E3S Web of Conferences **1**, 15001 (2013)
DOI: 10.1051/e3sconf/20130115001
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Methylmercury Accumulation in Rice Grain (*Oryza sativa* L.): Environment and Genotype Controls

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Abstract. In 2010, 50 *indica* rice varieties were cultivated in three sites in southwestern China along a contamination gradient (background, moderately-contaminated and highly-contaminated sites) to determine environment and genotype controls on MeHg accumulation in polished white rice and bran. Rice grain MeHg concentrations were significantly higher in the moderately-contaminated site compared to the other two sites (ANOVA, $p<0.0001$). Lower rice grain MeHg concentrations in the highly-contaminated site possibly reflected differences in surface water pH (highly-contaminated site: pH 11, other two sites: pH 7.6-8.0). More alkaline conditions at the highly-contaminated site possibly decreased the bioavailability of MeHg and/or other trace elements, thus lowering the uptake of MeHg from paddy soil to rice grain. Polished white rice MeHg concentrations were significantly associated with rice genotype ($p<0001$), indicating there may be genetic markers associated with the translocation of MeHg from the maternal tissue to the filial tissue (i.e., from the bran to the polished grain). Additionally, low MeHg-accumulating rice varieties were identified, which decreased MeHg exposure up to 69%, and may be recommended to farmers to mitigate MeHg accumulation in rice grain.

Key words: methylmercury, genotype, rice, bioavailability, mitigation

Introduction

Mercury (Hg) is a global pollutant and potent neurotoxin. China is the world's highest emitter of Hg primarily due to reliance on coal combustion for power and residential heating (Pacyna et al., 2010). China is also the largest producer of rice, generating 29% of the global rice supply in 2009 (IRRI, 2012). In Guizhou province, southwestern China, a 600-year legacy of Hg mining contaminated the soil, water and air (Feng et al., 2008). Although Hg mining officially ended in 2002, mine tailings are routinely smelted in the surrounding countryside, releasing fugitive Hg emissions to nearby rice paddies (Li et al., 2009). Fish ingestion is the primary human exposure pathway for methylmercury (MeHg); however, in some villages in the Hg mining region of Guizhou province, rice ingestion is also an important MeHg exposure pathway (Feng et al., 2008; Horvat et al., 2003; Rothenberg et al., 2011; Zhang et al., 2010).

The primary aim of this study was to investigate environment and genotype controls on MeHg accumulation in rice grain, and to identify mitigation strategies for communities where rice is a staple food and Hg contamination is elevated. To the best of our knowledge, this is the first study to address the contribution of genotype to MeHg accumulation in white rice, and the first study to report bran MeHg concentrations.

Materials and Methods

Three rice paddies were selected in Guizhou province, southwestern China, including the background site (located at the Guizhou Rice Research Institute) and the moderately- and highly-contaminated sites (both located in the Hg mining area). In April 2010, 50 *indica* rice varieties were germinated at the Guizhou Rice Research Institute and then transplanted to the rice paddies in the Hg mining area. In August 2010 before rice paddies were drained, sediment cores were extracted from the 3 paddy fields to determine pore water and paddy soil (0-2 cm depth) concentrations of total Hg (THg) and MeHg. At harvest, rice seeds were collected within each site, then de-hulled and polished, yielding bran and polished white rice samples for analyses.

THg was analyzed in pore water following EPA Method 1631, using cold vapor atomic fluorescence spectrometry (CVAFS) (USEPA, 2002), and THg in paddy soil, bran and white rice was analyzed using thermal decomposition and atomic absorption spectormetry following EPA Method 7473 (USEPA, 2007). Pore water MeHg concentrations were analyzed by distillation, ethylation, pyrolysis, separation by gas chromatography and CVAFS following EPA Method 1630 (USEPA, 2001). Paddy soil, bran and white rice MeHg concentrations were analyzed following solvent extraction (Liang et al., 1996, 2004), then MeHg was quantified using the same methods described for pore water MeHg concentrations following EPA Method 1630.

Results and Discussion

Pore water and paddy soil THg and MeHg concentrations were poor predictors of rice grain THg and MeHg concentrations. Highest rice grain THg and MeHg concentrations were observed in the moderately-contaminated site for all 50 rice varieties, despite lower THg concentrations in pore water and paddy soil. At the moderately-contaminated site, average white rice THg concentrations were 6.6 and 42 times higher compared to the highly-contaminated and background sites, respectively, while average white rice MeHg concentrations were 6.3 and 32 times higher compared to the highly-contaminated and background sites, respectively. The following hypotheses are considered. Although Hg may be toxic to plants (Patra and Sharma, 2000), in situ pore water THg concentrations at the highly-contaminated site were 2-6 orders of magnitude lower compared to Hg concentrations typically used by researchers to investigate Hg phytotoxicity (e.g. Patra and Sharma, 2000), indicating pore water THg concentrations at the highly-contaminated site were not likely high enough to stress rice plants and inhibit the translocation of Hg species from paddy soil to rice grain. Instead, site-level differences with respect to surface water pH may affect Hg bioavailability. The highly-contaminated site was located downstream from several calcine piles and surface water pH was more alkaline (pH 11) compared to the moderately-contaminated (pH 7.5) and background (pH 8.0) sites. Highly alkaline conditions possibly reduced the bioavailability of Hg species (e.g., Haitzer et al., 2003), thus limiting the uptake of MeHg from paddy soil by rice roots.

The contribution of rice genotype was assessed by standardizing concentrations of MeHg and inorganic Hg^{2+} (IHG=THg-MeHg), i.e., subtracting the site-level mean and dividing by the site-level standard deviation. Rice genotype was important for explaining variability in white rice MeHg concentrations (ANOVA, $p<0.001$), but was not important for explaining white rice IHg concentrations or concentrations of bran MeHg and IHg. Results suggest there may be genetic markers associated with the translocation of MeHg from the maternal tissue (i.e., bran) to the filial tissue (i.e., white rice).

The primary goal of this study was to establish mitigation strategies for rice farmers living in Hg-impacted regions. Low MeHg-accumulating rice varieties were identified, which will reduce MeHg exposure up to 69%, thus improving the health of farmers and surrounding communities, which depend on rice as a staple food.

Conclusions

Both environment and genotype controls contributed to MeHg accumulation in polished white rice. More alkaline conditions at the highly-contaminated site possibly reduced the bioavailability of Hg species, preventing MeHg uptake in rice grain. Efforts to improve the nutritional quality of rice grain through identification of genetic markers associated with the uptake of methylated species (e.g., organo-arsenic species) should also consider the effect on MeHg accumulation. Lastly, this study identified low MeHg-accumulating rice varieties commonly grown in southwestern China, which may be recommended to rice farmers to reduce MeHg exposure through rice ingestion by up to 69%.

Acknowledgements

S.E.R. was supported by the U.S. National Science Foundation International Research Fellowship Program (grant 0802014) and S.E.R. and X.F. were supported by the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Guiyang, China.

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