Present and Future Mercury Concentrations in Chinese Rice: Insights From Modeling

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Abstract We construct a rice paddy biogeochemical cycle model to investigate processes governing rice mercury sources and to understand factors influencing spatiotemporal variability in Chinese rice mercury concentrations. The rice paddy model takes atmospheric mercury deposition, simulated from a global atmospheric chemistry transport model (GEOS-Chem), and soil and irrigable surface water mercury concentrations obtained from literature and calculates rice inorganic (IHg) and methylmercury (MeHg) concentrations. We use ranges of GEOS-Chem-simulated future atmospheric mercury deposition—no policy and strict policy to regulate mercury emissions from Chinese coal-fired power plants under the Minamata Convention on Mercury—to simulate future rice IHg and MeHg concentrations. Sensitivity analyses suggest that rice IHg and MeHg concentrations are more sensitive to the process of soil desorption than infiltration of recently introduced mercury (atmospheric and irrigation source). The rate of internal methylation via microbial activity has the largest modeled influence on rice MeHg concentration. We find that soil mercury, rather than atmospheric deposition, explains observed spatial variability in rice IHg and MeHg concentrations and captures locations of rice mercury hot spots (>20 ng/g; China National Standard Limit). Under our future scenarios, the Chinese median rice IHg and MeHg concentration increases by 13% and decrease by 18% under no policy and strict policy, respectively. Regions with the largest percentage decline in rice IHg and MeHg concentrations under strict policy are in central China, which have high rice mercury concentrations, rice production, and consumption. Our study suggests that addressing Chinese rice mercury contamination requires attention to contaminated soil and regulation of anthropogenic mercury emissions.

1. Introduction

Atmospheric mercury emissions from anthropogenic activities and their subsequent deposition pose significant health risks to humans and wildlife (Mergler et al., 2007). China currently contributes >30% of global anthropogenic mercury emissions as a result of increasing population, industrial activities, and economic development (Pacyna et al., 2010). The dominant mercury emission sources in China are coal combustion, nonferrous metal smelting, cement production, and iron and steel production (L. Zhang et al., 2015). Mercury-contaminated sites including those influenced by abandoned and active mercury mining activities also mobilize mercury to the local atmosphere and nearby geochemical reservoirs of soil, sediment, and water (Horvat et al., 2003; P. Li et al., 2008; Qiu, Feng, Wang, & Shang, 2006; Qiu, Feng, Wang, & Xiao, 2006; Qiu et al., 2009, 2012, 2013). The distribution of various mercury sources and deposition patterns caused by meteorology and atmospheric chemistry result in spatially distinct mercury contamination levels and human health risks in China (P. Li et al., 2009; L. Zhang & Wong, 2007).

Exposure to methylmercury (MeHg), the most toxic and bioaccumulative form of mercury, via rice ingestion is a growing public health concern in China. China is the largest producer and consumer of rice in the world (Food and Agriculture Organization of the United Nations, 2013). A compilation of worldwide total mercury (THg) and MeHg concentrations in rice has shown that high rice MeHg concentrations, which can lead to MeHg intake exceeding the reference dose of 0.1 μg/kg body weight/day (Rice et al., 2000), occur in China and in particular in Guizhou province, which is characterized by large mercury mines (Rothenberg et al., 2014). Measurements of methylation rates and environmental parameters have suggested that irrigated rice
paddies are conducive to microbially mediated MeHg production (Marvin-DiPasquale et al., 2014; Rothenberg & Feng, 2012; Windham-Myers, Fleck, et al., 2014; Zhao et al., 2016). Root exudates of carbon and oxygen from the rice rhizosphere have been shown to enhance MeHg production, compared to other permanent and seasonal wetlands, by supporting microbial diversity and by promoting sulfate production (Marvin-DiPasquale et al., 2014; Windham-Myers, Marvin-DiPasquale, et al., 2014; Windham-Myers, Fleck, et al., 2014). Sulfate acts as an electron acceptor for sulfate-reducing microbes, which mediate MeHg production (Gilmour et al., 1992). Efficient translocation of MeHg through root membranes and rice grain also contributes to elevated rice MeHg levels (Meng et al., 2014). The proportion of total mercury present as MeHg (% MeHg of THg) has been shown to range between 8.1 and 75% (Rothenberg et al., 2014). The wide range in rice % MeHg (of THg) is likely attributed to multiple mercury sources and complex biogeochemical processes in rice paddies as well as rice variety, which affect the MeHg production, bioavailability, and bioaccumulation to rice grain.

Understanding mercury sources, biogeochemical processes, and fate in rice paddies is important for evaluating the spatial extent of potential risks and for implementing mercury management practices for rice in China. Previous studies that have examined the speciation, biogeochemical controls, and bioaccumulation of mercury in rice paddies have been conducted primarily in active and abandoned mercury mining sites in Guizhou province, China (Horvat et al., 2003; Huang et al., 2011; L. Li et al., 2010; P. Li et al., 2008; Meng et al., 2010, 2011, 2012, 2014; Qiu et al., 2008; Rothenberg & Feng, 2012; Savik et al., 2011; H. Zhang, Feng, Larsen, Shang, & Li, 2010; Zhao et al., 2016), and in laboratory settings (Y. R. Liu et al., 2016; Shu et al., 2016; H. Zhu et al., 2015, 2016). These studies have suggested that rice mercury may originate either from irrigation water contaminated by mercury ore and calcine deposits near mercury mining sites or from previously deposited or legacy mercury in soil. Recent studies that distinguished the relative contribution of rice mercury sources using mercury stable isotope measurements have suggested that ~20% of mercury in rice comes from foliage uptake (in the form of gaseous elemental Hg: Hg\(_0\)) and the remaining proportion (~80%) comes from soil (Feng et al., 2016; Strickman & Mitchell, 2017; R. Yin et al., 2013).

Regions influenced by mercury mining activities represent only a few of the 31 Chinese provinces and municipalities (i.e., Guizhou, Hunan, and Shaanxi). Geographical surveys of rice THg and MeHg levels across China show comparably elevated levels in regions impacted by other sources of mercury (i.e., waste recycling and incineration plants, coal-fired power plants, lead and zinc smelters, and urbanization) (Y. Fang et al., 2014; Fu et al., 2008; Hang et al., 2009; Haiyan & Stuanes, 2003; B. Li et al., 2013; P. Li et al., 2010; Li, Feng, Yuan, et al., 2012; Qian et al., 2010; Shi et al., 2005). Some previous work has suggested that recently deposited mercury from the atmosphere is more bioavailable for microbial methylation and uptake by rice than soil mercury. Evidence for atmospheric sources of both THg and MeHg in rice include increasing trends in rice and paddy soil THg and MeHg levels over the rice growing periods in areas where atmospheric mercury deposition is high and soil mercury concentration is similar to the Chinese background level (Meng et al., 2011, 2012). Other studies have observed decreasing trends in rice MeHg levels with increasing distance away from mercury point sources (Qiu, Feng, Wang, & Shang, 2006; Qiu et al., 2012, 2013). The relative importance of various mercury sources and biogeochemical processes governing these sources in rice paddies remains uncertain.

Here we use a rice paddy biogeochemical cycle model of mercury, together with a global scale atmospheric chemistry transport model for mercury, to (1) identify locations of high atmospheric mercury deposition to rice paddies in China, (2) investigate processes governing the relative importance of mercury sources in rice, and (3) understand factors influencing spatiotemporal variability in rice mercury levels across China. We compare model analyses with available measurements of mercury in rice paddies to identify processes of high uncertainty and variability. We then use our model to project future rice mercury concentrations in China under policy and no-policy emissions scenarios.

2. Materials and Methods

To address the objectives above, we construct a rice paddy biogeochemical cycle model of mercury. This rice paddy model is used to simulate sources, biogeochemical processes, and fate of mercury in rice paddies and to assess uncertainties in simulated processes. The rice paddy model takes atmospheric mercury deposition, here simulated from a global atmospheric chemistry transport model, and soil and irrigable surface water mercury concentrations from the literature to evaluate spatiotemporal variability in rice mercury sources and concentrations. Throughout this study, we refer to recently introduced mercury as that deposited
from the atmosphere and through irrigation input. Soil mercury represents mercury deposited previously from the atmosphere or legacy mercury.

2.1. Rice Paddy Area and Production

To identify locations of high atmospheric mercury deposition to rice paddies in China, we obtain year 2010 rice production and rice paddy area information from Z. Liu et al. (2013). Z. Liu et al. (2013) combine three data sets to evaluate and verify Chinese rice production and percent area occupied by rice paddy in 10 km × 10 km grid cells: (1) agricultural statistics released by the Ministry of Agriculture, China, (2) the National Land Cover Dataset of China interpreted from the Landsat TM satellite data, and (3) the global crop spatial distribution obtained from the Monthly Irrigated and Rainfed Crop Areas (2000). The combined data from Z. Liu et al. (2013) show a total rice paddy area of 3 × 10^5 km^2 (3 × 10^7 ha) and rice production of 2 × 10^8 tons in year 2010. This information is used to map rice production and percent rice paddy area on a provincial level (Figure 1).

2.2. Atmospheric Chemistry Transport Model

We use GEOS-Chem v.9-02, a global atmospheric chemistry transport model for mercury, to simulate present and projected future anthropogenic mercury emissions and deposition to Chinese rice paddies under the implementation of the global treaty on mercury, the Minamata Convention on Mercury. Briefly, GEOS-Chem provides gridded simulations of three atmospheric mercury species (elemental mercury; Hg^0, gaseous oxidized mercury; Hg^2+, and particulate-bound mercury; Hg_p) and accounts for atmospheric processes including emission, re-emission, transport, oxidation, photochemical reduction, and deposition (Amos et al., 2012; Giang et al., 2015; Holmes et al., 2010; Selin et al., 2007; Selin & Jacob, 2008; Soerensen et al., 2010; Strode et al., 2007). The model uses present-day meteorology from the NASA Goddard Earth Observing System (GEOS-5). The model has been validated extensively by comparing the observed mercury emissions and deposition to those predicted based on the model (e.g., Amos et al., 2012; Holmes et al., 2010; Muntean et al., 2014; Selin & Jacob, 2008; Soerensen et al., 2010). We use present (year 2006 emission inventories with simulated gross deposition results (wet and dry deposition of Hg^0, Hg^2+, and Hg_p) archived for year 2010–2012 meteorology) and future atmospheric mercury emission and deposition (year 2050

Figure 1. China provincial maps of percent rice area (%), rice production (million tons), and present (wet, dry, and total; μg/m²/yr) and future (Future_High and Future_Low; μg/m²/yr) atmospheric mercury deposition simulated by GEOS-Chem. Regions of high atmospheric mercury deposition are Henan (1), Anhui (2), Jiangxi (3), Hunan (4), Guizhou (5), Chongqing (6), and Hubei (7).
emissions with the same 2010–2012 meteorology) estimates from Giang et al. (2015). Future atmospheric mercury emission estimates are scaled based on (1) the level of Minamata Convention-consistent technology stringencies to limit mercury emissions from Chinese coal-fired power plants and (2) the level of future energy transition away from fossil fuel based on the Intergovernmental Panel on Climate Change Special Report on Emissions Scenarios scenarios (A1B and B1). In this study, we use the highest and lowest emission scenarios from Giang et al. (2015) to project future atmospheric mercury deposition to Chinese rice paddies (Figure 1). The highest emission scenario combines A1B and the absence of Minamata Convention-consistent technological changes (referred to as Future_High) and the lowest emission scenario combines B1 and a strict interpretation of Minamata Convention-consistent technological changes to Chinese coal-fired power plants (referred to as Future_Low).

2.3. Rice Paddy Model

We construct a rice paddy model to simulate sources, biogeochemical processes, and fate of inorganic mercury (IHg) and MeHg. We consider the sum of IHg and MeHg as THg. IHg is defined as both dissolved (free ion and soluble complexes) and particulate-bound species of Hg⁰, Hg²⁺, and Hg₂⁻. MeHg refers to both dissolved and particulate-bound organometallic Hg, which is the toxic form of mercury discussed in section 1. The overall structure of the rice paddy model is illustrated in Figure 2. The rice paddy model (equivalent to 1 ha of rice paddy) consists of five reservoirs: the flooded water column, pore water, topsoil, subsoil, and rice plants. The model uses depths of 15 cm (flooded water column), 20 cm (pore water), 20 cm (topsoil), and 50 cm (subsoil), and soil densities of 1.5 g/cm³ (topsoil) and 1.4 g/cm³ (subsoil). These values are consistent with those observed in typical rice paddies (Chen et al., 2002; Dittmar et al., 2007; Maclean et al., 2013; Rothenberg & Feng, 2012). The model takes atmospheric mercury deposition and mercury concentration of irrigation water as input. Atmospheric deposition is calculated using GEOS-Chem and assumes input of only IHg. The relative contribution of Hg⁰ uptake via foliage to rice is constrained from previous mercury stable isotope measurements (Feng et al., 2016; Strickman & Mitchell, 2017; R. Yin et al., 2013) and not modeled explicitly. We consider this fraction only when evaluating the model-simulated rice THg and MeHg concentrations against measurements from China. Irrigation supplies both IHg and MeHg, which are calculated using (1) THg concentration and % MeHg (of THg) measurements of surface water obtained from various locations in China (Table 1), (2) the volume of water required to generate a flooded water column calculated from the model dimension, and (3) the average number of irrigation periods (~6) required to maintain the flooded water column over ~5 months of rice growing (Maclean et al., 2013). We use surface water mercury concentrations given that surface water is the major source of irrigation to Chinese rice paddies (X. Zhu et al., 2013). Mercury...
transfer between the model reservoirs and biogeochemical rates within individual reservoirs are based on first-order differential equations; \( \frac{dM}{dt} = k \times M \). M (kg) represents either IHg or MeHg reservoir masses, and \( k \) (yr\(^{-1}\)) represents time-invariant rate coefficients. Table 1 summarizes all mercury inputs and rate coefficients \( (k) \) implemented in the rice paddy model as well as their uncertainty ranges; these are described further below.

Prior to simulating sources, biogeochemical processes, and fate of IHg and MeHg in rice paddies, we initialize the rice paddy reservoirs with relatively low mercury concentrations consistent with preindustrial background values (Selin et al., 2008). The model is run to steady state under average present-day conditions.

| Reservoirs Processes | Parameters | Base model | Minimum | Maximum | References |
|----------------------|------------|------------|---------|---------|------------|
| Atmospheric deposition (IHg) | Input (kg/ha/yr) | 5.9 \times 10^{-4} | 3.9 \times 10^{-4} | 1.4 \times 10^{-4} | 0.3 \times 10^{-4} | 9.7 \times 10^{-4} | 0.216 | GEOS-Chem simulation (F. Fang et al., 2004; Horvat et al., 2003; Li, Feng, Qiu, et al., 2012; Lin et al., 2010; Qiu, Feng, Wang, & Shang, 2006; Qiu, Feng, Wang, & Xiao, 2006; Qiu et al., 2009, 2012, 2013; Rothenberg & Feng, 2012; L. Zhang & Wong, 2007) |
| Irrigation (IHg) | | | | | | | | (Horvat et al., 2003; Li, Feng, Qiu, et al., 2012; Qiu et al., 2009, 2012, 2013; Rothenberg & Feng, 2012) |
| Irrigation (MeHg) | | | | | | | | (Horvat et al., 2003; Li, Feng, Qiu, et al., 2012; Qiu et al., 2009, 2012, 2013; Rothenberg & Feng, 2012) |
| Flooded water column | | | | | | | | | (Bachand et al., 2014; Kim et al., 2014) |
| Rate coefficient (yr\(^{-1}\)) | Runoff | \( k_{\text{runoff}} \) | 2.5 | 2.5 | 12 | (Bachand et al., 2014; Kim et al., 2014) |
| | Evasion | \( k_{\text{evasion}} \) | 0.80 | 0 | 1.2 | (Agnan et al., 2016; X. Wang et al., 2016) |
| | Photodegradation | \( k_{\text{photodegradation}} \) | 10 | 10 | 32 | (Fleck et al., 2014) |
| | Infiltration | \( f_{\text{dissolved}} \) | 70 | | | (Alpers et al., 2014) |
| | Infiltration (MeHg) | | | | | | (Alpers et al., 2014) |
| | Methylation | \( k_{\text{methylation}} \) | 0.40 | 1.2 \times 10^{-2} | 32 | (Marvin-DiPasquale et al., 2014; Zhao et al., 2016) |
| | Demethylation | \( k_{\text{demethylation}} \) | 10 | 4 | 40 | (Drott et al., 2008; Tjerngren et al., 2012) |
| | Diffusion (IHg) | \( k_{\text{diffusion}} \) | 8 | 1 | 8 | (Rothenberg & Feng, 2012) |
| | Diffusion (MeHg) | \( k_{\text{diffusion}} \) | 11 | 9 | 11 | (Rothenberg & Feng, 2012) |
| | Seepage | | 0.15 | 0.15 | 4.9 | (Bicknell, 2000) |
| Rate coefficient (yr\(^{-1}\)) | Adsorption (IHg) | \( f_{\text{dissolved}} \) | 1.4 \times 10^{-2} | 1.9 \times 10^{-3} | 5.0 \times 10^{-2} | (Meng et al., 2011, 2012) |
| | Adsorption (MeHg) | | 2.8 | 0.50 | 9 | (Meng et al., 2011, 2012) |
| | Desorption | \( f_{\text{dissolved}} \) | 10 | | | (Meng et al., 2011, 2012) |
| | Desorption (MeHg) | | 1.4 \times 10^{-2} | 1.9 \times 10^{-3} | 5.0 \times 10^{-2} | (Liao et al., 2009; Y. Yin et al., 1997) |
| Rate coefficient (yr\(^{-1}\)) | Burial | \( k_{\text{burial}} \) | 6.0 \times 10^{-5} | | | (Amos et al., 2013; Selin et al., 2008; Smith-Downey et al., 2010) |
| | Recycling to subsoil (IHg) | \( k_{\text{recycling to subsoil}} \) | 1.0 \times 10^{-3} | 5.0 \times 10^{-4} | 2.0 \times 10^{-3} | (Amos et al., 2013; Selin et al., 2008; Smith-Downey et al., 2010) |
| | Recycling to topsoil (IHg) | \( k_{\text{recycling to topsoil}} \) | 9.0 \times 10^{-4} | 4.0 \times 10^{-4} | 1.0 \times 10^{-3} | (Amos et al., 2013; Selin et al., 2008; Smith-Downey et al., 2010) |
| | Recycling to topsoil (MeHg) | \( k_{\text{recycling to topsoil}} \) | 4.0 \times 10^{-4} | 5.0 \times 10^{-5} | 1.1 \times 10^{-3} | (Amos et al., 2013; Selin et al., 2008; Smith-Downey et al., 2010) |
| | All recycling | \( f_{\text{decomposition}} \) | 20 | | | (Smith-Downey et al., 2010) |
| Rate coefficient (yr\(^{-1}\)) | Root absorption (IHg) | \( k_{\text{root absorption}} \) | 5 | 5 | 12 | (Meng et al., 2012) |
| | Root absorption (MeHg) | \( k_{\text{root absorption}} \) | 50 | 13 | 487 | (J. Liu et al., 2012; Meng et al., 2011; Windham-Myers, Marvin-DiPasquale, et al., 2014) |
atmospheric deposition (GEOS-Chem-simulated atmospheric mercury deposition spatially averaged by province/municipality; 59 μg/m²/yr or 5.9 × 10⁻⁴ kg/ha/yr) and irrigation input (literature reported Chinese background surface water THg concentration of 0.044 μg/L, % MeHg of THg = 0.20%) (L. Zhang & Wong, 2007). We then compare the steady state mercury concentrations with present-day global average values in soil (topsoil = 70 ng THg/g and subsoil = 40 ng THg/g) (Selin et al., 2008). We then compare mercury lifetimes with previous model estimates, which estimated 10–1,000 years in the topsoil and subsoil, respectively (Amos et al., 2013; Selin et al., 2008; Smith-Downey et al., 2010). Rothenberg and Feng (2012) observed mercury lifetimes of hours to days and ranges of THg and MeHg concentrations of 10⁻¹ to 10² ng/L and 10⁻² to 10⁻¹ ng/L, respectively, in both the flooded water column and pore water in Chinese rice paddies. These values are used to calibrate uncertain parameters in the model as described further below.

The model is then used dynamically to simulate sources, biogeochemical processes, and fate of IHg and MeHg in rice paddies. The dynamic run is used to evaluate the overall performance of the rice paddy model. We run the model for 5 months, representing the time duration from seedling plantation to harvest (Maclean et al., 2013). To estimate the mercury concentration for the edible portion of rice (i.e., rice grain mercury concentration from the total rice plant simulated by the rice paddy model), we use previously estimated % IHg (of THg; 10%) and % MeHg (of THg; 95%) accumulation to rice grain from the rice plant (Meng et al., 2011), the average rice plant per area (21 plants/m²) (Rothenberg & Feng, 2012), and the average rice grain weight per plant (13.7 g) (H. Zhu et al., 2016). The estimated rice THg and MeHg concentrations, the model-simulated THg and MeHg concentrations in individual reservoirs, and their % MeHg (of THg) values are compared with available measurements for model evaluation (section 3.3). Sensitivity analyses are conducted to evaluate model uncertainties (section 3.4). Below, we provide details of how individual model parameters are derived and implemented in the rice paddy model.

2.3.1. Flooded Water Column

Most rice paddies in China are cultivated under continuously flooded conditions (Maclean et al., 2013; Rothenberg et al., 2014). IHg and MeHg are introduced to the flooded water column via atmospheric deposition and irrigation input. Once IHg enters the flooded water column, a portion of this IHg is exported via runoff, evaded into the atmosphere, or infiltrated into the pore water. MeHg can also be photochemically degraded in the flooded water column.

We use the rate of hydrologic outflow estimated in rice paddies to derive the rate of runoff (k runoff) for IHg and MeHg. The rate of hydrologic outflow represents the rate of change in water depth in the flooded water column caused by runoff. In Californian rice paddies, the hydrologic outflow has been estimated to be less than 0.50 cm/d (Bachand et al., 2014). Similar rates have been determined by Kim et al. (2014), who reported 0.10 to 0.45 cm/d and 0.10 to 0.30 cm/d in Korean rice paddies, respectively. We use the depth information of the flooded water column (15 cm) and a rate of hydrologic outflow of 0.10 cm/day to estimate the timescale of mercury removal via runoff (t runoff in days). We use the timescale information to calculate k runoff for our model (1/t runoff = k runoff in d⁻¹; shown as yr⁻¹ in Table 1).

Removal of IHg and MeHg takes place by evasion to the atmosphere and photochemical degradation, respectively. In rice paddies, these processes are thought to be relatively slow due to dense leaf canopy (Fleck et al., 2014; X. Wang et al., 2016; Windham-Myers, Fleck, et al., 2014). We use data compiled by X. Wang et al. (2016) and Agnan et al. (2016) in Chinese rice paddies (0 to 1.5 ng/m²/h) and water-saturated vegetated wetlands (0.20 ng/m²/h), respectively, to obtain uncertainty ranges in Hg⁰ evasion flux. We use the flooded water column IHg concentration and divide by a Hg⁰ evasion flux of 1.0 ng/m²/h to estimate the rate of evasion (k evasion) for the model. To estimate the rate of MeHg photochemical degradation (k photodegradation), we use the flooded water column MeHg concentration and divide by a photochemical degradation flux of 1.0 ng/m²/d measured in Californian rice paddies (Fleck et al., 2014).

Infiltration transfers recently introduced mercury into deeper reservoirs. The infiltration rate represents the rate of change in water depth in the flooded water column caused by downward water percolation through pore water. Given the lack of available mercury-specific infiltration rates, we use the infiltration rate for water to estimate the rate of infiltration (k infiltration) for IHg and MeHg. Infiltration rates for water estimated in Californian, Taiwanese, and Korean rice paddies have a relatively narrow range of 0.51 to 0.81 cm/d (Bachand et al., 2014; Chen et al., 2002; Kim et al., 2014). We divide the depth information of the flooded
water column (15 cm) by an infiltration rate of 0.78 cm/d to estimate the first-order timescale and the rate of mercury removal via infiltration ($t_{\text{infiltration}}$ in days, where $1/t_{\text{infiltration}} = k_{\text{infiltration}}$).

Not all mercury in the flooded water column is transferred to pore water via infiltration. It is likely that most dissolved mercury infiltrates pore water, while mercury associated with particles of topsoil undergo suspension and resuspension at the topsoil-water interface. We apply a dissolved fraction ($f_{\text{dissolved}}$) of 70% and 60% for IHg and MeHg, respectively, to $k_{\text{infiltration}}$ (i.e., $k_{\text{infiltration}} \times f_{\text{dissolved}} \times M_{\text{flooded water column}}$) to simulate transfer of only dissolved mercury species via infiltration (Figure 2 and Table 1). These values are derived from Alpers et al. (2014), who measured dissolved and particulate IHg and MeHg concentrations in the flooded water column of Californian rice paddies.

### 2.3.2. Pore Water

We define pore water as a reservoir containing dissolved fractions of IHg and MeHg within the top 20 cm of the soil column (topsoil). Once mercury infiltrates the pore water, a portion of mercury is taken up by rice or adsorbed to particles of topsoil. The rate coefficients for mercury adsorption (and desorption) between the pore water and particles of topsoil are implemented in the topsoil reservoir and described in the section below. We treat the pore water and topsoil reservoirs separately in the rice paddy model to understand how recently introduced mercury sources via infiltration, in comparison to topsoil mercury via adsorption-desorption, govern rice mercury sources and concentrations.

As illustrated in Figure 2, the pore water receives mercury from two different sources—infiltration of recently introduced mercury and desorption of topsoil mercury. Rice roots are in direct contact with the pore water and can take up dissolved IHg and MeHg species during transpiration (Bachand et al., 2014; Rothenberg et al., 2014). Studies have suggested that microbial methylation and demethylation occur predominantly in the pore water, where the dissolved fractions of IHg and MeHg become bioavailable for microbial activities (J. Liu et al., 2012; Rothenberg et al., 2014; Su et al., 2016). We use the rate of methylation ($k_{\text{methylation}}$) measured in Chinese and Californian rice paddies for the rice paddy model (Marvin-DiPasquale et al., 2014; Zhao et al., 2016). A compilation of demethylation rates ($k_{\text{demethylation}}$) reported in many wetlands has shown more than an order of magnitude higher values than $k_{\text{methylation}}$ measured at the same sites (Drott et al., 2008; Tjerngren et al., 2012). Using the $k_{\text{methylation}}$ measured in rice paddies ($0.22 \times 10^{-3}$ d$^{-1}$) and the average ratio of $k_{\text{demethylation}}/k_{\text{methylation}}$ estimated from the compilation studies (~25), we calculate $k_{\text{demethylation}}$ for our model ($k_{\text{demethylation}}/0.22 \times 10^{-3}$ d$^{-1} = 25$).

A portion of IHg and MeHg is subjected to diffusion or the transfer of dissolved IHg and MeHg species back to the flooded water column. Rothenberg and Feng (2012), based on multiyear studies of mercury biogeochemical cycling in Chinese rice paddies, observed a rapid equilibration (within days) of IHg between the flooded water column and the pore water and a twofold higher MeHg concentration in the pore water than the flooded water column upon rice paddy irrigation. For model calibration, we adjust the rate of diffusion ($k_{\text{diffusion}}$) in our model to match IHg concentration between the flooded water column and the pore water and an approximately twofold higher MeHg concentration in the pore water than the flooded water column.

Seepage is another process that can cause IHg and MeHg removal from rice paddies. The mobility of mercury in soil depends on the soil physicochemical properties, which govern the partitioning of mercury between particulate and dissolved phases (Różański et al., 2016; Šipková et al., 2016). Because our rice paddy model assumes that all mercury in the pore water is already in the dissolved phase and represents the mercury subjected to the adsorption-desorption cycle between the topsoil and the pore water, we use the seepage rate for water obtained from clay and silt soil (Bicknell, 2000) to derive the seepage rates ($k_{\text{seepage}}$) for IHg and MeHg. The rate of seepage represents the rate of water movement through pore water that is attributable to seepage. We divide the depth information of the pore water (20 cm) by a seepage rate of $8.0 \times 10^{-3}$ cm/d to estimate the first-order timescale of mercury removal via seepage ($t_{\text{seepage}}$ in days). We use the timescale information to calculate the first-order seepage rate $k_{\text{seepage}}$ for our model ($1/t_{\text{seepage}} = k_{\text{seepage}}$).

### 2.3.3. Topsoil

The dominant processes governing mercury exchange between pore water and topsoil reservoirs are adsorption and desorption. The rates of these processes determine the relative contribution of soil mercury (previously deposited or legacy mercury in soil) and recently introduced mercury (that taken up directly from the pore water and those recycled through the topsoil reservoir via adsorption-desorption) to rice. A soil-pore
water partition coefficient (Log \( K_{d} \), L/kg), defined as the ratio of soil IHg and MeHg concentrations to their pore water concentrations, has been used extensively to estimate mercury concentrations in pore water (Allison & Allison, 2005). As illustrated in Figure 2, the pore water mercury concentrations are dynamically coupled with infiltration, diffusion, seepage, rice root absorption, microbial methylation-demethylation, and adsorption-desorption cycles. We implement these biogeochemical processes and rates independently in the rice paddy model rather than using a Log \( K_{d} \). We then compare the model estimated and observed Log \( K_{d} \) in Chinese rice paddies (Rothenberg & Feng, 2012) to further verify the biogeochemical processes implemented in our model in section 3.3.

The rates of adsorption and desorption (\( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \)) implemented in the rice paddy model are adjusted at steady state to represent the rates of adsorption and desorption required to achieve the feasible ranges of mercury attributable to soil in rice (referred to as percent soil mercury contribution to rice below) relative to that deposited recently from the atmosphere. We estimate the feasible range of percent soil mercury contribution to rice (5 to 60%) from rice paddy controlled plot studies that measured rice mercury concentrations under the same atmospheric mercury loading but under variable soil mercury concentrations (Meng et al., 2011, 2012). We use \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) estimated at 30% soil mercury contribution to rice or the median fraction estimated from Meng et al. (2011, 2012) for our model. The method describing the model calibration of \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) is shown further below (section 3.2). Previous experimental studies have collectively shown that ~10% of mercury is mobilized back into solution via desorption due to the strong binding affinity of mercury to organic carbon-rich clay and silt soil (i.e., rice paddy soil) (Liao et al., 2009; Y. Yin et al., 1997). We apply a recovery fraction (\( f_{\text{recovery}} \)) of 10% to \( k_{\text{desorption}} \) (i.e., \( k_{\text{desorption}} \times f_{\text{recovery}} \times M_{\text{topsoil}} \)) to simulate mercury transfer from the topsoil to the pore water reservoir via desorption (Figure 2 and Table 1).

### 2.3.4. Subsoil

The rate of recycling (\( k_{\text{recycling}} \)) between the topsoil and subsoil reservoirs implemented in the rice paddy model are adjusted at steady state to represent the rates required to achieve realistic mercury lifetimes in these reservoirs (Amos et al., 2013; Selin et al., 2008; Smith-Downey et al., 2010) and the mercury fraction attributable to subsoil in rice. While measurements of the subsoil mercury contribution to rice are unavailable, the direct subsoil mercury contribution to rice is most likely small to negligible (0–5%) during the lifetime of rice (~5 months). We use \( k_{\text{recycling}} \) estimated at 3% subsoil mercury contribution to rice for our model. The uncertainties of these fractions are described below. We apply a fraction \( f_{\text{decomposition}} \) of 20% to \( k_{\text{recycling}} \) (i.e., \( k_{\text{recycling}} \times f_{\text{decomposition}} \times M_{\text{topsoil and subsoil}} \)) for the fraction of mercury available for recycling via organic carbon decomposition (Figure 2 and Table 1). The \( f_{\text{decomposition}} \) implemented in the rice paddy model is slightly higher than that used in modeling forest ecosystems (16%) (Smith-Downey et al., 2010) given the higher organic carbon content in rice paddy soil (Rothenberg et al., 2014).

Burial represents mercury exported indefinitely from rice paddies via vertical or lateral seepage or that transferred to even deeper reservoirs. For the rate of burial (\( k_{\text{burial}} \), we derive this value using previously estimated mercury lifetimes in subsoil (Amos et al., 2013; Selin et al., 2008; Smith-Downey et al., 2010) given the lack of previous estimates constraining this process in rice paddies.

### 2.3.5. Rice

Mercury uptake via rice root occurs primarily from pore water (Bachand et al., 2014; Rothenberg et al., 2014). Rice MeHg uptake fluxes have previously been estimated from Chinese and Californian rice paddies (2.4 to 89 ng/m²/d) (J. Liu et al., 2012; Meng et al., 2011; Windham-Myers, Marvin-DiPasquale, et al., 2014). We use the pore water MeHg concentration and divide by a rice MeHg uptake flux of 9.2 ng/m²/d to estimate the rate of root MeHg absorption (\( k_{\text{root absorption for MeHg}} \)) for our model. We estimate rice IHg uptake flux from Meng et al. (2012), who measured IHg concentrations in rice during multiple stages of the growth phase. The estimated flux of 153 ng/m²/d and the pore water IHg concentration are used to derive the rate of root IHg absorption (\( k_{\text{root absorption for IHg}} \)) for the model.

### 2.4. Measurement Constraints

We compile multiple sets of mercury and rice paddy relevant measurements to evaluate the rice paddy model. Table 2 summarizes the observed THg and MeHg concentrations, and % MeHg (of THg) values in rice paddy reservoirs. The flooded water column and pore water values represent the ranges gathered from rice
Table 2
List of Model Simulated (This Study) and Observed THg and MeHg Concentrations and % MeHg (of THg) in Rice Paddy Reservoirs

| THg (ng/L or ng/g) | MeHg (ng/L or ng/g) | % MeHg (of THg) | References |
|-------------------|---------------------|-----------------|------------|
| Flooded water column | 75 | 0.20 | 0.27 | This study (Rothenberg & Feng, 2012; Zhao et al., 2016) |
| 40–728 | 0.10–7.8 | 0.14–1.8 | (J. Liu et al., 2012; Rothenberg & Feng, 2012; Su et al., 2016; Zhao et al., 2016) |
| Pore water | 73 | 0.40 | 0.54 | This study (J. Liu et al., 2012; Rothenberg & Feng, 2012; Su et al., 2016; Zhao et al., 2016) |
| 7–430 | 0–11 | | |
| Topsoil | 79 | 0.40 | 0.50 | This study (S. Wang et al., 2016) (Zheng et al., 1994) |
| 3–150,000ᵃ (agricultural soil average 108) | 65–70ᵇ (Chinese background soil) | 0.39–0.98 | (Marvin-DiPasquale et al., 2014; Su et al., 2016) |
| Subsoil | 49 | 0.20 | 0.41 | This study (Amos et al., 2013; Selin et al., 2008) |
| ~40 | | | |
| aResults representing the ranges and average Chinese agricultural soil THg concentrations. bResults representing the range of Chinese background soil THg concentration.

2.5. Model Simulations

Table 3 lists the various rice paddy model simulations performed in this study. Simulation types are divided into the five categories of (1) model calibration (CAL), (2) standard model simulation (BASE), (3) spatial variability assessment (SP_Atm, SP_Soil, SP_Both), (4) sensitivity analyses (SE_10%, SE_Uncertainty, SE_Process, SE_Input, SE_MeHg), and (5) future rice mercury concentration projections (Med_Future, SP_Future). We describe the methods for these simulations in order.

As noted in section 2.3.3, the model calibration (CAL) is conducted at steady state to adjust $k_{adsorption}$ and $k_{desorption}$ to match the feasible range of percent soil mercury contribution to rice (Meng et al., 2011, 2012). The ratio of $k_{adsorption}$ to $k_{desorption}$ controls percent soil mercury contribution to rice, while the absolute value of these parameters influences the rice paddy reservoir mercury concentrations. In CAL, we conduct a series of simulations to select values of $k_{adsorption}$ and $k_{desorption}$ to match steady state reservoir mercury concentrations and range of percent soil contribution to rice, and use those selected values for the BASE simulation. We describe the process in section 3.

Mercury concentrations generated from the fully calibrated model in BASE are used to evaluate the rice paddy model. As noted in section 2.3, the BASE simulation represents the 5 month dynamic run of the standard model simulation (different from steady state simulations) under Chinese provincial average atmospheric mercury deposition, steady state soil mercury concentration, and Chinese background surface water mercury concentration. The BASE simulation uses the Base Model rate coefficients as illustrated in Table 1. Throughout this study, we alter specific model parameters from BASE as described below and in Table 3 to perform remaining tests.
The model-simulated spatial variability in rice THg and MeHg concentrations is assessed under variable atmospheric mercury deposition (in the form of IHg) and soil mercury concentrations corresponding to each 4° × 5° latitude-longitude grid cell (the GEOS-Chem grid size used in our atmospheric simulations). Throughout these model simulations, we keep the rate coefficients consistent with BASE. In SP_Atm, we run the rice paddy model under constant soil mercury concentrations (steady state concentrations) with variable GEOS-Chem-simulated atmospheric mercury deposition. In SP_Soil, we run the rice paddy model under constant atmospheric deposition (GEOS-Chem-simulated Chinese provincial average) with variable soil mercury concentrations. Soil THg concentrations are obtained from S. Wang et al. (2016), who reported spatial distribution of agricultural topsoil THg concentrations across China. We apply 0.56% or the median rice paddy topsoil % MeHg (of THg) value (Marvin-DiPasquale et al., 2014; Su et al., 2016) to estimate topsoil MeHg concentrations across China. Finally, in SP_Both, we run the rice paddy model under both variable atmospheric mercury deposition and soil mercury concentrations.

Sensitivity analyses are conducted to understand how individual model parameters influence rice IHg and MeHg sources and concentrations. We first modify mercury inputs, concentrations, and rate coefficients individually from BASE using the uncertainty ranges from literature (minimum and maximum in Table 1; SE_Uncertainty) and by forcing ±10% changes (SE_10%) to assess the overall changes in rice IHg and MeHg concentrations. In SP_Process, we focus on source-relevant processes of infiltration and desorption to evaluate the changes in rice IHg and MeHg concentrations. For SE_Process, we keep the mercury inputs and concentrations consistent with BASE and modify \( k_{\text{infiltration}} \) and \( k_{\text{desorption}} \) using the uncertainty range from Table 1 and the range estimated from percent soil mercury contribution to rice (CAL), respectively. In SE_Input, we assess the changes in percent soil mercury contribution to rice using the observed range of Chinese soil mercury concentration and atmospheric mercury deposition. For soil THg and MeHg concentrations, we use the range from S. Wang et al. (2016) or values consistent with those used for the spatial variability assessment (THg = 65 to 1,000 ng/g and % MeHg of THg = 0.56%). We use the GEOS-Chem-simulated Chinese provincial range in atmospheric mercury deposition (14 to 97 \( \mu g/m^2/yr \); Figure 1). For SE_Input, we

### Table 3

| Types of Model Simulations Performed on the Rice Paddy Model |
|---------------------------------------------------------------|
| **Model simulation type** | **Simulation code** | **Simulation test sensitive to** | **Changes to simulation** | **Simulation results** |
|----------------------------|---------------------|--------------------------------|---------------------------|-----------------------|
| Model calibration         | CAL                 | \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) | Ranges of % soil mercury contribution (5–60%) from Meng et al. (2011, 2012) | Figure 3            |
| Standard model simulation | BASE                | Rice [IHg] and [MeHg]         | None                      | Figure 4            |
| Spatial variability assessment | SP_Atm            | Rice [THg] and [MeHg]         | Gridded atmospheric mercury deposition from GEOS-Chem | Figure 4            |
|                            | SP_Soil             | Rice [THg] and [MeHg]         | Gridded soil [IHg] and [MeHg] from S. Wang et al. (2016) | Figure 4            |
|                            | SP_Both             | Rice [THg] and [MeHg]         | Atmospheric mercury deposition and soil [IHg] and [MeHg] | Figure 4            |
| Sensitivity analyses       | SE_Uncertainty      | Rice [IHg] and [MeHg]         | Uncertainties ranges in Table 1 (min/max) for mercury inputs, concentrations, and rate coefficients | Figure 5            |
|                            | SE_10%              | Rice [IHg] and [MeHg]         | ±10% perturbation in mercury inputs, concentrations, and rate coefficients | Figure 5            |
|                            | SE_MeHg             | Rice [MeHg]                   | \( k_{\text{infiltration}} \) for IHg without \( k_{\text{desorption}} \) and \( k_{\text{infiltration}} \) for MeHg, \( k_{\text{desorption}} \) for IHg without \( k_{\text{infiltration}} \) and \( k_{\text{desorption}} \) for MeHg | Figure 6            |
|                            | SE_Process           | Rice [IHg] and [MeHg]         | Uncertainty range in \( k_{\text{infiltration}} \) and CAL estimated range of \( k_{\text{desorption}} \) | Figure 7            |
|                            | SE_Input             | % Soil mercury contribution to rice | GEOS-Chem-simulated range in atmospheric mercury deposition and the range of soil [IHg] and [MeHg] from S. Wang et al. (2016) | Figure 8            |
| Future rice mercury concentration projections | Med_Future | Soil [IHg] and [MeHg], Rice [IHg] and [MeHg] | GEOS-Chem-simulated future atmospheric mercury deposition scenarios (Future_High and Future_Low) | Figure 9            |
|                            | SP_Future           | Rice [THg] and [MeHg]         | Gridded future atmospheric mercury deposition scenarios (Future_High and Future_Low) and soil [IHg] and [MeHg] from S. Wang et al. (2016) | Figure 10           |
keep the rate coefficients consistent with BASE and allow rice IHg and MeHg concentrations to change with the soil mercury concentrations and atmospheric mercury deposition to calculate the resulting percent soil mercury contribution to rice. In SE_MeHg, we identify the most influential IHg source for microbial methylation and rice uptake. To do this, we increase IHg supply via \( k_{\text{infiltration}} \) to the rice paddy at \( k_{\text{desorption}} = 0 \) (both IHg and MeHg) and at \( k_{\text{infiltration}} = 0 \) for MeHg to simulate the changes in rice MeHg concentration. In another test, we increase IHg supply via \( k_{\text{desorption}} \) at \( k_{\text{infiltration}} = 0 \) (both IHg and MeHg) and at \( k_{\text{desorption}} = 0 \) for MeHg to simulate the changes in rice MeHg concentration. For SE_MeHg, we keep the mercury inputs and concentrations consistent with BASE and compare the model-simulated rice MeHg concentrations to identify IHg sources sensitive to microbial methylation and uptake by rice.

We use GEOS-Chem-simulated future atmospheric mercury deposition scenarios of Future_High and Future_Low to project changes in Chinese soil and rice mercury concentrations. Throughout these model simulations, we keep the rate coefficients consistent with BASE. In Med_Future, steady state soil IHg and MeHg concentrations and the median Chinese rice IHg and MeHg concentrations are treated as baselines given that these concentrations represent present-day median observations over China. For each future atmospheric mercury scenario, we assume annual linear changes in atmospheric deposition from year 2020 (consistent with present-day estimates and the beginning of the Minamata Convention enforcements) to 2050. We apply these annual linear changes in atmospheric mercury deposition to the rice paddy model and run the model dynamically to simulate annual changes in both steady state soil IHg and MeHg concentrations and the median Chinese rice IHg and MeHg concentrations. In SP_Future, we use soil THg and MeHg concentrations obtained from S. Wang et al. (2016) and apply GEOS-Chem-simulated future atmospheric mercury deposition scenarios corresponding to each 4° × 5° latitude-longitude grid cell. For each grid cell, we assume annual linear changes in atmospheric deposition from year 2020 to 2050. We apply these annual changes in atmospheric mercury deposition to the rice paddy model to evaluate the future spatial variability in rice THg and MeHg concentrations.

3. Results
3.1. Atmospheric Deposition to Rice Paddies

Figure 1 shows percent rice area, rice production, and present and future (total, wet, and dry) atmospheric mercury deposition at a provincial level in China as simulated by GEOS-Chem. Model simulations of present-day atmospheric mercury deposition show that the regions of high percent rice area and large rice production are generally colocated with regions of high atmospheric mercury deposition. The critical locations where atmospheric mercury deposition to rice paddies are high are in central China (Henan, Anhui, Jiangxi, Hunan, Guizhou, Chongqing, and Hubei). These areas together represent 33% and 48% of the total Chinese rice area and rice production, respectively, and receive on average nearly 2 times higher atmospheric mercury deposition (94 \( \mu g/m^2/yr \)) than the rest of China (51 \( \mu g/m^2/yr \)).

Model-simulated present-day wet and dry deposition show similar spatial distribution as the model-simulated present-day total atmospheric mercury deposition (Figure 1). Precipitation flux (kg/m²/yr) from GEOS-5 demonstrates a strong latitudinal gradient across China (i.e., decreasing precipitation with increasing latitude). Given that rice grows most actively in humid subtropical climates, the precipitation pattern explains the higher magnitude of wet deposition to regions of dense rice paddies. Elevated dry deposition to central China is the result of surface type as implemented in GEOS-Chem. A compilation of dry deposition velocities across various surface type has shown that water-saturated vegetated canopies such as rice paddies and wet deciduous forest canopies have higher dry deposition velocities than bare soil, grassland, and wetlands (L. Zhang et al., 2009). Deciduous forests and croplands are densely aggregated in central China (J. Liu et al., 2003). This suggests that GEOS-Chem adequately captures the surface type and the dry deposition over central China.

In the model-simulated future atmospheric mercury deposition, regions of high atmospheric mercury deposition do not change under future scenarios (Future_High and Future_Low scenarios for year 2050; Figure 1). The magnitude of atmospheric mercury deposition, however, increases (Future_High: −23% to +86% and average: +27% by province/municipality) or decreases (Future_Low: −59% to +5% and average: −30% by province/municipality) depending on the absence or presence of strict policies and technologies to regulate mercury emissions from Chinese coal-fired power plants. The implications of policy-relevant mercury
emissions and deposition changes in China are discussed in detail in Giang et al. (2015). In this study, we use the Future_High and Future_Low scenario estimates combined with the rice paddy model to project future rice THg and MeHg concentrations (section 3.5).

### 3.2. Rice Paddy Model Calibration

Adsorption and desorption are the most uncertain parameters in the rice paddy model due to measurement uncertainties. In CAL, we adjust the rates for adsorption and desorption at steady state to match the feasible range of percent soil mercury contribution to rice. As illustrated in Figure 3, under constant $k_{adsorption}$ (IHg = 3.3 yr\(^{-1}\), MeHg = 2.8 yr\(^{-1}\)), increasing $k_{desorption}$ causes the top reservoir (pore water and flooded water column) and the bottom reservoir (topsoil and subsoil) IHg and MeHg concentrations to increase and decrease, respectively, from the steady state values (dotted gray line). Under varying range of $k_{desorption}$, we perform a series of simulations to adjust $k_{adsorption}$ to match steady state mercury concentrations in the rice paddy reservoirs and the feasible range of percent soil Hg contribution to rice (5–60%). The model-simulated $k_{adsorption}$ and $k_{desorption}$ necessary to match steady state reservoir mercury concentrations and the ratios of $k_{adsorption}/k_{desorption}$ for IHg and MeHg corresponding to the feasible range of percent soil mercury contribution to rice are shown in Table 4.

Achieving 5 to 60% soil mercury contribution to rice at steady state results in wide ranges of $k_{adsorption}$ (IHg: 0.60 to 11 and MeHg: 0.50 to 9.1 yr\(^{-1}\)), and $k_{desorption}$ (IHg and MeHg: 1.9 × 10\(^{-3}\) to 5.0 × 10\(^{-2}\) yr\(^{-1}\)), and relatively narrow ranges in $k_{adsorption}/k_{desorption}$ ratios (IHg: 220 to 316 and MeHg: 182 to 263, Table 4). Our BASE rate coefficients for $k_{adsorption}$ (IHg: 3.3 and MeHg: 2.8 yr\(^{-1}\)) and $k_{desorption}$ (IHg and MeHg: 1.4 × 10\(^{-2}\) yr\(^{-1}\)) represent the values that correspond to 30% soil mercury contribution to rice in CAL. Applying $k_{adsorption}$ and $k_{desorption}$ to our 5 month dynamic standard model simulation of BASE results in 39% and 35% soil IHg and MeHg contribution to rice, respectively, consistent with the median fraction estimated from the rice

![Figure 3. Changes in rice paddy reservoir IHg and MeHg concentrations with increasing $k_{desorption}$ during model calibration (CAL). The $k_{adsorption}$ values for IHg and MeHg are held constant at 3.3 and 2.8 yr\(^{-1}\), respectively (30% soil mercury contribution to rice). The dotted lines represent the $k_{desorption}$ value (0.014 yr\(^{-1}\)) when the rice paddy reservoir IHg and MeHg concentrations are at steady state.](image_url)
paddy controlled plot studies (Meng et al., 2011, 2012). The relatively narrow ranges in $k_{\text{adsorption}}/k_{\text{desorption}}$ ratios under varying percent soil mercury contribution to rice suggest that $k_{\text{adsorption}}$ and $k_{\text{desorption}}$ are tightly coupled and that an increase in $k_{\text{desorption}}$ to enhance soil mercury contribution to rice requires increased supply of pore water mercury via $k_{\text{adsorption}}$. In addition, a lower $k_{\text{adsorption}}$ for MeHg than IHg is necessary to reproduce steady state mercury concentrations and mercury lifetimes in the reservoirs. The lower $k_{\text{adsorption}}$ for MeHg than IHg captures the binding efficiencies of MeHg and IHg to soil particles. Positively charged IHg cations have higher binding efficiencies to negatively charged organic matters on soil particles (i.e., humus, clay minerals) than neutrally charged MeHg (Różański et al., 2016).

We further evaluate $k_{\text{adsorption}}$ and $k_{\text{desorption}}$ by comparing between the model-calibrated (CAL) and experimentally derived values. The experimental values are from controlled experimental settings of spiking high concentrations of mercury to various types of soil-solution mixtures (Liao et al., 2009; Y. Yin et al., 1997). The CAL ranges of $k_{\text{adsorption}}$ and $k_{\text{desorption}}$ are much lower than experimentally derived values of $k_{\text{adsorption}}$ (1,250 to 13,141 yr$^{-1}$) and $k_{\text{desorption}}$ (465 to 5,263 yr$^{-1}$). The ratios of $k_{\text{adsorption}}/k_{\text{desorption}}$ determined from CAL are approximately tenfold larger than those observed in the same experimental settings. Applying the experimental values of $k_{\text{adsorption}}$ (465 to 5,263 yr$^{-1}$) to the rice paddy model results in 100% soil mercury contribution to rice and orders of $10^5$ to $10^{12}$-fold reduction in mercury concentrations in the topsoil and subsoil reservoirs compared to the steady state values. Applying the experimental values of $k_{\text{adsorption}}$ (1,250 to 13,141 yr$^{-1}$) together with the experimental $k_{\text{desorption}}$ results in 100% soil mercury contribution to rice and orders of $10^3$ to $10^5$-fold reduction in the topsoil and subsoil reservoir mercury concentrations, which are inconsistent with available measurements (Table 2). This suggests that $k_{\text{adsorption}}$ and $k_{\text{desorption}}$ measured in experimental settings may be too rapid to explain the observed reservoir mercury concentrations. The experimental $k_{\text{adsorption}}$ and $k_{\text{desorption}}$ resulting in 100% soil mercury contribution to rice also suggest that all mercury infiltrated to the pore water are rapidly adsorbed to particles of topsoil rather than being taken up by rice. We discuss why these rapid $k_{\text{adsorption}}$ and $k_{\text{desorption}}$ are unlikely to occur in natural rice paddies in the discussion section.

### 3.3. Model Evaluation

We use THg and MeHg concentrations simulated from BASE (5 month dynamic standard model simulation) to evaluate the overall performance of the rice paddy model. The comparison between the BASE-simulated concentrations and observations is presented in Table 2. The BASE THg and MeHg concentrations and % MeHg (of THg) in the pore water and the flooded water column fall within the wide ranges of the observed values in rice paddies (Table 2) (J. Liu et al., 2012; Rothenberg & Feng, 2012; Su et al., 2016; Zhao et al., 2016). For topsoil, the BASE THg concentration and % MeHg (of THg) fall within the ranges of the observed values in rice paddies (Marvin-DiPasquale et al., 2014; Su et al., 2016) and correspond with the average Chinese agricultural topsoil mercury concentration reported by S. Wang et al. (2016). Soil-pore water partition coefficients estimated using the BASE-simulated soil and pore water THg (Log $K_d = 3.0$) and MeHg (Log $K_d = 3.0$) concentrations are similar for MeHg but slightly lower for THg than those estimated from Chinese rice paddies (THg: Log $K_d = 4.1$ to 5.8 and MeHg: Log $K_d = 2.0$ to 4.1) (Rothenberg & Feng, 2012).

With respect to rice mercury concentrations, the BASE-simulated THg (14 ng/g) and MeHg (4.7 ng/g) concentrations and % MeHg (of THg: 34%) after 5 months agree well with the median value reported in China (Table S1). The model slightly underestimates the rice THg concentration, likely due to the lack of gaseous Hg$^0$ uptake via foliage. Assuming that an additional ~20% of IHg in rice comes from gaseous Hg$^0$ uptake via foliage (Feng et al., 2016; Strickman & Mitchell, 2017; R. Yin et al., 2013), our estimates show rice THg concentration of 16 ng/g and % MeHg (of THg) of 30%, which correspond more closely with the observed median value in China.

We compare the observed and model-simulated spatial variability in rice THg and MeHg concentrations (SP_Atm, SP_Soil, and SP_Both) to further evaluate the rice paddy model. As illustrated in Figure 4 (in dotted circles), we plot the observed rice THg and MeHg concentrations using the available latitude-longitude coordinate information from Table S1. For those without coordinates, the concentrations are plotted using the information of sampling towns or cities or simply on the geographical center of the province/municipality (italicized in Table S1). The linear regressions between the observed and model-simulated THg and MeHg concentrations under our simulations varying both atmospheric and soil concentrations (SP_Both, based
on 4° × 5° latitude-longitude grid cell averages) show correlations for THg of $r^2 = 0.41$ and for MeHg of $r^2 = 0.61$. This suggests that our rice paddy model can reproduce some variability in observed rice THg and MeHg concentrations across China. We also note that using $k_{\text{adsorption}}$ and $k_{\text{desorption}}$ estimated at 5% and 60% soil mercury contribution to rice (CAL) do not significantly improve the overall correlations between the observed and model-simulated rice THg and MeHg concentrations across China (5%; $r^2 = 0.24$ and $r^2 = 0.46$ for THg and MeHg at 60%; $r^2 = 0.43$ and $r^2 = 0.62$ for THg and MeHg).

Under our simulation varying only atmospheric deposition (SP_Atm), rice THg and MeHg concentrations demonstrate relatively narrow ranges across China (THg: 12 to 15 ng/g and MeHg: 3.9 to 4.9 ng/g). The linear regressions between the observed and SP_Atm rice THg and MeHg concentrations show virtually no correlation (THg: $r^2 = 0.0005$ and MeHg: $r^2 = 0.02$). The linear regressions between the observed and model-simulated rice THg and MeHg concentrations under varying soil THg and MeHg concentrations (SP_Soil) show a similar correlation (THg: $r^2 = 0.43$ and MeHg: $r^2 = 0.62$) with SP_Both. The SP_Soil rice THg and MeHg concentrations show wide ranges across China (THg: 13 to 45 ng/g and MeHg: 4.5 to 17 ng/g) and are within the observed ranges of 7.5 to 103 ng/g and 1.6 to 20 ng/g for rice THg and MeHg (grid cell averages), respectively. We find that soil MeHg concentration is particularly effective in predicting the observed rice MeHg concentrations. Rice THg concentrations simulated from SP_Soil capture locations of rice mercury hot spots or those exceeding the China’s National Standard Limit of 20 ng THg/g in rice (China E. P. A., 2005). Based on the reported spatial distribution of agricultural topsoil THg concentrations across China (S. Wang et al., 2016), these regions have soil THg concentration >400 ng/g.

Additionally, we compare the observed and model-simulated bioaccumulation factor (BAF) or the ratio of rice to soil THg and MeHg concentrations. Rothenberg et al. (2014), based on the compilation study of rice THg and MeHg concentrations from China, found mean BAFs of 0.32 (range $1.2 \times 10^{-4}$ to 15) and 5.5 (range 0.20 to 34) for THg and MeHg, respectively. The BAFs estimated using the SP_Soil rice THg and MeHg concentrations and soil THg and MeHg concentrations reported by S. Wang et al. (2016) are within these ranges (THg: $1.0 \times 10^{-2}$ to 0.60, mean = 0.14, MeHg: 0.71 to 12, and mean = 4.9).

### 3.4. Sensitivity Analyses

We perform multiple types of sensitivity analyses to identify processes and factors governing rice mercury sources and concentrations (SE_10%, SE_Uncertainty, SE_MeHg, SE_Process, and SE_Input). Figure 5 shows the results of sensitivity analyses, which are based on ±10% perturbations (upper panels; SE_10%) and uncertainty ranges from literature in mercury inputs, concentrations, and rate coefficients from BASE (lower panels; SE_Uncertainty). The SE_10% shows that rice IHg concentration is most sensitive to the process of $k_{\text{root absorption}}$ for IHg. Rice MeHg concentration is most sensitive to microbial methylation with ±10%
perturbation in $k_{\text{methylation}}$ resulting in ±8.7% change in rice MeHg concentration. Among the ranges of available measurements, BASE uses a relatively low $k_{\text{methylation}}$. We find that $k_{\text{methylation}}$ between 0.06 and 5.3 yr$^{-1}$ is needed to reproduce the observed rice MeHg concentrations in China (Table S1). Changes in other model terms result in less than ±4% change in rice IHg and MeHg concentrations. Rice IHg and MeHg concentrations are slightly more sensitive to $k_{\text{filtration}}$ and atmospheric mercury deposition than $k_{\text{desorption}}$ and soil IHg and MeHg concentrations. Changes in $k_{\text{recycling}}$ and $k_{\text{burial}}$ from the deeper reservoir of the subsoil have no influence on rice IHg and MeHg concentrations during the lifetime of rice (5 months).

In SE_MeHg, we further assess the modeled influential IHg sources for microbial methylation and uptake by rice. As illustrated in Figure 6, rice MeHg concentration is more sensitive to IHg infiltration ($k_{\text{filtration}}$) than to IHg desorption ($k_{\text{desorption}}$). Under the narrow uncertainty range of $k_{\text{filtration}}$, rice MeHg concentration changes from 2.8 to 3.4 ng/g compared to the change in rice MeHg concentration from 0.95 to 3.0 ng/g under

![Figure 5](image1.png)

**Figure 5.** Results of sensitivity analyses representing percent changes (%) in rice IHg and MeHg concentrations under (1) ±10% perturbations (upper panel; SE_10%) and (2) uncertainty ranges from literature of individual mercury inputs, concentrations, and rate coefficients (lower panel; SE_Uncertainty). The percent changes (%) in rice IHg and MeHg from SE_Uncertainty are shown on a log scale.

![Figure 6](image2.png)

**Figure 6.** Model-simulated changes in rice MeHg concentration with changes in $k_{\text{filtration}}$ and $k_{\text{desorption}}$ for IHg (SE_MeHg). The shaded area and the dotted line for $k_{\text{filtration}}$ represent the uncertainty range from literature and the BASE model implemented value, respectively. The shaded area and the dotted line for $k_{\text{desorption}}$ represent the feasible range of percent soil mercury contribution to rice (5–60%) (Meng et al., 2011, 2012) and the BASE model implemented value (30%), respectively.
the range of $k_{\text{desorption}}$ estimated by percent soil mercury contribution to rice (CAL). This is consistent with previous studies that have suggested recently introduced IHg, relative to soil IHg, is more bioavailable for microbial methylation and uptake by rice (Meng et al., 2010, 2012; Qiu et al., 2013; Zhao et al., 2016).

The SE_Uncertainty simulations using the uncertainty ranges from literature show that irrigation input has a substantial effect on both rice IHg and MeHg concentrations (lower panels; Figure 5). Varying surface water mercury concentrations are not used in the spatial variability assessment given that these values are reported primarily near active and abandoned mercury mining sites in Guizhou province, with few measurements representing background concentrations in China (Table 1). Using the Guizhou surface water mercury concentrations, we evaluate the potential importance of contaminated irrigation water as a source of mercury to rice. The surface water THg and MeHg concentrations in Guizhou demonstrate average values of $\sim 1.7 \mu g/L$ and $\sim 0.10 \mu g/L$, respectively (Horvat et al., 2003; P. Li, Feng, Qiu, et al., 2012; Lin et al., 2010; Qiu et al., 2009, 2013), compared to the Chinese average values of $\sim 0.29 \mu g/L$ and $\sim 5.0 \times 10^{-4} \mu g/L$, respectively (L. Zhang & Wong, 2007). We run the rice paddy model under constant soil mercury concentrations and GEOS-Chem-simulated atmospheric mercury deposition as BASE and apply elevated surface water mercury concentrations consistent with those observed in Guizhou (THg = 1.7 $\mu g/L$ and MeHg = 0.10 $\mu g/L$). We find rice THg and MeHg concentrations of 86 ng/g and 42 ng/g, respectively, which are within the ranges of those observed in contaminated mining sites in Guizhou (Table S1). We discuss below the potential importance of irrigation water as a source of IHg and MeHg to rice in certain parts of China.

In SE_Process, we focus on $k_{\text{infiltration}}$ and $k_{\text{desorption}}$ to evaluate how these source-relevant processes influence rice IHg and MeHg concentrations within their feasible uncertainty ranges. As shown in Figure 2, $k_{\text{infiltration}}$ and $k_{\text{desorption}}$ are the primary pathways that supply recently introduced mercury and soil mercury to the pore water and subsequently to rice. We use the uncertainty range of $k_{\text{infiltration}}$ (Table 1) and the range of $k_{\text{desorption}}$ estimated using percent soil mercury contribution to rice (CAL) to evaluate the resulting changes in rice IHg and MeHg concentrations. As illustrated in the shaded area of Figure 7, there is a larger uncertainty range of $k_{\text{desorption}}$ than $k_{\text{infiltration}}$. Under these uncertainty ranges, the changes in $k_{\text{infiltration}}$ result in rice IHg and MeHg concentrations of 7.9–9.2 ng/g and 4.0–4.8 ng/g, respectively. The changes in $k_{\text{desorption}}$ result in rice IHg and MeHg concentrations of 7.6–13 ng/g and 3.8–7.3 ng/g, respectively. This suggests that both rice IHg and MeHg concentrations are more sensitive to the change in $k_{\text{desorption}}$ than $k_{\text{infiltration}}$, which acts as a limiting factor for supplying recently introduced IHg and MeHg sources to rice.

In SE_Process, we also observe nonlinear responses in rice IHg and MeHg concentrations with increasing $k_{\text{infiltration}}$ but not with $k_{\text{desorption}}$. The nonlinear responses in rice IHg and MeHg concentrations with increasing $k_{\text{infiltration}}$ are the result of inadequate supply of recently introduced mercury sources relative to increasing $k_{\text{infiltration}}$. This suggests that under constant atmospheric and irrigation mercury supply into the rice paddy system, increasing $k_{\text{infiltration}}$ has a declining relative influence on rice IHg and MeHg concentrations. Under constant soil mercury concentration, rice IHg and MeHg concentrations increase linearly with increasing $k_{\text{desorption}}$. 

![Figure 7. Model-simulated changes in rice IHg (blue) and MeHg (red) concentrations with changes in $k_{\text{infiltration}}$ and $k_{\text{desorption}}$ (SE_Process). The shaded area and the dotted line for $k_{\text{infiltration}}$ represent the uncertainty range from literature and the BASE model implemented value, respectively. The shaded area and the dotted line for $k_{\text{desorption}}$ represent the feasible range of percent soil mercury contribution to rice (5–60%) (Meng et al., 2011, 2012) and the BASE model implemented value (30%), respectively.](image-url)
In addition to the changes in rate coefficients, concentrations of mercury in soil and the magnitude of atmospheric mercury deposition can influence the relative contribution of various IHg and MeHg sources to rice. In CAL, we determine potential ranges of \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) using the feasible range of percent soil mercury contribution to rice under a fixed soil mercury concentrations and atmospheric mercury deposition. In SE_Input, we use the \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) consistent with our standard model simulation of BASE (30% soil mercury contribution to rice) to assess how the observed ranges of Chinese soil IHg and MeHg concentrations (S. Wang et al., 2016) and GEOS-Chem-simulated atmospheric mercury deposition influence percent soil mercury contribution to rice. The results of SE_Input show that both percent soil IHg and MeHg contribution to rice are more sensitive to the changes in soil IHg and MeHg concentrations than to the magnitude of atmospheric mercury deposition (Figure 8). Increasing soil IHg and MeHg concentrations using the observed range of Chinese soil mercury concentration results in increasing percent soil mercury contribution to rice: from 37 to 64% for IHg and from 32% to 64% MeHg. Increasing atmospheric mercury deposition using the GEOS-Chem-simulated range of Chinese atmospheric mercury deposition results in reduction in percent soil mercury contribution to rice: from 48% to 36% for IHg and from 42% to 31% for MeHg. Under the Chinese average atmospheric mercury deposition and irrigation input (consistent with BASE), the soil IHg and MeHg concentrations at which percent soil mercury contribution to rice begin to exceed 50% are 250 ng/g and 1.5 ng/g for IHg and MeHg, respectively. This suggests that the relative contribution of mercury sources to rice can shift more rapidly with the extent of soil IHg and MeHg contamination than atmospheric mercury deposition.

### 3.5. Future Rice Mercury Concentrations

Future rice and soil mercury concentration simulated using the median Chinese rice IHg and MeHg concentrations and steady state soil IHg and MeHg concentrations as baselines (Med_future) show relatively small changes in soil IHg and MeHg concentrations but measurable changes in rice IHg and MeHg concentrations by year 2050 (Figure 9). Under Future_High of 86% increase in atmospheric mercury deposition, both rice IHg and MeHg concentrations increase by 18%. Under Future_Low of 59% reduction in atmospheric mercury deposition, both rice IHg and MeHg concentrations decrease by 13%.
Future spatial variability in rice THg and MeHg concentrations of SP_Future are shown in Figure 10 as percent changes in rice THg and MeHg concentrations from the present-day spatial variability of SP_Both ((SP_Future – SP_Both)/SP_Both × 100 = percent change). Rice THg and MeHg concentrations increase under Future_High (+0.8 to +8.6% by grid cell) and decrease under Future_Low (−11% to −0.6% by grid cell). The regions with relatively large percent increase (> 5.0%) in rice THg and MeHg concentrations under Future_High occur in Beijing, Jiangsu, and Guangdong provinces. The regions with relatively large percent reduction (>−9.0%) in rice THg and MeHg concentrations under Future_Low occur in central China (Chongqing, Hubei, and Hunan).

Figure 9. Model-simulated future soil and rice lHg and MeHg concentrations (Med_Future) under Future_High (red; −23% to +86%) and Future_Low (blue; −59% to +5%).

Figure 10. Model-simulated spatial variability in percent change (%) in future rice THg and MeHg concentrations (SP_Future) from the present-day simulation of SP_Both.
4. Discussion

In this study, we use multiple modeling approaches to elucidate important processes and factors governing mercury sources and concentrations in rice at multiple spatiotemporal scales. We focus on how mercury inputs, soil mercury concentration, and their associated processes influence rice mercury sources and concentrations. The evaluation of the rice paddy model shows that our model reproduces concentrations in the range of observed values and can reproduce some spatial variability in rice across China. Sensitivity analyses of the rice paddy model suggest that soil mercury concentration and the process of desorption explain the observed spatial variability in Chinese rice mercury concentrations. Our future simulations show that policies that influence atmospherically deposited mercury to Chinese rice paddies can alter future rice mercury concentrations.

Our rice paddy model suggests that a portion of IHg and MeHg in rice comes directly from recently introduced sources via infiltration rather than recycling through the topsoil reservoir via the adsorption-desorption cycle. The influence of atmospheric sources of IHg and MeHg to rice has been a topic of debate in the literature (Meng et al., 2011, 2012; Qiu et al., 2013; Zhao et al., 2016). The processes of adsorption and desorption, which control the relative contribution of soil versus recently introduced IHg and MeHg to rice, are characterized by measurement uncertainties in rice paddies. In this study, we divide the pore water and topsoil reservoirs to understand how recently introduced mercury sources, in comparison to topsoil mercury, influence rice mercury sources and concentrations. Moreover, by comparing between the model constrained (CAL) and experimental values of \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \), we find that the relatively slow \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) constrained by the feasible range of percent soil mercury contribution to rice explain the observed reservoir mercury concentrations, rather than the experimental values, which result in 100% soil mercury contribution to rice (section 3.2). Rapid \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) are plausible only under laboratory settings given that these rates are determined by spiking unreasonably high mercury concentrations and by physically mixing soil-solution mixtures, which can facilitate these processes. Particularly for \( k_{\text{desorption}} \), experimental studies have suggested that \( k_{\text{desorption}} \) is dependent on soil pH and organic content, which determines the binding site and affinity for mercury to soil particles (Feng et al., 2016; Liao et al., 2009; Y. Yin et al., 1997). D. Wang et al. (1997) documented decreasing mercury concentrations in plants with increasing soil organic content and attributed this to strong binding affinity between mercury and organic matter. Given the high organic content of rice paddy soil, a relatively slower rate of \( k_{\text{desorption}} \) appears to explain an approximately tenfold higher \( k_{\text{adsorption}}/k_{\text{desorption}} \) ratio than the experimentally derived \( k_{\text{adsorption}}/k_{\text{desorption}} \) ratio (section 3.2). We suggest that further measurement studies using rice paddy soil are required to better constrain \( k_{\text{adsorption}} \) and \( k_{\text{desorption}} \) in rice paddies.

The sensitivity simulations of SE_10% using the standard model (BASE) suggest that the process of infiltration \( (k_{\text{infiltration}}) \) is indeed more influential in determining rice IHg concentration than adsorption and desorption \( (k_{\text{adsorption}} \text{ and } k_{\text{desorption}} \text{ Figure 5}) \). Rice root absorption \( (k_{\text{root absorption}}) \) also has the largest modeled influence on rice IHg concentration (SE_10%; Figure 5), suggesting that IHg infiltrated from the flooded water column is taken up rapidly via rice roots. This is consistent with the transpiration activity driven by the dense rice paddy root system in the pore water. A majority of rice roots including fine root hairs, which provide large surface area for water and nutrient transpiration (Raven et al., 2005), exist in the pore water space and within 20 cm of the soil column (Yoshida & Hasegawa, 1982). Rice root densities have been estimated to be much higher than other crops such as wheat, soybean, and maize (Yoshida & Hasegawa, 1982). Bachand et al. (2014) have also suggested, based on data from Californian rice paddies, that the transpiration-driven activity by rice roots has the dominant influence on water infiltration in rice paddies.

For MeHg, external MeHg input via atmospheric deposition, irrigation, and soil MeHg constitute only a small portion of the total MeHg in rice compared to the internal production as illustrated by the largest model influence of \( k_{\text{methylation}} \) on rice MeHg concentration (SE_10%; Figure 5). Many previous studies have observed active microbial methylation in irrigated rice paddies (Marvin-DiPasquale et al., 2014; Rothenberg & Feng, 2012; Zhao et al., 2016). J. Liu et al. (2012) observed a significant positive correlation between MeHg concentration in the pore water and MeHg concentration in Chinese rice and attributed this to internal MeHg production in the pore water. With regard to sources available for microbial methylation, a number of studies have suggested that recently deposited mercury from the atmosphere (in the form of IHg) is more bioavailable for methylation and uptake by rice than soil IHg (Meng et al., 2011, 2012; Qiu et al., 2013; Zhao et al.,
In particular, Meng et al. (2011, 2012) in rice paddy controlled plot studies observed significant increase in rice paddy soil THg and MeHg concentrations over the rice growing period at sites where atmospheric mercury deposition is high but not at sites with relatively high soil THg and MeHg concentrations. Given that atmospheric deposition was the main source of mercury input to soil, the increase in paddy soil MeHg concentration was explained by the microbial methylation of atmospherically deposited mercury. Our sensitivity analyses of SE_10% show a consistent finding that rice MeHg concentration is slightly more sensitive to the changes in atmospheric deposition in the form of IHg than soil MeHg concentration (Figure 5). In SE_MeHg, IHg supply to the pore water via infiltration has a larger model influence on rice MeHg concentration than IHg adsorption from soil (Figure 6).

While the rate of infiltration is well constrained by measurement studies in rice paddies, the wide ranges of \( k_{\text{desorption}} \) estimated using percent soil mercury contribution result in greater variation in simulated rice IHg and MeHg concentrations. In SE_Process, varying \( k_{\text{infiltration}} \) and \( k_{\text{desorption}} \) within the feasible uncertainty range, both rice IHg and MeHg concentrations increase linearly with \( k_{\text{desorption}} \), but not with \( k_{\text{infiltration}} \), which is limited by both the uncertainty range and the magnitude of recently introduced IHg and MeHg to the system (Figure 7). Our rice paddy model uses \( k_{\text{infiltration}} \) measured in Californian, Taiwanese, and Korean rice paddies (Table 1). The narrow uncertainty range in \( k_{\text{infiltration}} \) has been attributed to similar soil type (i.e., silt and clay) and porosity across rice paddies (Chen et al., 2002; Kim et al., 2014). In contrast, many environmental factors have been shown to enhance \( k_{\text{desorption}} \) in rice paddies. Previous studies have suggested that soil acidity in rice paddies, which is generated by oxygen leakage during root exudation, can facilitate soil mercury desorption (Feng et al., 2016; Shu et al., 2016; Su et al., 2016). For MeHg, high concentrations of pore water dissolved organic carbon, which is generated from tissue leaching and decay, can promote MeHg partitioning into pore water and enhance its bioavailability for uptake by rice (Rothenberg et al., 2014). While our model assessment of \( k_{\text{desorption}} \) does not take these environmental factors into consideration, the wide range in \( k_{\text{desorption}} \) and its potential sensitivity to various environmental factors suggest that rice IHg and MeHg concentrations are more sensitive to the process of desorption than infiltration.

The strong influence of soil mercury as a source to rice is shown by SE_Input, where varying the range of observed Chinese soil IHg and MeHg concentrations have larger relative influence on the simulated percent soil mercury contribution to rice than the observed range of Chinese atmospheric mercury deposition (Figure 8). The modeled spatial variability of rice THg and MeHg concentrations also suggests that soil THg and MeHg concentrations (SP_Soil), rather than direct atmospheric mercury deposition (SP_Atm), explain the observed rice THg and MeHg concentrations across China (Figure 4). The locations of rice mercury hot spots or those that exceed 40 ng THg/g in rice occur predominantly in central China and near active and abandoned mercury mines (Guizhou, Hunan, and Shanxi) (B. Li et al., 2013; Qiu et al., 2012; Rothenberg et al., 2014). Other areas that exceed the China’s National Standard Limit of 20 ng THg/g in rice are characterized by high bedrock mercury concentration (Guangxi), elevated atmospheric mercury deposition (Fujian and Liaoning), and artisanal as well as large-scale gold mining (Jiangxi) (S. Wang et al., 2016; L. Zhang et al., 2015). This suggests that the activities that lead to rice and soil mercury contamination (>400 ng THg/g) are not limited to mercury mining activities. The remaining regions in China are largely characterized by atmospheric mercury point sources including coal combustion, nonferrous metal smelting, cement production, and iron and steel production (L. Zhang et al., 2015). Based on the reported spatial distribution of Chinese agricultural soil THg concentration (S. Wang et al., 2016), these regions have soil THg concentration ranging between 65 and 300 ng/g. This range is consistent with the Chinese average soil THg concentration or those used for BASE (~79 ng/g) and the SE_Input estimated concentration at which percent soil mercury contribution to rice begins to exceed 50% (~250 ng/g; Figure 8).

Similar to IHg, the extent of soil MeHg contamination, rather than internal MeHg production via microbial activity, has a larger relative influence on rice MeHg sources and concentrations. As illustrated in SE_Input, in regions of elevated soil MeHg concentration (>1.5 ng/g), the desorption of soil MeHg outcompetes the internal microbial methylation of atmospherically deposited mercury (Figure 8). Soil MeHg better predicts the observed rice MeHg concentration (Figure 4) as well as the observed BAFs than IHg (section 3.3). We attribute this to little external MeHg input to the rice paddy system. The contribution of various IHg sources (i.e., atmospheric deposition, irrigation, soil, and foliage uptake) to rice has much greater spatial variability. For MeHg, there is a little external input, with the rest originating from internal production via microbial methylation and soil desorption.
The unexplained variance between the observed and model-simulated (SP_Soil; THg: $r^2 = 0.41$, MeHg; $r^2 = 0.61$) spatial variability in rice THg and MeHg concentrations may be related to the geographical differences in environmental factors governing the rate of mercury biogeochemical processes as well as the biogeochemical differences between contaminated and background regions. For instance, Feng et al. (2016) suggested that, while soil acidity caused by root exudation can increase the rate of $k_{\text{desorption}}$ in many rice paddies, the high sulfide content in mine-contaminated soil (i.e., calcine) can limit active soil mercury desorption. Rothenberg et al. (2014) suggested that the biogeochemical differences between contaminated and background soil as well as the geographical differences in rice variety may determine the extent of mercury transpiration and bioaccumulation in rice. Given the limited number of measurements available on mercury speciation, transport, and biogeochemical fluxes and rates in rice paddies, many rate coefficients derived to construct the rice paddy model in this study were gathered from mercury mine-contaminated rice paddies in China and California (Table 1). These limitations may also explain some discrepancies between the observed and model-simulated rice THg and MeHg concentrations. In addition, J. S. Zhu et al. (2013) observed significant positive relationships between mercury evasion flux and solar radiation, and water temperature in Chinese rice paddies. The relationship between environmental factors and the rate of biogeochemical processes for mercury in rice paddies are, however, limited to a few studies and thus not considered in our model. We suggest that more measurement studies are needed to constrain the spatial variability of rice THg and MeHg concentrations in China.

Our results suggest that targeted mercury management in rice paddies requires precise understanding of biogeochemical processes and factors that contribute to the spatial variability in rice mercury sources and concentrations. In regions that have background to average soil mercury concentration, rice IHg and MeHg concentrations are controlled by the processes of infiltration and methylation of recently deposited mercury from the atmosphere. The relative importance of IHg and MeHg sources to rice can shift from atmospheric to soil mercury at sites with elevated soil mercury concentration and with environmental factors that enhance $k_{\text{desorption}}$. Based on the side-by-side comparison of contaminated versus uncontaminated sites in China, Rothenberg et al. (2014) suggested that the extent of rice mercury contamination is related to proximity to active mercury pollution sources rather than diffuse regional mercury sources. Our results provide an additional insight that soil mercury impacted by various anthropogenic activities including local mercury and gold mining activities as well as previously deposited mercury from atmospheric point sources explain the observed spatial variability of rice THg and MeHg concentrations in China.

Identifying a targeted mercury management strategy can nevertheless remain challenging, for instance, in central China, where the regions of rice mercury hot spots, high water and soil THg and MeHg concentrations, and large atmospheric mercury deposition are colocated. The contribution of irrigation water contaminated by mercury ore and calcine deposits may overwhelm the effect of other sources as well the effect of internal microbial methylation as illustrated by the SE_Uncertainty, where applying the elevated Guizhou (central China) surface water mercury concentrations to the rice paddy model reproduces observed Guizhou rice THg and MeHg concentrations. Based on the reported surface water mercury concentrations in Guizhou, the locations of severely contaminated surface water are, however, concentrated over a few stream reaches near major mercury mines (i.e., Wanshan, Wuchuan, and Tongren) (F. Fang et al., 2004; Horvat et al., 2003; P. Li, Feng, Qiu, et al., 2012; Lin et al., 2010; Qiu, Feng, Wang, & Shang, 2006, Qiu et al., 2009, 2012, 2013; Rothenberg & Feng, 2012). In addition to the potential importance of irrigation water as a source of mercury to rice, hydrologic management such as the alternating wetting and drying cycle, which is widely being implemented in China to reduce water consumption and methane emissions, has been shown to reduce rice MeHg concentrations substantially compared to a continuously flooded condition (Rothenberg et al., 2016). Our model simulates rice IHg and MeHg concentrations under a continuously flooded condition given that many sites, which reported mercury speciation, transport, and biogeochemical fluxes and rates and those used in our model (Table 1), represent a continuously flooded condition. We suggest that future investigation on the influence of hydrologic management on rice MeHg concentrations can help identify site-specific remediation strategies for rice MeHg in China.

Our simulated future median Chinese rice IHg and MeHg concentrations from Med_Future show that the absence (Future_High) or presence (Future_Low) of strict policies and technologies to regulate mercury emissions from Chinese coal-fired power plants can have measurable influence on rice IHg and MeHg concentrations (Med_Future, Figure 9). Given the small changes in Chinese average soil IHg and MeHg concentrations...
during the time frame of our model simulation (year 2020 to 2050), the changes in the median Chinese rice I$_{Hg}$ and Me$_{Hg}$ concentration predominantly reflect the changes of atmospheric mercury deposition. Soil I$_{Hg}$ and Me$_{Hg}$ concentrations are subject to small changes given the long mercury lifetime in the topsoil reservoir. Larger changes in soil I$_{Hg}$ concentrations than Me$_{Hg}$ can be explained by negligible Me$_{Hg}$ input via the GEOS-Chem-simulated atmospheric deposition. This suggests that the accumulation of previously deposited mercury in soil is unlikely to affect the median Chinese rice I$_{Hg}$ and Me$_{Hg}$ concentrations at least during our assessment timescale.

Our future spatial variability assessment of percent changes in rice TH$_{Hg}$ and Me$_{Hg}$ concentrations shows that the regulation of atmospheric mercury emissions from Chinese coal-fired power plants can have measurable health benefits to Chinese populations exposed to dietary mercury via rice ingestion (SP_Future, Figure 10). Under Future_High, the regions subject to relatively large percent increase (>5.0%) in rice TH$_{Hg}$ and Me$_{Hg}$ concentrations are characterized by regions of either low rice production (Beijing; Figure 1) or low observed rice TH$_{Hg}$ and Me$_{Hg}$ concentrations (Jiangsu and Guangdong; Table 2). In contrast, central China (Chongqing, Hubei, and Hunan) characterized by rice mercury hot spots, high soil TH$_{Hg}$ and Me$_{Hg}$ concentrations, and large rice production exhibits relatively large percent reduction (>9.0%) in rice TH$_{Hg}$ and Me$_{Hg}$ concentrations under Future_Low. A recent survey of Chinese provincial rice consumption level reported rice consumption levels of 475, 395, and 591 g/d/person in Chongqing, Hubei, and Hunan, respectively, which are larger than the Chinese average rice consumption level of ~300 g/d/person (De Steur et al., 2010). H. Zhang, Feng, Larssen, Qiu and Vogt (2010) also suggested that, in certain parts of central China and in particular in Guizhou province, rice ingestion is the dominant Me$_{Hg}$ exposure pathway compared to fish consumption. We suggest that understanding future public health risks from mercury via rice ingestion requires knowledge about the spatial variability in rice production, consumption, and the changes in rice TH$_{Hg}$ and Me$_{Hg}$ concentrations across China.

Our future assessments likely underestimate the potential health benefits under the implementation of the Minamata Convention on Mercury. In this study, we focus on Future_High and Future_Low to capture ranges of future rice TH$_{Hg}$ and Me$_{Hg}$ concentrations under the absence or strict regulation of atmospheric mercury emissions from Chinese coal-fired power plants. While coal-fired power plants are the dominant mercury emission source in China, our present-day spatial variability assessment (SP_Soil) clearly demonstrates that multiple anthropogenic activities and sources can pose rice TH$_{Hg}$ and Me$_{Hg}$ contamination in China. In fact, the Minamata Convention on Mercury includes a number of provisions related to the regulation of anthropogenic mercury emissions from a variety of power and industrial sectors. The convention also includes specific provisions to ban mercury mining activities and remediate contaminated sites, which may substantially reduce rice TH$_{Hg}$ and Me$_{Hg}$ concentrations and further improve health benefits for populations near mercury mining sites. Additionally, we predict that the changes in surface water mercury concentration with the regulation of atmospheric mercury emissions will alter the relative contribution of irrigation mercury source to rice. M. Liu et al. (2016) estimated that 97% of the total mercury found in Chinese surface water has an atmospheric origin (i.e., recently deposited mercury from the atmosphere and the associated runoff from land). Future studies that evaluate the changes in various anthropogenic mercury emissions, releases, and other activities will help better quantify future public health risks originating via rice ingestion in China.

5. Conclusion

In this study, we use models to elucidate important processes and factors governing mercury sources to rice at multiple spatiotemporal scales. Our rice paddy model considers multiple mercury sources (atmospheric deposition, soil, and irrigation water). These sources have varying magnitude, pathways, and timescales for rice uptake. We show that the relative importance of various mercury sources to rice depends on both soil mercury concentration and the rate of desorption. Both soil TH$_{Hg}$ and Me$_{Hg}$ reproduce some spatial variability as well as rice mercury hot spots across China. The sources that contaminate soil are linked to various anthropogenic activities including local mercury and gold mining activities and previously deposited mercury from atmospheric point sources. We find that, in central China, the regions of large atmospheric deposition, high soil mercury concentration, high rice mercury concentrations, and large rice production and consumption are colocated. This indicates that a precise understanding of mercury sources and biogeochemical processes is necessary to identify a targeted mercury management strategy. In the future, central
China is subject to the largest reduction in atmospheric mercury deposition and possibly the largest increase in health benefits under the strict policy to regulate mercury emissions from Chinese coal-fired power plants. These future assessments are likely underestimated if we consider multiple provisions that regulate anthropogenic activities under the implementation of the Minamata Convention on Mercury. Our study suggests that addressing rice mercury contamination in China requires both attention to contaminated soil and regulation of anthropogenic mercury emissions. Measurement studies targeting adsorption and desorption as well as the environmental factors affecting the rate of various biogeochemical processes in rice paddies will improve our understanding of the spatiotemporal resolution of rice THg and MeHg concentrations and public health risks in China.

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