brown-breasted bulbul (−1.15 ± 0.14 ‰), whereas the insectivorous spot-breasted scimitar

Table 2
Concentrations and isotopic compositions of Hg in bird feathers from rice paddy habitat.

Birds (ID, diets)	N	THg	MeHg%[a]	N	Δ^{199}Hg	Δ^{201}Hg	δ^{202}Hg
		μg/g	%		‰	‰	‰
Spot-breasted Scimitar Babbler (01-Sb, PI)	5	110 ± 48	93.8 ± 2.61	3	0.12 ± 0.03	0.09 ± 0.03	−1.91 ± 0.24
Streak-breasted Scimitar Babbler (02-Sb, PI)	5	26.4 ± 4.3	96.5 ± 2.66	2	0.33 ± 0.08	0.33 ± 0.5	−1.40 ± 0.03
Hwamei (03-Hw, PI)	5	54.5 ± 13.6	89.0 ± 7.41	3	0.28 ± 0.03	0.30 ± 0.03	−1.24 ± 0.14
Chestnut-headed Tesia (04-Ch, PI)	4	78.1 ± 14.5	95.1 ± 1.81	3	0.43 ± 0.06	0.37 ± 0.08	−1.18 ± 0.13
Brown-breasted Bulbul (05-Bb, PF)	4	15.1 ± 13.5	85.7 ± 3.58	2	0.40 ± 0.05	0.40 ± 0.11	−1.15 ± 0.14
Collared Finchbill (06-Cf, PF)	4	8.49 ± 1.65	91.6 ± 7.45	2	0.33 ± 0.08	0.23 ± 0.07	−1.25 ± 0.18
Tree sparrow (07-Ts, PG)	6	16.3 ± 3.4	93.1 ± 2.64	3	0.44 ± 0.02	0.31 ± 0.03	−1.12 ± 0.01
Common kingfisher (08-Ck, PP)	6	9.93 ± 1.33	93.5 ± 4.94	4	0.51 ± 0.04	0.48 ± 0.05	−0.75 ± 0.11
Russet Sparrow nestlings	40	2.54 ± 1.09	72.2 ± 13.9	3	0.46 ± 0.21	0.29 ± 0.11	−1.34 ± 0.26

Note: PI is primarily insectivorous, PF is primarily frugivorous, PG is primarily granivorous, PP is primarily piscivorous.
[a] Except for Brown-breasted Bulbul and russet Sparrow nestlings, MeHg% in other songbirds were cited from previous reported data in Abeysinghe et al. (2017).

babbler (−1.40 ± 0.03 ‰) and streak-breasted scimitar babbler (−1.91 ± 0.24 ‰) had lower values.

As shown in Fig. 1, different MDFs were observed in different trophic transfers, such as from rice leaves to grasshoppers (+0.92 ‰) and katydids (+1.35 ‰), and from rice grains to rice green stink bugs (−0.18 ‰). Compared with their diets, the granivorous and frugivorous songbirds showed large MDFs of +0.93 ‰ (tree sparrow), +2.23 ‰ (brown-breasted bulbul), and +2.13 ‰ (collared finchbill), whereas the piscivorous common kingfisher and arachnophagous chestnut-headed tesia had small MDFs of +0.25 ‰ (from sharpbelly), +0.30 ‰ (from riparian spider, *Tetragnatha nitens*), and +0.03 ‰ (from upland spider, *Argiope bruennichi*). This difference in MDF might be caused by the large variation of MeHg% in prey/diets and consumers. When the MeHg% in diets and consumers were relatively higher, a smaller MDF was observed.

3.2.2. MIF

Δ^{199}Hg in paddy soils (0.04 ± 0.02 ‰), rice leaves (−0.05 ± 0.01 ‰), and rice grains (−0.06 ± 001 ‰) were close to the previously reported values of 0.05 ± 0.01 ‰ in soil, −0.18 ± 0.05 ‰ to −0.07 ± 0.02 ‰ in rice leaves, and 0.05 ± 0.02 ‰ to 0.11 ± 0.03 ‰ in rice grains, respectively (Qin et al., 2020; Feng et al., 2016). Among the invertebrates, water beetles showed the highest value for Δ^{199}Hg (0.54 ± 0.09 ‰), whereas the lowest value for Δ^{199}Hg was observed in an upland spider (*Argiope bruennichi*, −0.09 ± 0.003 ‰). Songbird feathers were characterized by relatively high Δ^{199}Hg values, ranging from 0.28 ± 0.03 ‰ to 0.51 ± 0.04 ‰, except those of the spot-breasted scimitar babbler (0.12 ± 0.03 ‰). The feathers of the piscivorous common kingfisher, granivorous tree sparrow, and insectivorous chestnut-headed tesia showed

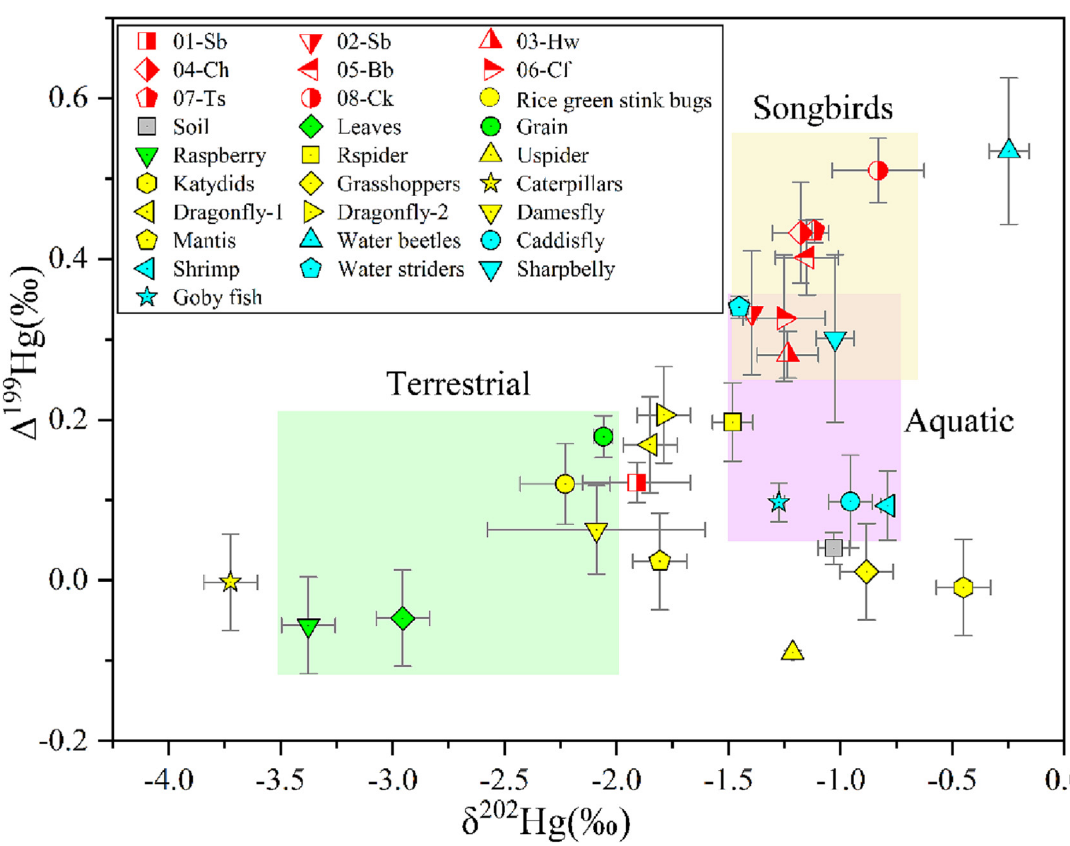

Fig. 1. Δ^{199}Hg versus δ^{202}Hg in rice paddy soil and different taxa of organisms at each trophic level in the Wanshan Hg mining area. Symbols for songbirds are listed in Table 2. Rspider is riparian spider, Uspider is upland spider. The symbol colors are as follows: white and red – songbirds; green – rice plants; yellow – terrestrial invertebrates; and blue – fish and aquatic invertebrates. Rectangles represent terrestrial (green) and aquatic (purple) Hg sources and songbirds (yellow).

the three highest Δ^{199}Hg values of 0.51 ± 0.04 ‰, 0.44 ± 0.02 ‰, and 0.43 ‰ ± 0.06 ‰, respectively.

Relatively smaller MIF values were observed in the transfers from rice leaves or rice grains to herbivorous invertebrates, such as from rice leaves to katydids (+0.10 ‰) or grasshoppers (+0.07 ‰), and from rice grains to rice green stink bugs (+0.18 ‰). These MIF values are consistent with the MIFs from grasshoppers (+0.18 ‰) and katydids (+0.15 ‰) to the riparian spider *Tetragnatha nitens*. In comparison, relatively large MIFs were observed during the trophic transfers from the diet or prey to terrestrial songbirds, such as from rice grains to tree sparrow (+0.50 ‰), spiders to chestnut-headed tesia (+0.23 ‰ and 0.52 ‰), and raspberry to brown-breasted bulbul (+0.46 ‰) and collared finchbill (+0.39 ‰).

The linear fitting slope (0.98 ± 0.03; Fig. 2) of Δ^{199}Hg versus Δ^{201}Hg in the terrestrial food chain samples (including feathers) were much closer to the slope of divalent Hg (Hg^{2+}) photochemical reduction (1.00 ± 0.01) than that of MeHg photodegradation (1.36 ± 0.04) reported by Bergquist and Blum (2007). However, the linear fitting for songbird feathers (excluding those of the common kingfisher) also showed a similar slope (1.03 ± 0.14; Fig. S3) to that for the terrestrial food chain samples, which was much lower than the slope (1.29 ± 0.22) for upland buzzard feathers on the Tibetan Plateau, where MIF is controlled mainly by MeHg photodegradation (Liu et al., 2020). Thus, in the present study, the MIF in terrestrial food chains around rice paddies may have mainly originated from the photochemical reactions of Hg^{2+}, and some Hg has undergone a photochemical reduction process before entering the food chain.

3.2.3. Estimated MeHg isotope ratios

In this study, because the p value of the linear fitting of δ^{202}Hg was >0.5, the linear fitted Δ^{199}Hg of IHg and MeHg in the aquatic food chains were 0.03 ‰ ($\Delta^{199}Hg_{IHg\text{-}aqua.}$, f_{MeHg} = 0) and 0.49 ‰ ($\Delta^{199}Hg_{MeHg\text{-}aqua.}$, f_{MeHg} = 1), respectively (Fig. S4). The Hg isotopic compositions in the rice leaves (−2.99 ± 0.05 ‰ and − 0.05 ± 0.01 ‰) can be regarded as the IHg isotope ratios ($\delta^{202}Hg_{IHg\text{-}terr.}$ and $\Delta^{199}Hg_{IHg\text{-}terr.}$) in the terrestrial habitat or food chains. In this way, the MeHg isotopic compositions in the organisms at each trophic level were estimated and listed in Table 1. Given the measured $\Delta^{199}Hg_{MeHg}$ values in rice grains (0.13 ± 0.06 ‰) reported by Qin et al. (2020) and Li et al. (2017), the estimated $\Delta^{199}Hg_{MeHg}$ values in rice green stink bugs (0.12 ‰), common kingfisher (0.51 ± 0.04 ‰), and sharpbelly (0.41 ‰), we observed negligible MIF (−0.01 ‰ and + 0.10 ‰) in the trophic transfers from diets to rice green stink bugs and common kingfisher, respectively, suggesting that MIF of MeHg is absent during the trophic transfer in both aquatic and terrestrial food chains.

3.3. Explanation of the large MIFs between songbirds and their diets

In the present study, we observed large MIFs of MeHg isotope ratios between herbivorous and granivorous songbirds and their diets, except for insectivorous songbirds. In addition to dietary intake, the authors of previous studies have reported that distinct foraging zones, changes in feeding behavior or nutritional stress, or differences in specific Hg isotope ratios across tissues and organs (Kwon et al., 2013; Renedo et al., 2018a, 2021) may cause Hg isotopic compositions variations. However, the feathers of russet sparrow nestlings in artificial nest boxes in the same area, which fed on invertebrates around the rice paddies, showed similar Δ^{199}Hg (0.46 ‰ ± 0.21 ‰, Hg occurring mainly as MeHg) to that of the other songbirds analyzed. Therefore, considering the limited foraging territories, abundant invertebrates, plant seeds, and fruits around the rice paddies, it is unlikely that changes in foraging zones, animal movements, or nutritional stress caused such large MIFs. Moreover, although little is known about the differences in the specific Hg isotopic compositions in the blood and feathers of terrestrial songbirds, the similar $\Delta^{199}Hg_{MeHg}$ values observed in the common kingfisher, wild fish (sharpbelly), and the aquatic habitat suggest that the MIF of MeHg isotope ratios in non-migratory songbird feathers can also be used to accurately identify the MeHg isotope compositions in their diets. Thus, the differences in tissue- or organ-specific isotopic compositions also did not cause the large MIFs of MeHg isotopes observed in this study.

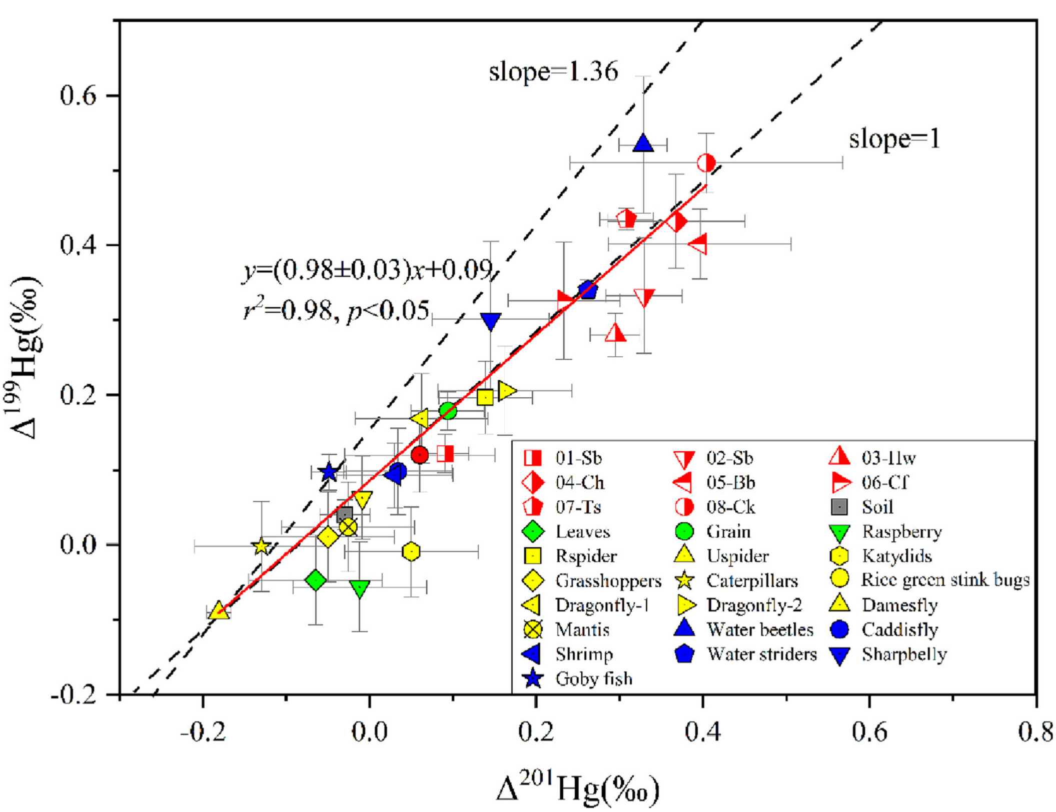

Fig. 2. Relationship between Δ^{199}Hg and Δ^{201}Hg in soil and samples from taxa (without fish or aquatic invertebrates).

Tsui et al. (2018) reported that terrestrial songbirds can acquire MeHg from beyond their habitats, particularly the aquatic habitat around which they were captured. Therefore, it is possible that the terrestrial songbirds in our study obtained Hg of aquatic origin from habitats or food chains rather than rice paddies. However, because the very low MeHg% (~0) and the relatively low MIF of the measured MeHg isotopic compositions in the rice plants (0.08–0.17 ‰, $\Delta^{199}Hg_{MeHg}$; Li et al., 2017, Qin et al., 2020) and the much lower MIF of THg isotopic compositions (~0 ‰, $\Delta^{199}Hg$) in rice plants, corn, and vegetables (Feng et al., 2016; Chang et al., 2021; Sun et al., 2019; Du et al., 2018) in Hg mining areas (Table S5), only Hg of aquatic origin or from aquatic or riparian invertebrates that is characterized by relatively high values of $\Delta^{199}Hg$ (0.17 ‰–0.53 ‰), can explain the large MIF values in songbirds, particularly herbivorous and granivorous songbirds. Therefore, we conclude that the subsidy (such as the predation of emergent insects and carnivorous spiders) of Hg that accumulated in riparian predators (spiders) is the most likely explanation of such large MIFs in terrestrial songbirds.

3.4. Identification of MeHg sources in songbirds

Based on the estimated MIF of MeHg ($\Delta^{199}Hg_{MeHg}$) and the reported $\delta^{13}C$ and $\delta^{15}N$ of organisms in both terrestrial (Abeysinghe et al., 2017) and aquatic food chains around rice paddies, we found that the MIF of MeHg ($\Delta^{199}Hg_{MeHg}$) showed a narrower range, which can be used to reveal the MeHg sources (Fig. S5). Therefore, based on the values of $\Delta^{199}Hg_{MeHg}$, the two end-members of MeHg sources of terrestrial MeHg (with average values of 0.13 ‰ for rice grains and leaves) and aquatic MeHg (0.49 ‰) were identified (Fig. 3), and the contributions of these two MeHg sources to songbirds were estimated (Table 3).

Table 3
Estimated contribution proportions of two MeHg sources in songbird samples.

Sample	Aquatic MeHg		Terrestrial MeHg	
	Range	Average	Range	Average
Spot-breasted Scimitar Babbler	−7.5– 5.8	−2.3	94.2– 108	102
Streak-breasted Scimitar Babbler	41.6– 72.3	56.9	27.7– 58.4	43.1
Hwamei	33.6– 49.8	42.4	50.2– 66.4	57.6
Chestnut-headed Tesia	65.0– 98.8	84.9	1.2– 35.0	15.1
Brown-breasted Bulbul	41.7– 72.2	57.0	27.8– 58.3	43.0
Collared Finchbill	67.1– 85.6	76.3	14.4– 32.9	23.7
Tree Sparrow	80.8– 88.4	85.6	12.4– 19.2	14.4
Common Kingfisher	89.4– 115	106	−14.6– 10.6	−6.1

As shown in Table 3, almost all the MeHg (106 %) in the piscivorous common kingfisher came from an aquatic source. In contrast, most of studied terrestrial songbirds studied were characterized by high MeHg contributions from aquatic MeHg source that is consistent with a recent study of other terrestrial songbirds by Wu et al. (2022). Aquatic MeHg contributed 86 % (range 81 %–88 %) and 84.9 % (range 65 %–99 %) of the MeHg in the granivorous tree sparrow and insectivorous chestnut-headed tesia, respectively, whereas the two MeHg sources made nearly equivalent contributions to the insectivorous streak-breasted scimitar babbler, hwamei, and the frugivorous brown-breasted bulbul. Nearly all the MeHg (102 %) in the insectivorous spot-breasted scimitar babbler came from a terrestrial MeHg source, which may reflect variability across sampling sites or prey within these species. For example, birds living around Hg mines or artificial Hg retorting contaminated areas far from aquatic habitats and who feed mainly on terrestrial invertebrates that are less impacted by aquatic origin Hg.

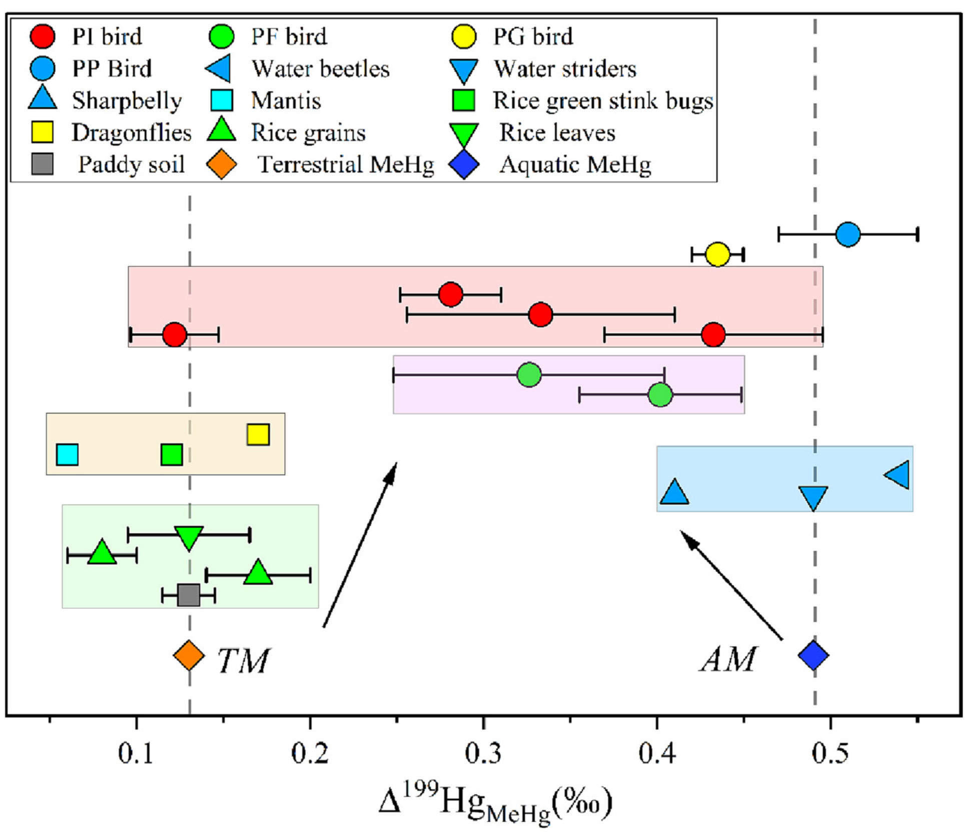

Fig. 3. Estimated MeHg isotopic compositions in songbirds and invertebrates in Hg contaminated rice paddy ecosystem. The MeHg isotope ratios in paddy soil, rice leaves, and rice grain were reported in Qin et al. (2020) and Li et al. (2017). PI, PF, PG, and PP are introduced in Table 2. Rectangles colored green, red, purple, yellow, and blue represents the MeHg isotope ratios in terrestrial plants, terrestrial insectivorous songbirds (except the spot-breasted scimitar babbler), terrestrial frugivorous songbirds, and aquatic invertebrates samples. AM and TM are aquatic MeHg and terrestrial MeHg endmembers, respectively.

The compositions of songbird diets usually change dynamically during their different life stages or in different seasons. For instance, the granivorous tree sparrow consumes more invertebrates in summer or the breeding season and more seeds or grains in winter (Holland et al., 2006; Ai et al., 2019). Moreover, the riparian spider (*Tetragnatha nitens*) always consumes high proportions of aquatic prey (Speir et al., 2014; Ortega-Rodriguez et al., 2019; Jackson et al., 2021) and receives nearly equivalent proportions of MeHg from aquatic and upland terrestrial habitats (Tsui et al., 2012). They therefore pose an elevated risk of MeHg exposure to arachnophagous songbirds (Beaubien et al., 2020). Thus, aquatic invertebrates can also be consumed by riparian predators like spiders, and transport aquatic MeHg to terrestrial songbirds indirectly, including herbivorous and granivorous songbirds (Cristol et al., 2008; Jackson et al., 2021; Wu et al., 2022).

3.5. Limitations and implications for aquatic MeHg subsidy to songbirds

The extremely high MeHg concentration in terrestrial songbird feathers has caused increasing concern about the extensive bioaccumulation and biomagnification of MeHg in terrestrial food chains in Hg mining contaminated areas. In this study, we demonstrated that the extensive MeHg biomagnification in Hg-mining-contaminated rice paddy ecosystems is not simply controlled by MeHg of terrestrial origin, and that the contribution of aquatic origin Hg must be considered when evaluating environmental Hg pollution and the exposure of wildlife, even when the apex predators do not directly prey on aquatic or riparian invertebrates.

Although Rosera et al. (2022) reported that a binary mixing model estimated MeHg isotope ratios were close to the directly measured values, the comparability of isotopic compositions obtained with the two methods still remains an unavoidable challenge. Thus, for a comprehensive interpretation of MeHg sources in rice paddy food chains, especially the trophic levels with low MeHg%, we recommend the compound-specific isotope analyses of MeHg in biological samples (Li et al., 2017; Rosera et al., 2020; Qin et al., 2020; Zhang et al., 2021) in related works in the future. Furthermore, given that we have only discussed the MeHg sources and transfer in songbirds and food chains, analyzing IHg isotope ratios would extend the understanding of Hg biomagnification and its biogeochemical behaviors in terrestrial songbirds and food chains.

4. Conclusions

In this study, large MIFs of both Hg and MeHg isotope ratios were observed between terrestrial granivorous and frugivorous songbirds and their diets. We first identified the large MIF of both Hg and MeHg isotope ratios between terrestrial granivorous and frugivorous songbirds and their diets. In Hg-contaminated rice paddy ecosystems, aquatic MeHg and Hg that are characterized by high positive MIF of both the THg and MeHg isotope ratios, contributed a comparable proportion of MeHg to those terrestrial songbirds, particularly granivorous and frugivorous songbirds. This suggests that MIF of the MeHg in resident songbird feathers can be used as an efficient tool to reconstruct MeHg sources in resident songbirds. Overall, these findings have extended the understanding of the Hg sources in terrestrial songbirds, and have demonstrated that the MeHg in terrestrial songbirds is not simply controlled by terrestrial origin MeHg, and that the subsidy of MeHg from aquatic habitats should be taken into consideration. Moreover, because we only discussed MeHg sources and feather samples from songbirds, future studies of IHg isotopes, different types of samples (blood and other organs or tissues), and long-term monitoring would extend our understanding of the sources and transfer of Hg in songbirds, and give some advice to the inescapable biodiversity protection of wildlife in Hg contaminated areas.

CRediT authorship contribution statement

Zhidong Xu: Conceptualization, Methodology, Writing- Original Draft, Writing - Review & Editing, Funding acquisition; **Qinhui Lu**: Investigation, Methodology; **Xiaohang Xu**: Visualization, Investigation. **Longchao Liang**: Investigation, Methodology; **Kasun S. Abeysinghe**: Investigation, Methodology; **Zhuo Chen**: Reviewing and Editing, Supervision; **Guangle Qiu**: Writing- Reviewing and Editing, Supervision, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests.

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Appendix A. Supplementary data

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