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Investigation of biogeochemical controls on the formation, uptake and accumulation of methylmercury in rice paddies in the vicinity of a coal-fired power plant and a municipal solid waste incinerator in Taiwan

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HIGHLIGHTS

- Field campaigns at paddies over a rice-growing season were conducted.
- High Hg-methylation potential occurred at the rice mid-growing season.
- Detection of *hgcA* in all soil samples confirmed the prevalence of Hg-methylators.
- Sulfate-reducers might have been the principal Hg-methylators at the study sites.
- Pore-water chemical speciation controls the uptake of methylmercury in rice roots.

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ABSTRACT

Recent studies have shown that rice consumption is another critical route of human exposure to methylmercury (MeHg), the most toxic and accumulative form of mercury (Hg) in the food web. Yet, the mechanisms that underlie the production and accumulation of MeHg in the paddy ecosystem are still poorly understood. In 2013 and 2014, we conducted field campaigns and laboratory experiments over a rice growing season to examine Hg and MeHg cycling, as well as associated biogeochemistry in a suite of paddies close to a municipal solid waste incinerator and a coal-fired power plant station in Taiwan. Concentrations of total Hg and MeHg in paddy soil and rice grain at both sites were low and found not to exceed the control standards for farmland soil and edible rice in Taiwan. However, seasonal variations of MeHg concentrations observed in pore water samples indicate that the *in situ* bioavailability of inorganic Hg and activity of Hg-methylating microbes in the rhizosphere increased from the early-season and peaked at the mid-season, presumably due to the anoxia created under flooded conditions and root exudation of organic compounds. The presence of Hg-methylators was also confirmed by the *hgcA* gene detected in all root soil samples. Subsequent methylation tests performed by incubating the root soil with inorganic Hg and an inhibitor or stimulant specific for certain microbes further revealed that sulfate-reducers might have been the principal Hg-methylting guild at the study sites. Interestingly, results of hydroponic experiments conducted by cultivating rice in a defined nutrient solution amended with fixed MeHg and varying levels of MeHg-binding ligands suggested that chemical speciation in soil pore water may play a key role in controlling MeHg accumulation in rice, and both passive and active transport pathways seem to take place in the uptake of MeHg in rice roots.

1. Introduction

Mercury (Hg) is a highly toxic trace element that has been recognized internationally as a global priority pollutant present in

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various environmental compartments and foods at levels posing a significant threat to human health and wildlife reproduction (Mason et al., 1995). Current inventories of Hg emissions show that anthropogenic activities are the major sources of Hg inputs to the environment, and the release of Hg primarily comes from a number of combustion sectors, including municipal solid waste-, sewage sludge-, hazardous waste- and hospital-incinerators, industrial manufacturing plants, and fossil fuel-burning power utilities (Keeler et al., 2006; UNEP, 2008). Of these sources, coal combustion and solid waste incineration have been regarded as two of the leading contributors in the total Hg emissions (Wang et al., 2004). Once released (primarily in its inorganic forms), reactive gaseous Hg, which is comprised of Hg(II) species, as well as particulate-bound Hg including both particle-associated Hg(0) and Hg(II) species, may be deposited on local surface environments due to their relatively short atmospheric residence time (Carpi, 1997). Consequently, apart from other potential sources, soil surface and vegetation of agricultural land proximate to an operating combustion facility likely receive additional inputs of Hg.

Following deposition, the relatively less-toxic inorganic Hg species may undergo transformations by certain guilds of anaerobic microorganisms, in particular sulfate-reducing bacteria (SRB), iron-reducing bacteria (FeRB) and methanogens (MPA), to methylmercury (MeHg), a potent neurotoxin that has received considerable attention due to its strong tendency to readily accumulate in concentration in food chains (Bloom, 1992; Kraepiel et al., 2003). However, the degree to which the chemical, biological, and physical parameters in an ecosystem to promote conditions favoring microbial methylation is known to be a much stronger determinant of MeHg accumulation in biota within the food web than the total amount of Hg in the ecosystem (Benoit et al., 2003). Of different ecosystems, wetlands have been recognized as important sites for Hg methylation owing to a supply of organic matter from rotting vegetation and flooded conditions that enhance anoxia therefore promoting the *in situ* activity of Hg methylating microbes (St. Louis et al., 1994, 1996; Heyes et al., 2000). In paddy fields, given that water is stored in the field during most of the rice growing season, from an ecological point of view, rice paddies indeed function similarly to wetlands (Molles, 2010). As a result, paddy fields, in particular lowland flooded rice paddies, are considered potential “hotspots” of MeHg production (Qiu et al., 2008).

In fact, aside from intake of fish (particularly the piscivorous fish), fish products and marine mammals that has long been considered the primary pathway for human and wildlife exposure to MeHg (Kraepiel et al., 2003), elevated concentrations of Hg and MeHg in rice grown from local areas near Hg releasing sources (predominantly from mining and certain inland areas in China) where consumption of fish is scarce have been reported (Horvat et al., 2003; Feng et al., 2008; Li et al., 2008; Zhang et al., 2010b), raising the question that ingestion of rice may be the major MeHg exposure route for the population in those areas, one of the routes in the terrestrial food web that has been considered negligible (Zhang et al., 2010a). Indeed, a statistically significant correlation between the human hair Hg levels and estimated rice MeHg intake for those local residents has been demonstrated (Feng et al., 2008). Further investigations not only reveal that compared to rice, other crop plants including corn, rape, tobacco and cabbage grown locally in the same study area show 10–100 fold lower MeHg in the edible portion (Qiu et al., 2008), but also indicate that of rice tissues, seeds (i.e., brown rice) have the highest capacity to accumulate MeHg (Meng et al., 2010).

Notably, in contrast to MeHg, the bioaccumulation factors (BAFs) for inorganic Hg in rice is much lower (ranging from 800 to 40,000 times less than that of MeHg), and no clear relationship was observed between the BAF of MeHg and the BAF of inorganic Hg, implying that different accumulation mechanisms may exist for MeHg and inorganic Hg in the rice grain (Zhang et al., 2010b). Subsequent investigations of the bioaccumulation pathway(s) of inorganic and methylated forms of Hg in rice have confirmed that (i) for inorganic Hg, although soil is the major source of root inorganic-Hg content, root surface actually acts as a potential Hg barrier, and it is the atmospheric input of these Hg species that plays a more important role in regulating the amount of Hg in the aboveground parts of the rice plant (Meng et al., 2012); (ii) for MeHg, during the rice growing season it is primarily taken up from roots of the rice plant, then translocated to the aboveground tissues (leaves and stalks), and eventually the vast majority of MeHg is stored in grains, with a very small portion of it retained in the root (Meng et al., 2011).

Despite the substantial progress that has been made over the past few years in characterizing total Hg/MeHg distribution in the rice plant and understanding the potential risk associated with the consumption of rice enriched with MeHg, we do not yet have a complete picture of the mechanisms that underlie the formation, uptake and accumulation of MeHg in the paddy ecosystem. In light of the fact (i) that rice is a staple food in Taiwan (also throughout Asia) but there is a paucity of data on rice Hg from Taiwan (Lin et al., 2004; Rothenberg et al., 2014), and (ii) that the potential for maternal MeHg exposure (even at low-level) through ingestion of rice may subsequently impact health of the offspring (Rothenberg et al., 2011, 2013), it is important to conduct thorough investigations of this exposure pathway by examining why rice paddies are conductive for Hg methylation, which major biogeochemical factors may have been involved in this process, and also how additional inputs resulted from anthropogenic perturbations may eventually lead to the potential accumulation of Hg and MeHg in rice.

In this study, paddy fields within the agricultural area of the Beitou Municipal Solid Waste (MSW) Incinerator and the Taichung Coal-Fired Power Plant Station were chosen to sample surface water, topsoil and root soil during a full rice-growing season in 2013 and 2014, respectively. Total Hg, MeHg, as well as ancillary geochemical/microbiological parameters of soil, porewater, and rice grains were measured. In addition, laboratory incubation tests including microcosm and hydroponic experiments were carried out to (i) probe the primary Hg methylators in the rhizosphere of the study sites, and to (ii) explore the influence of pore water coordination chemistry on the uptake of MeHg in rice roots.

2. Materials and methods

2.1. Field locations and sampling

The Beitou MSW Incinerator is located close to the convergence zone of the Keelung and Danshuei Rivers in northern Taiwan, where mangrove-covered coastal wetlands are featured. Most of the agricultural area facing the incinerator is cultivated with rice, irrigated with water from the Wufen-Port Creek, the Sulfur-Port Creek, and the Pair Creek. The Taichung Coal-Fired Power Plant Station is situated near the Taichung Port and is close the Dadu Estuary in central Taiwan. Similar to the farmland of the Beitou Incinerator, rice plantation is the primary land use in the agricultural area of the Taichung Power Plant Station, and the irrigation water may originate from the Wu River. It is noted that previous studies surveying heavy metal content in farmlands throughout Taiwan did not list both areas as Hg-contaminated sites (Lin et al., 2004).

Four and two paddy fields in the vicinity of the Beitou Incinerator and Taichung Power Plant Station were chosen respectively to collect samples from Feb to Jul in 2013 and 2014 (Fig. 1). At the