Pure Appl. Chem., Vol. 84, No. 2, pp. 281–289, 2012.
http://dx.doi.org/10.1351/PAC-CON-11-09-16

Methylmercury in rice (*Oryza sativa L.*) grown from the Xunyang Hg mining area, Shaanxi province, northwestern China*

Guangle Qiu[1], Xinbin Feng[1,‡], Bo Meng[1], and Xun Wang[1,2]

[1]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 55002, China; [2]Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Mercury (Hg) is a global pollutant and can transform into methylmercury (MeHg), a highly toxic and bioaccumulative organic form. Recent surveys showed that rice (*Oryza sativa L.*) rather than fish is the main source of human MeHg exposure in Hg mining and retorting regions in Guizhou province, southwestern China, where rice is a traditional staple food. Here we report that MeHg in rice grown at an active Hg mining and retorting region in Shaanxi province, northwestern China, characterized with different climate compared to Guizhou, contained levels up to 240 μg kg^{-1} MeHg in bran, 78 μg kg^{-1} MeHg in polished rice, and 30 μg kg^{-1} MeHg in hull, respectively. Although the polishing process may reduce MeHg content, the mass balance calculation showed that greater than 50 % of total MeHg mass can be observed in white rice (polished rice). The ongoing Hg retorting activities, which account for the high levels of ambient air Hg, result in high levels of MeHg in rice grains. Our results further demonstrate that the accumulation of MeHg is a common feature of rice.

Keywords: methylmercury; mercury mining activity; northwestern China; rice.

INTRODUCTION

Mercury (Hg) is a highly toxic element because of its accumulative and persistent character in the environment and biota. Its toxicity always depends on chemical forms [1]. Methylmercury (MeHg), an organic form, as the major causative agent in Minamata disease is well known for its bioaccumulation and biomagnification in fish. Consumption of fish is currently considered as the primary pathway of human exposure to MeHg, posing a worldwide human health threat [2,3]. Hg concentrations in most foodstuffs rather than fish are below 20 μg kg^{-1}, and mainly present in inorganic forms [4]. Under certain conditions, however, inorganic forms can be converted to organic forms [3,5]. Hence, the primary concern about Hg is the conversion from inorganic Hg to MeHg.

Recent bio-geochemical studies on Hg mining and retorting areas in China revealed that the rice is heavily contaminated with not only inorganic Hg but also MeHg [6–11]. And, therefore, human MeHg exposure would occur through rice ingestion in the region, where rice is a staple food. The concentrations of MeHg in edible parts (seed) of rice from Wanshan (the largest abandoned Hg mining site in China), for instance, were up to 140 μg kg^{-1} and up to 170 μg kg^{-1} from Tongren (an active artisanal Hg retorting site) [6,7]. A positive correlation between MeHg concentrations in inhabitants' hair and

---

Pure Appl. Chem. **84**, 169–333 (2012). A collection of invited papers based on presentations at the 4th International IUPAC Symposium on Trace Elements in Food (TEF-4), Aberdeen, UK, 19–22 June 2011.

‡Corresponding author: Tel.: +86-851-5891356; Fax: +86-851-5891609; E-mail: fengxinbin@vip.skleg.cn

rice consumption was observed, confirming that rice consumption is an important pathway of human MeHg exposure [8]. Estimated values of MeHg exposure to inhabitants through rice consumption exceed international guidelines, which contributes 94–96% of the total, and only 1–2% through fish [7,9].

Further, Meng et al. [10,11] demonstrated that the seed of rice has the highest accumulation for MeHg compared to other tissues and the paddy soil is the potential MeHg source. They found that MeHg in soil was firstly absorbed by roots and then translocated to the above-ground parts (stalk and leaf), and finally transferred to seed during the ripening period. Finally, it was revealed that the newly deposited Hg is more readily transformed to MeHg and accumulated in rice plants than Hg forms with an extended residence time in soil.

China is rich in Hg and has many large Hg mines, which are situated in Guizhou, Yunnan, Chongqing, Hunan, and Shaanxi provinces. Most of the Hg mines had experienced a long-term history of mining and retorting. To date, however, little data for MeHg in rice has been reported on other Hg mining and retorting sites except for Guizhou province. Therefore, the MeHg bioaccumulation and its distributions in rice plants grown in other Hg mining regions in China are still unknown. It is necessary to investigate MeHg in rice from other regions for a better understanding of its bio-geochemical processes impacted by Hg mining and retorting.

The Xunyang Hg deposit that is located in the southern part of Shaanxi province, northwestern China, currently is the largest active Hg-producing district in China. Hg mining and retorting at Xunyang was initiated in the Spring and Autumn and the Warring Periods (770 B.C.). Significant quantities of calcines were piled near Hg mine processing sites and retorting sites. To date, few geochemical studies relating to Hg contamination to the local environment has been conducted at Xunyang [12]. Total Hg concentrations in surface water emanating from calcines were recently reported to be up to 20 μg L^{-1}, total Hg concentrations in sediment were reported to reach up to 2100 mg kg^{-1}, and total Hg concentrations in soil collected from the vicinity of a retort in the Xunyang area are as high as 750 mg kg^{-1}.

To better understand MeHg bioaccumulation and distribution in rice plants, we measured MeHg concentrations in tissues of rice plants collected from Xunyang, the largest active Hg-producing district in northwestern China. The primary objectives are (1) to investigate MeHg concentrations and distribution in tissues of rice plants; (2) to demonstrate the accumulation of MeHg is a common feature of rice; and (3) to further understand potential bioaccumulation pathways of MeHg in rice plants.

EXPERIMENTAL

Study area

The Xunyang County (N: 32°29'–33°13', E: 108°58'–109°48') is located in the south of Shaanxi province, covering approximately 3550 km^2, with a population of 450 000. It has a northern, subtropical humid climate characterized with an average annual rainfall of 850 mm. The annual average temperature is 15.4 °C, with the highest value of 41.5 °C occurring in July.

Hg mineral deposits in Xunyang are located at Gongguan and Qingtonggou, covering an area of about 260 km^2. The dominant ore mineral is cinnabar, and Sb-rich minerals are also observed as associate minerals. The Hg mining activities in Xunyang are located at Gongguan and Qingtonggou, adjacent to the headwater of the Gongguan and Zhutong Rivers, respectively (Fig. 1). The Hg retorting facility, the largest active Hg-producing center in China, is located at Qingtonggou. A collection dam is located nearby the retorting site. Significant quantities of calcines were piled in spoil heaps in the dam. Mine drainage water flowing through the calcines and waste water discharged from the dam directly flow into the Zhutong River. Currently no retorting facility is observed at Gongguan, but large quantities of abandoned mine-wastes and waste rocks were uncontrollingly piled along the bank of the

Fig. 1 Map of the study area and the primary regions where rice MeHg studies (Guizhou province, gray) were conducted in China.

Gongguan River. Owing to the drainage and mine-wastes discharges from mining and retorting, the Gongguan and Zhutong Rivers were contaminated with Hg.

Materials

Forty-two rice grains as well as 10 whole rice plant samples (*Oryza sativa L.*) were collected from the vicinity of Hg mining areas (from mining sites of Gongguan and Qingtonggou, and retorting site of Qingtonggou) along the Gongguan and Zhutong Rivers during the rice harvest season in 2009 and 2010, respectively. Each sample comprised a composite of at least five subsamples within an area of about 5–10 m^2 in the same paddy field, and the amount of each sample was recorded. The collected rice samples were cropped on a regular basis for human consumption. The irrigating water of the sampled rice paddies was from the Gongguan and Zhutong Rivers, which were contaminated with Hg owing to Hg mining and retorting activities, respectively.

Sample preparation

The whole rice plant was divided into four fractions, namely, root, stalk, leaf, and seed. For the grain sample, its hull, bran, and polished rice were separated using a pestle and mortar in the laboratory. Then the mass of polished rice, bran, and hull were recorded, which generally account for 57, 12, and 31 % on average, respectively. All samples were cleaned using drinking water in situ followed by deionized water rinses after being brought back to the laboratory, and finally air-dried and stored in polyethylene bags to avoid cross-contamination. All samples were ground to 150 meshes per inch (IKA-A11 basic, IKA, Germany) prior to MeHg analyses.

Measurements

Approximately 0.2–0.3 g of a rice plant sample was digested using a KOH-methanol/solvent extraction technique for MeHg analysis [13]. In this process, samples were first digested with 25 % KOH/CH_3OH and heated at 75–80 °C in a water bath for 3 h. After that, the digests were acidified with concentrated HCl. Then MeHg in samples was extracted with methylene chloride as well as back-extracted from the solvent phase into water and aqueous phase ethylation. The ethylanalogue of MeHg, methylethyl mercury ($CH_3CH_3CH_2Hg$), was separated from solution by purging with N_2 onto a Tenax trap. The trapped $CH_3CH_3CH_2Hg$ 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 (800 °C) and analyzed by CVAFS (Brooks Rand model III, Brooks Rand Laboratories, Seattle, WA) following U.S. Environmental Protection Agency (EPA) method 1630 [13,14].

Quality assurance and quality control were determined using duplicates, method blanks, matrix spikes, and certified reference materials (TORT-2). The limit of determination was 0.003 μg kg^{-1} in rice samples. An average MeHg concentration of 151 ± 7.1 μg kg^{-1} ($n = 5$) was obtained from TORT-2 comparable with the certified value of 152 ± 13 μg kg^{-1}. Recoveries on matrix spikes of MeHg in samples were in the range of 83–120 %. The relative percentage difference was <10 % in duplicate samples.

RESULTS AND DISCUSSION

MeHg concentrations in grain, root, stalk, and leaf

MeHg concentrations varied widely in polished rice, bran, and hull of the grain. The highest concentrations of MeHg were observed in bran, ranging from 26 to 240 μg kg^{-1}, with a mean value of 69 μg kg^{-1}. The polished rice also exhibited high MeHg concentrations, ranging from 4.0 to 78 μg kg^{-1}, with a mean value of 17 μg kg^{-1}. The lowest concentrations of MeHg were found in hull, ranging from 3.0 to 30 μg kg^{-1}, with a mean value of 8.4 μg kg^{-1}.

White rice (polished rice) is more commonly consumed in the study area, and the mass for MeHg in the polished rice as well as the bran and hull were calculated. Data indicated that most of the MeHg is accumulated in polished rice, then bran, and the lowest is hull, which accounted for 52, 35.7, and 12.3 % of total MeHg mass, respectively. Although the polishing process may reduce the concentrations of trace elements [15,16], the largest mount of MeHg of the total is in the polished rice. However, because the left parts of bran and hull, in which the MeHg mass can reach 48 % of the total, will be fed to livestock, it will also cause health risks to humans through food chains.

Low concentrations of MeHg were found in other tissues of rice compared to that of grain, ranging from 0.55 to 3.4 μg kg^{-1} in leaf, 2.0 to 12 μg kg^{-1} in stalk, 1.8 to 13 μg kg^{-1} in root, respectively. The mean values of MeHg were 1.7 μg kg^{-1} in leaf, 4.7 μg kg^{-1} in stalk, and 5.2 μg kg^{-1} in root, respectively. Analytical data for MeHg concentrations in rice tissues exhibited the following distribution patterns: grain > root > stalk > leaf (Fig. 2), which was in agreement with previous results observed from the Guizhou province [11].

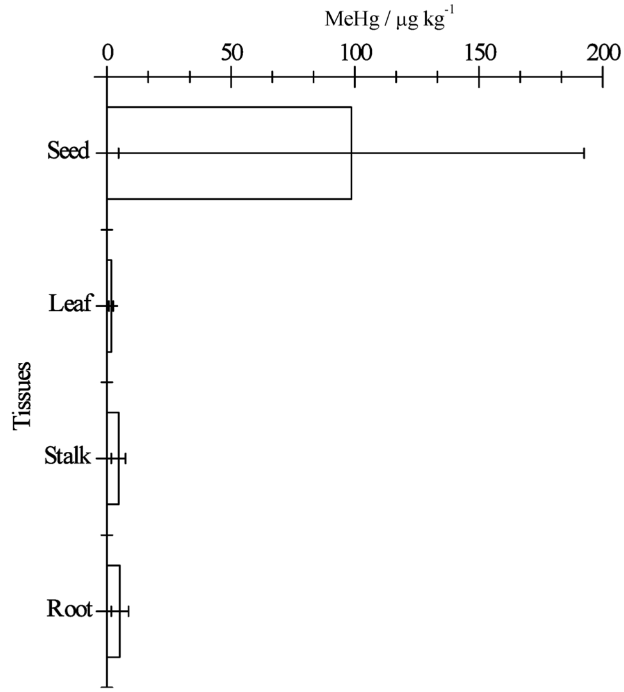

Fig. 2 MeHg concentrations in tissues of the rice grown from Xunyang Hg-Sb mining areas (MeHg in seed does not include bran and hull).

Our results for MeHg concentrations indicated that the rice grown in the Xunyang Hg mining and retorting areas was contaminated with MeHg in a certain level. In general, Hg concentrations in most crops are below 20 µg kg^{-1}, which is the maximum permissible limit recommended by Chinese National Standard Agency [17], and mainly in inorganic forms. The highest concentration of MeHg in grain was significantly higher than the food standard even for total Hg, posing a potential threat to the health of the residents [12].

Table 1 shows that significantly positive correlations between MeHg in root and grain (polished rice, bran, and hull) were observed. However, the correlations between MeHg concentration in stalk, leaf, and grain (polished rice, bran, and hull) were not significant. This implied that MeHg in root, rather than stalk and leaf, controls the distribution of MeHg in grain. Previous studies revealed that organic Hg in plant can be transported much more easily than inorganic Hg, and the phytochelatins, small peptides that detoxify plants from heavy metals can sequester Hg^{2+} but not MeHg [18,19]. Moreover, Meng et al. [10] demonstrated that MeHg in rice field, a wetland known as a net source of MeHg [20,21], was the only source of MeHg to root. Hence, the result indicates that MeHg in grain is associated with the MeHg level in root.

Table 1 Pearson's correlation matrix, giving the linear correlation coefficients (r) among the MeHg levels in tissues of rice plant (n = 10).

	Polished rice	Bran	Hull	Leaf	Stalk	Root
Polished rice	1					
Bran	0.995[a]	1				
Hull	0.950[a]	0.928[a]	1			
Leaf	0.279	0.255	0.323	1		
Stalk	0.281	0.216	0.361	0.657[b]	1	
Root	0.745[b]	0.685[b]	0.837[a]	0.460	0.611	1

[a]Correlation is significant at the 0.01 level (2-tailed).
[b]Correlation is significant at the 0.05 level (2-tailed).

Effect of active retorting on MeHg in rice grain

MeHg concentrations in rice grains (polished rice) collected around the Hg retorting site (Qingtonggou) were characterized by the highest concentration of 78 μg kg^{-1} adjacent to the retorting site, then decreased to 20 μg kg^{-1} at the site about 1 km away from the retorting site. And at the site about 15 km, MeHg concentrations in rice grain were below 10 μg kg^{-1} (Fig. 3).

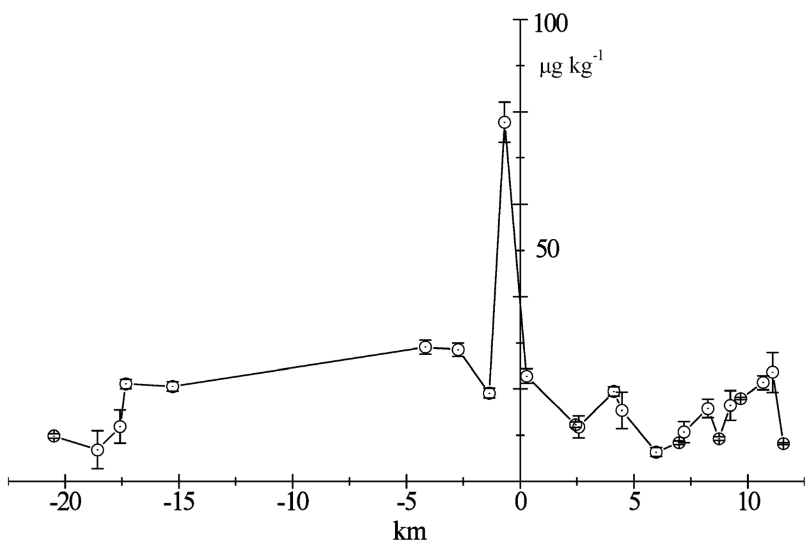

Fig. 3 Distribution of MeHg in seed distant from the Hg retorting site (0 km is the retorting site).

Meng et al. [11] considered that the high MeHg concentrations in soil at an ongoing mining site can be attributed to the newly deposited Hg, which is more readily transformed to MeHg [22]. And Harris et al. [23] demonstrated that an increase in Hg loading at rates resembling atmospheric deposition resulted in an increase in MeHg production and concentrations in aquatic fresh water biota. Hence, we suggest that the ongoing Hg retorting activities may result in high Hg deposition into adjacent rice paddies, which is more readily transformed into MeHg and bioaccumulated in rice grain, resulting in the high MeHg concentrations in seed.

Calculation of daily MeHg intake rate

The daily per capita consumption of rice in 2010 in China was 200 g dry weight per day for adults with an average weight of 60 kg, according to the National Bureau of Statistics of China. Assuming the absorption of MeHg in bodies was 100 %, we roughly calculated adult daily intake of MeHg via rice consumption. For an adult, routine consumption of 200 g per day of rice containing the average MeHg concentration of 17 μg kg^{-1} obtained in our study would provide MeHg intake of 0.057 μg kg^{-1} body weight per day. This value is lower than the new dietary reference dose (RfD) of 0.23 μg kg^{-1} body weight per day for MeHg recommended by the UN Committee [24] and the RfD of 0.1 μg kg^{-1} body weight per day for MeHg exposure recommended by the EPA [25]. For the peak value of 78 μg kg^{-1}, however, we could get extremely high MeHg intake of 0.26 μg kg^{-1} body weight per day, which exceeds the RfDs recommended by both the UN Committee and the EPA. This indicates that MeHg exposure through rice eating may constitute health risks to the local residents in Xunyang. Apparently, the groups living in Qingtonggou were heavily exposed to MeHg, which resulted from the abnormally high MeHg levels in rice. Therefore, the rice yielded from the Hg mines in Xunyang contained concentrations of this neurotoxin high enough to cause exposure risks to the local people.

Comparison of MeHg concentrations

The comparison of MeHg concentrations in rice among this study and other data from different regions in Guizhou province is shown in Table 2. It is shown that the rice grown from the sites impacted by both Hg mining and retorting (Wanshan, Tongren, Wuchuan, and Xunyang) and chemical and coal-fired facilities (Qingzhen) had higher MeHg concentrations than that from the control site (Huaxi). The highest MeHg concentrations were generally present in active Hg mining and retorting regions at Tongren, Xunyang, and Wanshan (closed in 2002). The documented maximum value was 174 μg kg^{-1} obtained from an active artisanal Hg retorting site in Gouxi, Tongren County. The MeHg levels in rice in the study area were highly elevated compared with other studies from other Hg mines except for the active artisanal retorting site, with an elevated average value of 17 μg kg^{-1}. Although only a small amount of data are available, a high MeHg concentration of 28 μg kg^{-1} was observed in rice grown from Qingzhen County, a region impacted by both a coal-fired power plant and a chemical plant.

Table 2 MeHg concentrations in rice grown from various sites in Guizhou and Shaanxi.

Location and description		MeHg/μg kg^{-1}				References
		Range	Mean	STD	N	
Guizhou	Abandoned Hg mining region at Wanshan	1.2–144	10.6	14.4	154	[6,7,9,11,26]
	Abandoned Hg mining region at Wuchuan	1.2–17.9	8.4	4.3	26	[27,39]
	Active artisanal Hg mining region at Tongren	10.1–174	45.3	34.7	40	[7,11]
	Coal-fired power plant & Chemical plant at Qingzhen	0.71–28	11.3	12.8	4	[6]
	Control site at Huaxi	1.8–4.5	2.9	1.0	11	[11]
Shaanxi	Active Hg mining region at Xunyang	3.9–77.8	17.1	10.8	52	This study

Elevated atmospheric Hg concentrations can be found in ambient air at those Hg mining and retorting sites during the process of cinnabar ores retorting [11,28–30]. Similarly, high concentrations of atmospheric Hg can also be observed around the coal-fired power plant and chemical plant, which emit Hg through exhausts [31–34]. High concentrations of Hg adjacent to cinnabar ores retorting sites will result in elevated Hg deposition fluxes. Those new deposits of Hg, which are more readily transformed to MeHg [10,11,23,35–38], may attribute to high levels of MeHg in rice.

CONCLUSIONS

Our study confirmed the occurrence of elevated MeHg in tissues of rice plant cultivated in Hg mining areas. The highest values of MeHg in grains were found at the retorting site, which is attributed to the serious Hg contamination in rice paddies through elevated Hg deposition. The results confirmed that rice grain has the highest ability to bioaccumulate MeHg compared to other parts of rice plant. More studies are needed to understand the bioavailability and uptake of MeHg from paddy soil to rice. Consequently, the systematic assessment of human exposure to MeHg and biomonitoring measurements remain to be further investigated in this region.

ACKNOWLEDGMENTS

This study is supported by Chinese Academy of Sciences (KZCX2-YW-JC101) and the Natural Science Foundation of China (41073098, 41030752, and 41173126).

REFERENCES

1. T. W. Clarkson. *J. Trace Elem. Exp. Med.* **11**, 303 (1998).
2. T. W. Clarkson. *Environ. Health Perspect.* **100**, 31 (1993).
3. WHO. International Programme on Chemical Safety, Environmental Health Criteria 101: Methylmercury, World Health Organization, Geneva (1990).
4. WHO. International Programme on Chemical Safety, Environmental Health Criteria 101: Inorganic Mercury, World Health Organization, Geneva (1991).
5. D. W. Boening. *Chemosphere* **40**, 1335 (2000).
6. M. Horvat, N. Nolde, V. Fajon, V. Jereb, M. Logar, S. Lojen, R. Jacimovic, I. Falnoga, L. Qu, J. Faganeli, D. Drobne. *Sci. Total Environ.* **304**, 231 (2003).
7. G. Qiu, X. Feng, P. Li, S. Wang, G. Li, L. Shang, X. Fu. *J. Agric. Food Chem.* **56**, 2465 (2008).
8. X. Feng, P. Li, G. Qiu, S. Wang, G. Li, L. Shang, B. Meng, H. Jiang, W. Bai, Z. Li, X. Fu. *Environ. Sci. Technol.* **42**, 326 (2008).
9. H. Zhang, X. Feng, T. Larssen, G. Qiu, R. D. Vogt. *Environ. Health Perspect.* **118**, 1183 (2010).
10. B. Meng, X. Feng, G. Qiu, Y. Cai, D. Wang, P. Li, L. Shang, J. Sommar. *J. Agric. Food Chem.* **58**, 4951 (2010).
11. B. Meng, X. Feng, G. Qiu, P. Liang, P. Li, C. Chen, L. Shang. *Environ. Sci. Technol.* **45**, 2711 (2011).
12. L. Zhang, Y. Jin, J. Lu, C. Zhang. *Appl. Geochem.* **24**, 950 (2009).
13. L. Liang, M. Horvat, E. Cernichiari, B. Gelein, S. Balogh. *Talanta* **43**, 1883 (1996).
14. U.S. EPA. *Method 1630. Methylmercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS*, Draft January 2001, pp. 1–41, U.S. Environmental Protection Agency, Washington, DC (2001).
15. C. P. Villareal, J. W. Maranville, B. O. Juliano. *Cereal Chem.* **68**, 437 (1991).
16. R. J. B. Heinemann, P. L. Fagundes, E. A. Pinto, M. V. C. Penteado, U. M. Lanfer-Marquez. *J. Food Compost. Anal.* **18**, 287 (2005).
17. CNSA. *Tolerance Limit of Mercury in Foods* (in Chinese), pp. 171–173, Chinese National Standard Agency (1994).
18. D. Schwesig, O. Krebs. *Plant Soil* **253**, 445 (2003).

19. E. M. Krupp, A. Mestrot, J. Wielgus, A. A. Meharg, J. Feldmann. *Chem. Commun.* **28**, 4257 (2009).
20. B. A. Branfireun, N. T. Roulet, C. A. Kelly, J. W. M. Rudd. *Global Biogeochem. Cycles* **13**, 743 (1999).
21. M. E. Galloway, B. A. Branfireun. *Sci. Total Environ.* **325**, 239 (2004).
22. B. A. Branfireun, D. P. Krabbenhoft, H. Hintelmann, R. J. Hunt, J. P. Hurley, J. W. M. Rudd. *Water Resour. Res.* **41**, 1 (2005).
23. R. C. Harris, J. W. M. Rudd, M. Amyot, C. L. Babiarz, K. G. Beaty, P. J. Blanchfield, R. A. Bodaly, B. A. Branfireun, C. C. Gilmour, J. A. Graydon, A. Heyes, H. Hintelmann, J. P. Hurley, C. A. Kelly, D. P. Krabbenhoft, S. E. Lindberg, R. P. Mason, M. J. Paterson, C. L. Podemski, A. Robinson, K. A. Sandilands, G. R. Southworth, V. L. S. Louis, M. T. Tate. *Proc. Natl. Acad. Sci. USA* **104**, 16586 (2007).
24. WHO. UN committee recommends new dietary intake limits for mercury. Available: <http://www.who.int/mediacentre/news/notes/2003/np20/en/index.html> (cited 16 September 2011) (2003).
25. U.S. EPA. *Mercury Study Report to Congress*, Report No. EPA-452/R-97-003, Environmental Protection Agency, Washington, DC (1997).
26. P. Li, X. Feng, G. Qiu, L. Shang, G. Li. *Environ. Geochem. Health.* **31**, 683 (2009).
27. P. Li, X. Feng, G. Qiu, L. Shang, S. Wang. *Sci. Total Environ.* **395**, 72 (2008).
28. S. Wang, X. Feng, G. Qiu, Z. Wei, T. Xiao. *Atmos. Environ.* **39**, 7459 (2005).
29. S. Wang, X. Feng, G. Qiu, X. Fu, Z. Wei. *Atmos. Environ.* **41**, 5584 (2007).
30. S. Wang, X. Feng, G. Qiu, L. Shang, P. Li, Z. Wei. *Atmos. Environ.* **41**, 5984 (2007).
31. L. Chen, Y. Duan, Y. Zhuo, L. Yang, L. Zhang, X. Yang, Q. Yao, Y. Jiang, X. Xu. *Fuel* **86**, 603 (2007).
32. S. Tang, X. Feng, J. Qiu, G. Yin, Z. Yang. *Environ. Res.* **105**, 175 (2007).
33. L. Zhang, Y. Zhuo, L. Chen, X. Xu, C. Chen. *Fuel Process. Technol.* **89**, 1033 (2008).
34. S. Wang, L. Zhang, G. Li, Y. Wu, J. Hao, N. Pirrone, F. Sprovieri, M. Ancora. *Atmos. Chem. Phys.* **10**, 1183 (2010).
35. H. Hintelmann, R. Harris, A. Heyes, J. P. Hurley, C. A. Kelly, D. P. Krabbenhoft, S. Lindberg, J. W. Rudd, K. J. Scott, V. L. St. Louis. *Environ. Sci. Technol.* **36**, 5034 (2002).
36. M. Paterson, P. Blanchfield, C. Podemski. *Can. J. Fish. Aquat. Sci.* **63**, 2213 (2006).
37. D. M. Orihel, M. J. Paterson, P. J. Blanchfield, R. A. Bodaly, H. Hintelmann. *Environ. Sci. Technol.* **41**, 4952 (2007).
38. D. M. Orihel, M. J. Paterson, P. J. Blanchfield, R. A. Bodaly, C. C. Gilmour, H. Hintelmann. *Environ. Pollut.* **154**, 77 (2008).
39. G. Qiu, X. Feng, S. Wang, L. Shang. *Environ. Pollut.* **142**, 549 (2006).

