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Mercury flow through an Asian rice-based food web☆

Kasun S. Abeysinghe [a, b, c, d], Guangle Qiu [a, *], Eben Goodale [c, **], Christopher W.N. Anderson [e], Kevin Bishop [f, g], David C. Evers [h], Morgan W. Goodale [h], Holger Hintelmann [i], Shengjie Liu [b, d], Christos Mammides [b], Rui-Chang Quan [b], Jin Wang [b, d], Pianpian Wu [g], Xiao-Hang Xu [a, d], Xiao-Dong Yang [b], Xinbin Feng [a]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China
[b] Key Laboratory of Tropical Forest Ecology, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, Menglun, Mengla, Yunnan 666303, China
[c] Guangxi Key Laboratory of Forest Ecology and Conservation (under state evaluation status), College of Forestry, Guangxi University, Nanning, Guangxi 530005, China
[d] Graduate School of Chinese Academy of Sciences, Beijing 100049, China
[e] Soil and Earth Sciences, Institute of Agriculture and Environment, Massey University, Palmerston North 4442, New Zealand
[f] Department of Earth Sciences, Uppsala University, Villavägen, Uppsala 16, 752 36, Sweden
[g] Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Lennart Hjelmsväg 9, Uppsala, SE 75007, Sweden
[h] Biodiversity Research Institute, 276 Canco Road, Portland, ME 04103, United States
[i] Trent University, Chemistry Department, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada

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ABSTRACT

Mercury (Hg) is a globally-distributed pollutant, toxic to humans and animals. Emissions are particularly high in Asia, and the source of exposure for humans there may also be different from other regions, including rice as well as fish consumption, particularly in contaminated areas. Yet the threats Asian wildlife face in rice-based ecosystems are as yet unclear. We sought to understand how Hg flows through rice-based food webs in historic mining and non-mining regions of Guizhou, China. We measured total Hg (THg) and methylmercury (MeHg) in soil, rice, 38 animal species (27 for MeHg) spanning multiple trophic levels, and examined the relationship between stable isotopes and Hg concentrations. Our results confirm biomagnification of THg/MeHg, with a high trophic magnification slope. Invertivorous songbirds had concentrations of THg in their feathers that were 15x and 3x the concentration reported to significantly impair reproduction, at mining and non-mining sites, respectively. High concentrations in specialist rice consumers and in granivorous birds, the later as high as in piscivorous birds, suggest rice is a primary source of exposure. Spiders had the highest THg concentrations among invertebrates and may represent a vector through which Hg is passed to vertebrates, especially songbirds. Our findings suggest there could be significant population level health effects and consequent biodiversity loss in sensitive ecosystems, like agricultural wetlands, across Asia, and invertivorous songbirds would be good subjects for further studies investigating this possibility.

1. Introduction

Mercury is a well-known threat to both human and wildlife health, even at low concentrations (Mergler et al., 2007; Scheuhammer et al., 2007). The majority of global anthropogenic emissions are to the atmosphere and originate from Asia, particularly China and India (Pacyna et al., 2010) and the proportion of global output contributed by Asia is expected to increase (Streets

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* Corresponding author. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China.
** Corresponding author. Guangxi Key Laboratory of Forest Ecology and Conservation (under state evaluation status), College of Forestry, Guangxi University, 100 Daxue Road, College of Forestry Office 519, Nanning, Guangxi 530005, China.
E-mail addresses: qiuguangle@vip.skleg.cn (G. Qiu), eben.goodale@outlook.com, ebengoodale@gxu.edu.cn (E. Goodale).

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et al., 2009). The number of locally contaminated sites in Asia is also substantial (Kocman et al., 2013). Yet biomonitoring studies in Asia have concentrated mostly on animals consumed by humans, such as fish (Liu et al., 2012, 2014; Pan et al., 2014), with a general lack of attention to full food webs which can be used to assess ecosystem health. Wildlife studies have focused on invertebrates (Zhang et al., 2010c), and herons and cranes (Burger and Gochfeld, 1993; Zhang et al., 2006; Luo et al., 2014), with few studies on top predators (Guo et al., 2000) or community-wide investigations (Hsu et al., 2006). For example, there have been no studies on passerine birds (hereafter "songbirds") in Asia. Songbirds have recently been found to be especially strong accumulators of Hg in terrestrial contaminated areas (Evers et al., 2005; Cristol et al., 2008; Jackson et al., 2015), and are prone to reproductive declines due to Hg (Heinz et al., 2009; Jackson et al., 2011).

Apart from high exposure, Asia may also have different patterns of ecosystem Hg flow compared to other parts of the world. In inland regions of China, human exposure to Hg comes more from rice than fish (Zhang et al., 2010a). Mercury concentrations in fish in China are relatively low, perhaps due to the prevalence of farmed fish of short lifespan and low trophic level (Cheng and Hu, 2012), and high fishing intensity on wild fish (Feng et al., 2008; Pan et al., 2014). In contrast, rice paddies are ephemeral wetlands that are regularly flooded, facilitating the methylation process that makes Hg more biologically available (Ackerman and Eagles-Smith, 2010; Rothenberg et al., 2014) and rice grains in particular accumulate MeHg (Qiu et al., 2008; Zhang et al., 2010b). The global distribution of rice cultivation, like that of Hg emissions, is concentrated in Asia (Rothenberg et al., 2014). Rice fields provide habitat for a variety of arthropods (Chen et al., 2013; Dalzochio et al., 2016), and their vertebrate predators (Fasola and Ruiz, 1996; Elphick, 2000). Therefore, there is substantial, but undocumented, potential risk of Hg exposure for wildlife in rice-based ecosystems throughout Asia, particularly in areas of known Hg contamination.

The objectives of the Minamata Convention (International Negotiating Committee, 2013) include protecting the environment, especially when the environment directly affects public health. In different parts of Asia, hunting of wildlife such as mammals and birds is common (Yiming and Wilcove, 2005; Liang et al., 2013; Sreekar et al., 2015), and therefore high levels of Hg in wildlife can directly expose people to Hg. Where animals are confined to specific areas and consume all their diet from that area, they can be used as bioindicators of the environmental risks to people in contaminated areas, even highly contaminated areas from which people have been evacuated, but in which the efficacy of restoration needs to be evaluated. Here we report on Hg levels in mining and non-mining regions of Guizhou Province, China, in soil, rice, and a range of resident (non-migratory) animals spanning the entire food web.

2. Methods

2.1. Ethical guidelines

All samples were obtained following an agreement between the Wanshan Mercury Mine District, Leigongshan District, and the Institute of Geochemistry, Chinese Academy of Sciences. Birds were mist netted with the permission of the Guizhou Forestry Department; no species in this study was on the protected species list of China.

2.2. Sampling sites

The mining region was the Wanshan Mercury Mining District, one of Asia's largest Hg mines, with a history of Hg production that spanned 3000 years until its closure in 2001 (Dai et al., 2012; Fig. S1). The non-mining region was the Leigongshan area, about 180 km away, with a similar geological and ecological setting, but no record of mining activities. At Wanshan, Hg mine-waste is today capped under concrete, but Hg concentrations in soil samples near these caps remain high (~80 μg/g, or parts per million [ppm] THg DW) (Feng et al., 2013), and Hg concentrations in the atmosphere are elevated due to *in situ* emissions from contaminated soil (Dai et al., 2012). Human habitations have been removed from areas near the most contaminated large-scale Hg tailings at Wukeng, although people continue to come to that area to conduct agriculture. In Leigongshan, the source for Hg is deposition from the atmosphere (Fu et al., 2009; Zhang et al., 2013).

2.3. Sample collection

In Wanshan, soil, rice, herbivorous and predatory invertebrates, and frogs (hereafter referred to as "taxa with multiple sites in Wanshan"), were sampled at five sites that had different soil contamination concentrations, including sites very close to large-scale Hg tailings, a site near a small-scale artisanal mine, and downstream sites as far as 20 km away from contamination point sources (Table 1, map in Fig. S1), between August and December, 2014. At the same time, we sampled a sixth site in Leigongshan. Within each site we concentrated sampling in a rice paddy area of approximately 500 m × 500 m. For soil and rice, we set out 7 to 13 replicate 1 m^2 sampling plots, spaced at least 50 m from each other. Within each sampling plot we took 12 subsamples of approximately 50 g of soil using a corer from the 0–20 cm soil depth and

Table 1
Sample species, collection sites and tissue type.

Taxa	Sampling scheme	Tissue[a]
Soil, rice, herbivorous and predatory insects, frogs	5 sites, 0–20 km, from mines in Wanshan[b] 1 site in Leigongshan	Frogs: leg muscles (DW) Other taxa: whole sample (DW)
Fish, rats, snakes	Within 500 m of most contaminated mine in Wanshan 1 site in Leigongshan	Fish: axial muscles (DW) Rats: hair (FW) Snakes: tail tissue (DW)
Kingfishers and passerine birds	Within 4 km of large-scale mines in Wanshan 1 site in Leigongshan	Feathers (FW)
Owls	Recently captured birds from Wanshan District (within 20 km from mines) recently captured birds, Leishan District	Feathers (FW)

[a] FW = freshweight; DW = dry weight.
[b] The five sites were: 1) within 500 m of Wukeng tailing, the most contaminated site; 2) within 500 m of Meizixi, another large mercury tailing; 3) Gouxi, a small-scale artisanal mining site, now abandoned, approximately 12 km from Wukeng, but not downstream; 4) Baiguoshu, a village 8–10 km downstream from Meizixi; 5) Shenchongkou, a village 20 km downstream from both Wukeng and Meizixi.