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Using Mercury Stable Isotopes to Quantify Directional Soil−Atmosphere Hg(0) Exchanges in Rice Paddy Ecosystems

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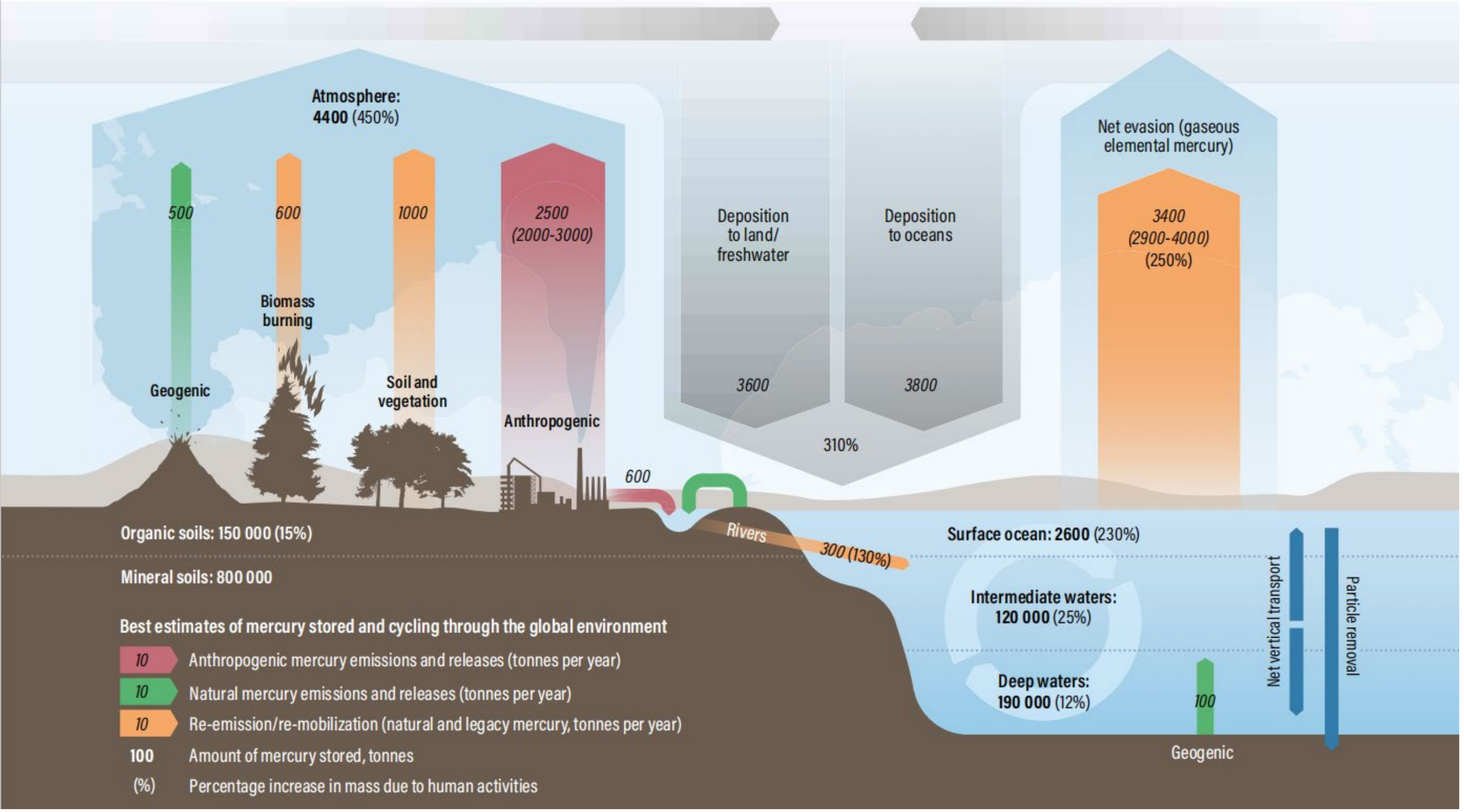
Outline

1. Background and objectives
2. Experimental design
3. Results and discussion
4. Conclusions

Background and objectives



The global mercury budget (UNEP, 2019)

- The present estimate of global natural Hg emission has large uncertainty (1700 to 2800 Mg a^{-1}) (Jiskraet al., 2015).
- Hg(0) emission from land surfaces plays an important natural Hg source (Wang et al., 2016).

Background and objectives

[20] Unbound elemental mercury does not significantly contribute to the total mercury found in background soils [*Skyllberg et al.*, 2000; *Friedli et al.*, 2007], so in our model all dry deposition of Hg^0 that is not permanently incorporated into leaf tissue is revolatilized to the atmosphere (hereafter referred to as revolatilization). Both dry and wet deposition of Hg(II) to leaf and soil surfaces are subject to photoreduction (if not permanently fixed by leaves), and we parameterize this flux (hereafter referred to as photoreduction) as a function of light intensity based on data reported by *Rolfhus and Fitzgerald* [2004],

$$f_{photoreduction} = 0.67 \cdot (1 - e^{-0.016 \cdot s}), \quad (3)$$

where $f_{photoreduction}$ is the fraction of Hg(II) deposited to leaf and soil surfaces that is reemitted to the atmosphere and *s* is the solar radiation flux (W m^{-2}). The remaining dry deposition of Hg(II) (minus leaf uptake and photoreduction) resides in the surface leaf/soil pool and is washed off in precipitation events (Figure 1). This is equivalent to the throughfall flux measured in field experiments.

(Smith-Downey et al., 2010)

Figure 2 shows the global tropospheric Hg budget from our GEOS-Chem simulation, including the rates of the major Hg^0 / Hg^{II} cycling pathways. The global tropospheric Hg reservoir is 3900 Mg, including 3500 Mg as Hg^0 and 400 Mg as Hg^{II}, smaller than the 4500 Mg reservoir in Holmes et al. (2010). In both cases, the reservoir was adjusted through the Hg^{II} photoreduction rate coefficient to match the observed annual mean TGM at long-term monitoring sites, mainly located at northern midlatitudes (Fig. 3). Holmes et al. (2010) used observations for 2000–2008 averaging 1.87 ± 1.00 ng m^{-3} STP ($p = 1$ atm, $T = 273$ K; $n = 39$ sites), whereas we use observations for 2007–2013 averaging 1.46 ± 0.25 ng m^{-3} STP ($n = 37$). Observed atmospheric concentrations in North America and Europe have

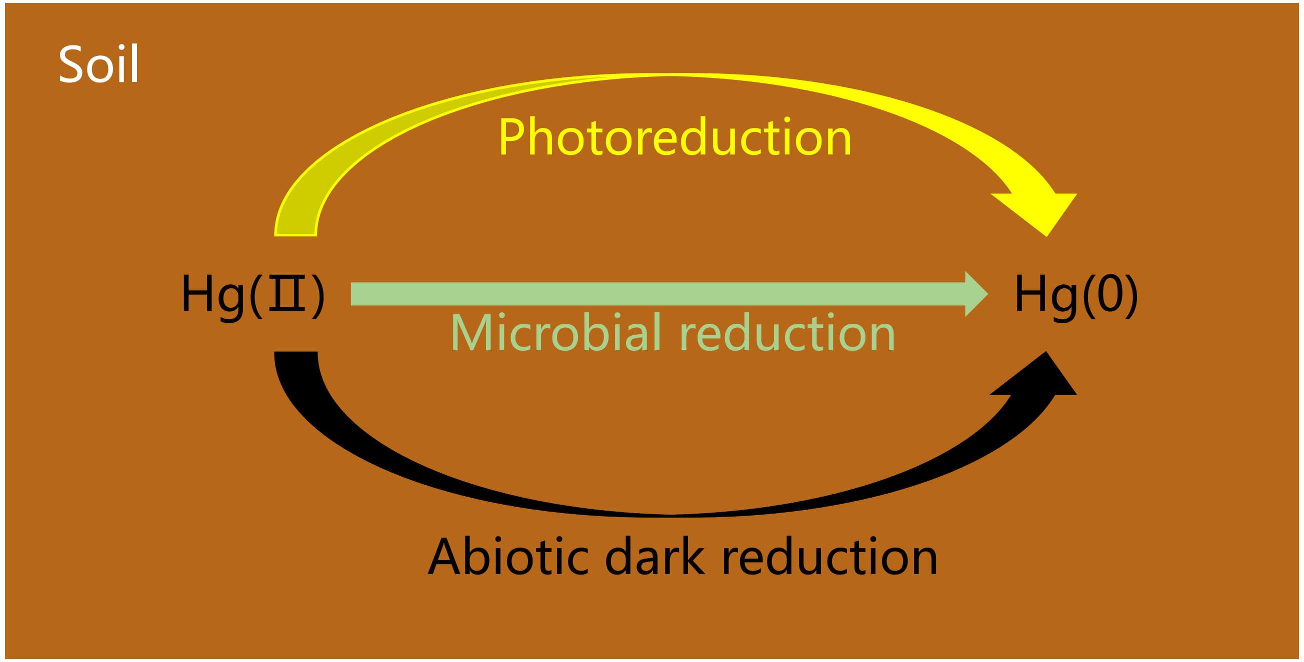
(Horowitz et al., 2017)

The soil pool and land-atmosphere exchange of Hg are simulated using the GTMM model[32]. The model has a horizontal resolution of 1°x1° and covers the top 30 cm of soils. The model takes the atmospheric deposition of both elemental and oxidized Hg from GEOS-Chem as input. This part of Hg is assumed to be loosely adsorbed to soil and leaf surfaces and undergoes photoreduction and revolatilization. Part of the Hg can reach to soil pool through litterfall. The model considers four soil Hg pools that are tied to carbon pools with characteristic turnover time ranged from 10^0 to 10^4 years. Hg bound to different soil carbon pools can be transformed between each other, and Hg is released to the atmosphere when the soil carbon is respired by microbial activities. The model is run for 30,000 years with atmospheric deposition at pre-industrial levels before ramped up with monthly deposition from 1840 to 2000[32].

(Zhang et al., 2021)

Solar radiation was considered the dominant factor for Hg reduction; therefore, soil Hg(0) emissions are primarily assessed based on the photoreduction process in chemical transport models

Background and objectives



The primary reduction pathways of Hg(Ⅱ) in soils

(Yuan et al., 2020; Jiskraet al., 2015)

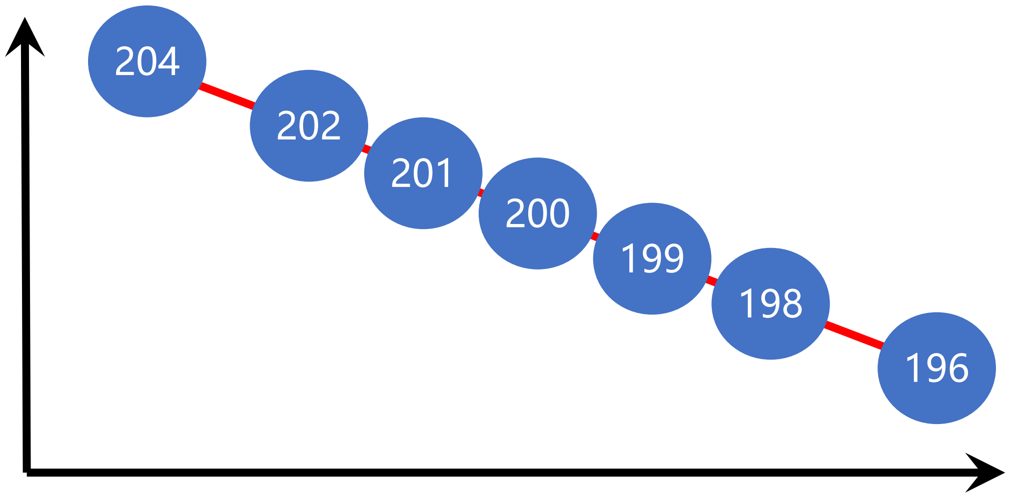
Photoreduction, **microbial reduction**, and **abiotic dark reduction** are considered the primary processes contributing to Hg(0) emissions from soils, neglecting later two processes could result in an underestimation of soil Hg(0) emissions.

Background and objectives

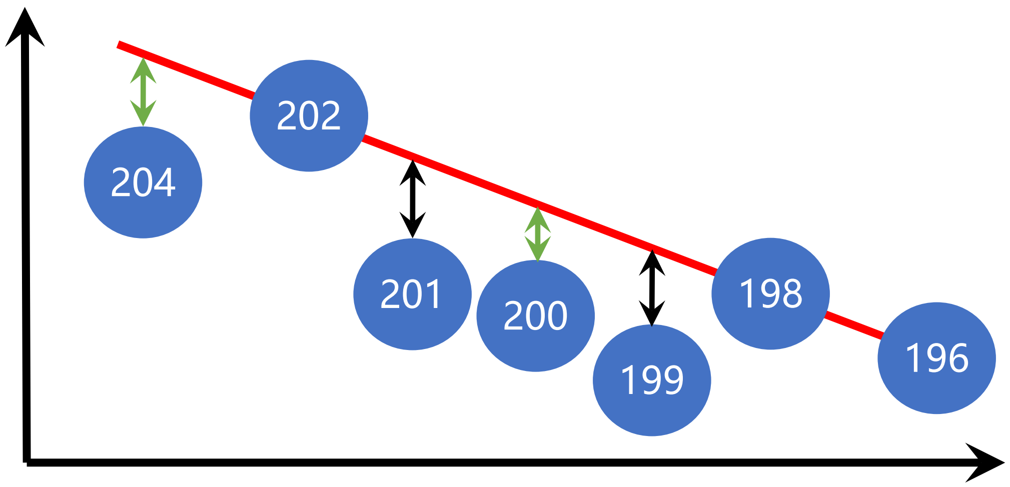
Rice paddies

- Hg(II) reduction in **rice paddy soils** can lower the concentration of substrates available for Hg-methylation and release the reduction product Hg(0) into the atmosphere.
- However, the relative importance of the differernt reduction processes for Hg(0) emissions from paddy soils remains elusive, mainly due to traditional observations of Hg(0) concentration and exchange flux not being able to distinguish Hg(0) emitted from different reduction processes

Background and objectives



Mass-dependent fractionations (MDF)



Mass-independent fractionations (MIF)

Mercury stable isotope is a useful tool for tracing and quantifying the sources and biogeochemical pathways of Hg innatural environments.

Background and objectives

Objectives:

1. Determine Hg isotope fractionation of microbial reductions, photoreductions, and abiotic dark reductions;
2. Characterize exchange fluxes and isotopic compositions of Hg(0) in the atmosphere−paddy soil exchange process using a dynamic flux chamber (DFC);
3. Quantify the relative contributions of different Hg(II) reduction processes to Hg(0) emissions from paddy soils.

Outline

Experimental design

Study area (109°11′27″ E, 27°33′48″ N)

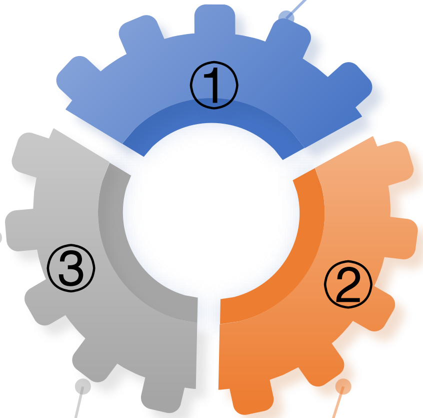
Field experiments were performed in a rice paddy located in the Wanshan Hg mining area in Guizhou Province, southwestern China.

Experimental design

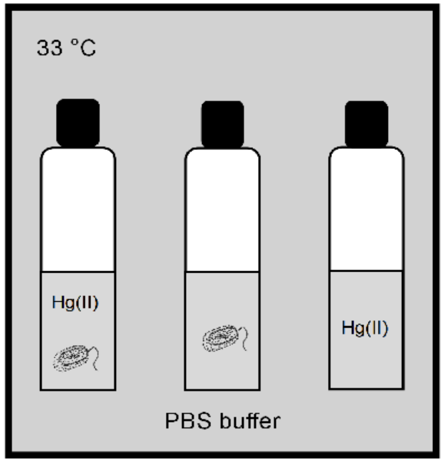
Three pre-experiments

③ During the night, the DFCs were covered by light-tight boxes to collect Hg(0) samples produced from the abiotic dark reduction process.

Photoreduction and abiotic dark reduction experiments



① The characteristics of isotope fractionation in microbial reduction process were studied by a pure culture experiment (*G. sulfurreducens* PCA).



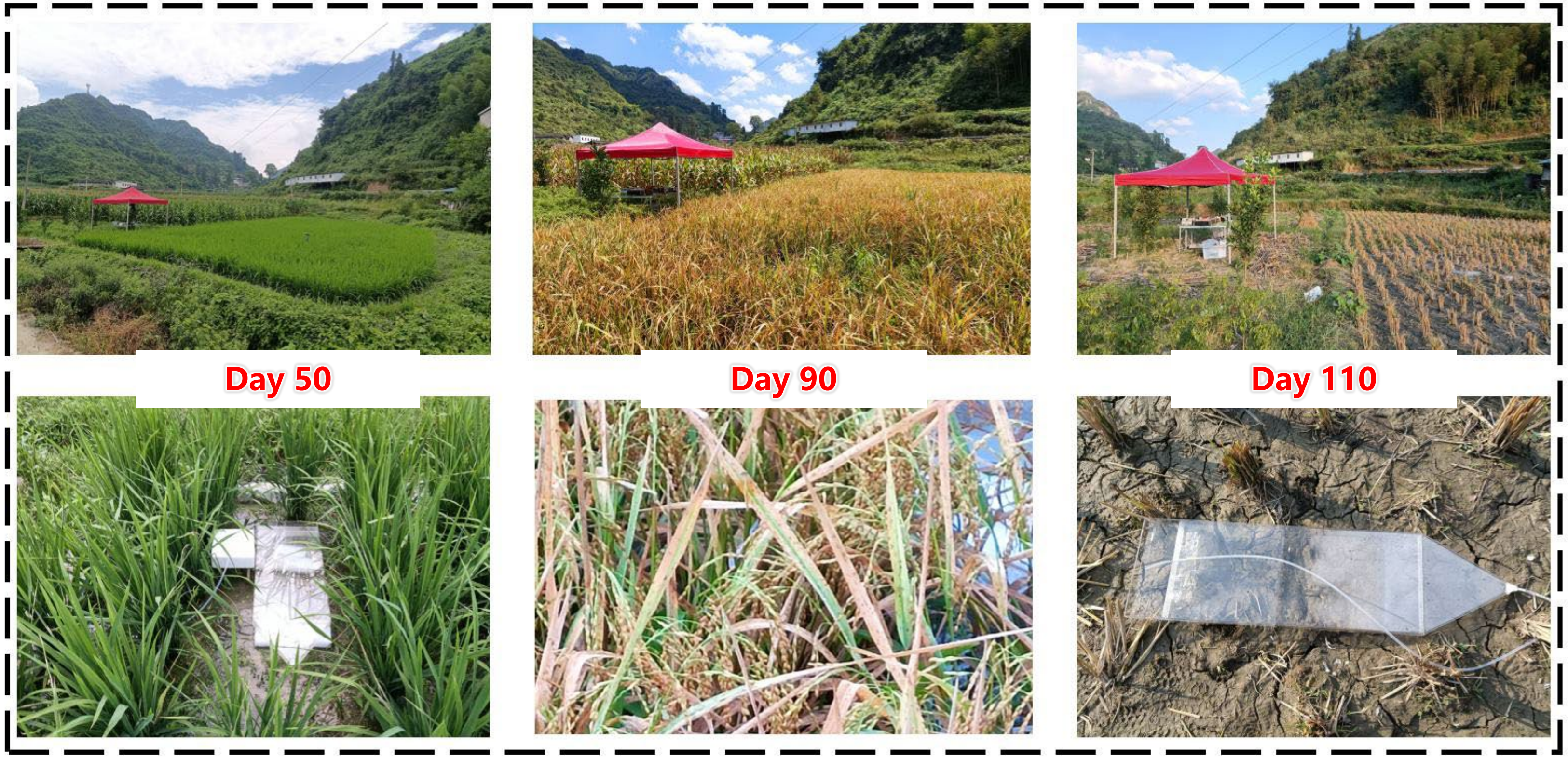
Pure culture experiment

② During the day, the DFCs were exposed to natural sunlight to collect Hg(0) samples produced from the photoreduction process.

All the samples were analyzed for Hg concentration and isotopic composition in the lab.

Experimental design

Sampling



Sampling in the rice paddy at different stages

Hg(0) exchange flux between the paddy soil and the atmosphere was measured in the rice paddy using the DFC method on the 50, 90, and 110th day after transplanting and first flooding.

Outline

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3. **Results and discussion**
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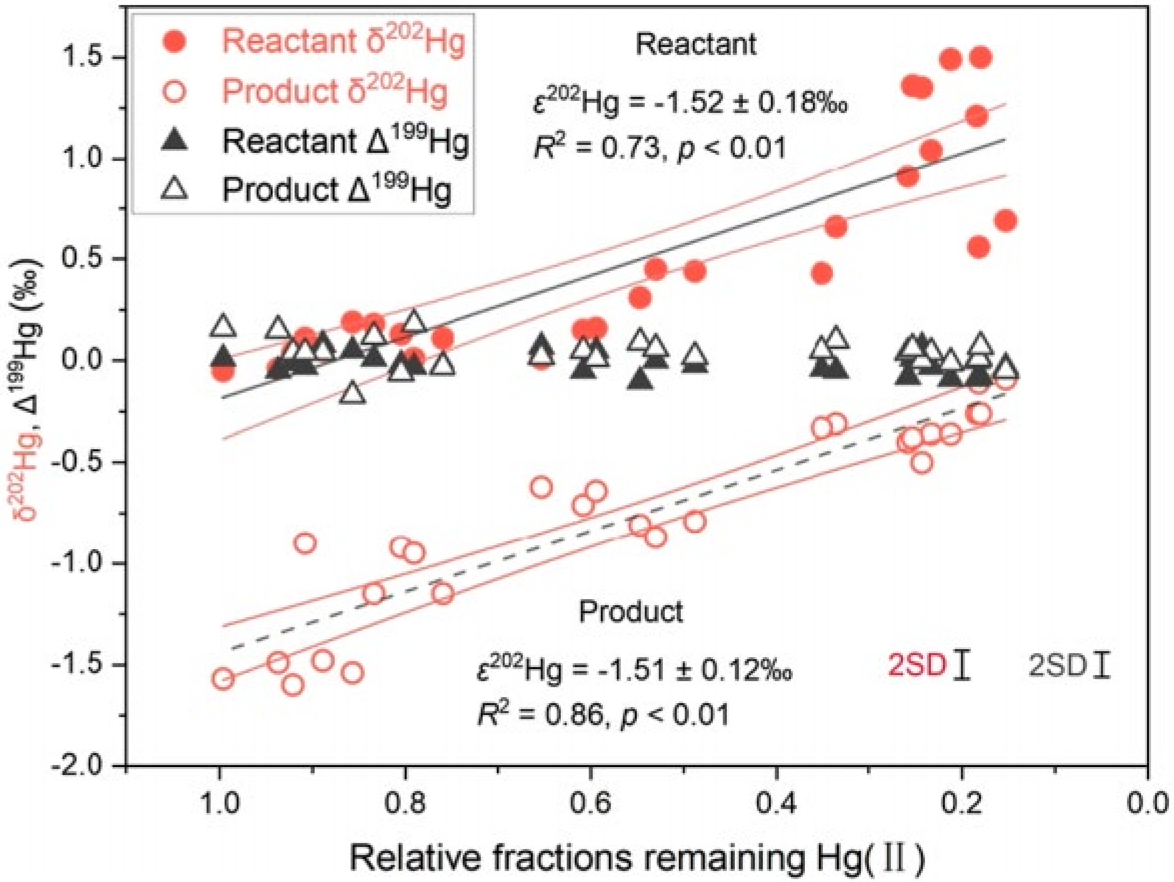
Results and discussion

1. microbial reduction process

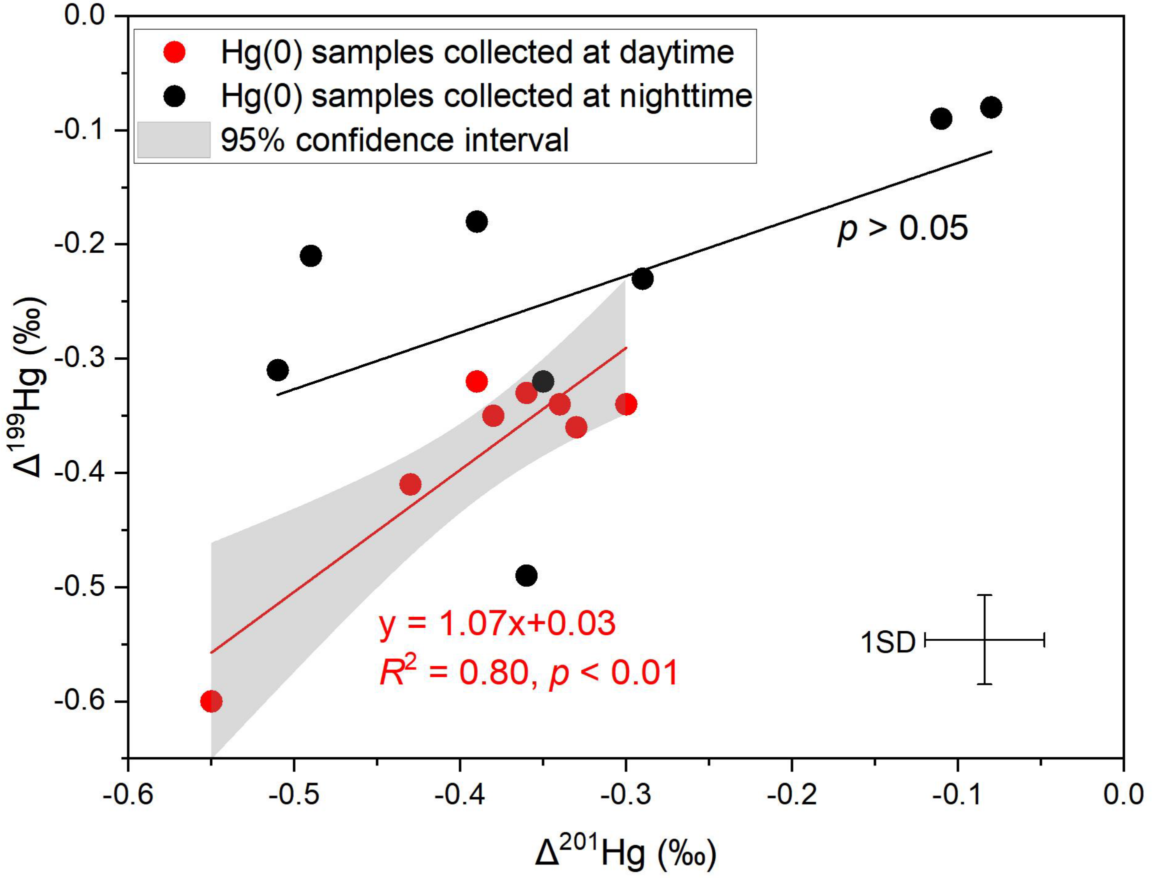


Mercury isotope fractionation characteristics during the microbial reduction of Hg(II)

- With progression of the experiment of Hg (II) reduction by bacteria, the Hg mass (94.3 ± 15.1%) and isotopes (δ^{202}Hg = −0.03 ± 0.10‰ and Δ^{199}Hg = −0.01 ± 0.06‰) **followed a mass balance throughout the experiment**, indicating the reliability of the experimental design and results.
- The Hg isotope enrichment factor (**ε^{202}Hg**) was **−1.51 ± 0.24‰** (2SD).

Results and discussion

2. Photoreduction and abiotic dark reduction processes in rice paddies



$\Delta^{199}Hg/\Delta^{201}Hg$ of Hg(0) collected during the day and the night.

- During the day (**Photoreduction**):

  $\delta^{202}Hg = -0.80 \pm 0.67‰$;

  $\Delta^{199}Hg = -0.38 \pm 0.18‰$ （2SD, n=8）

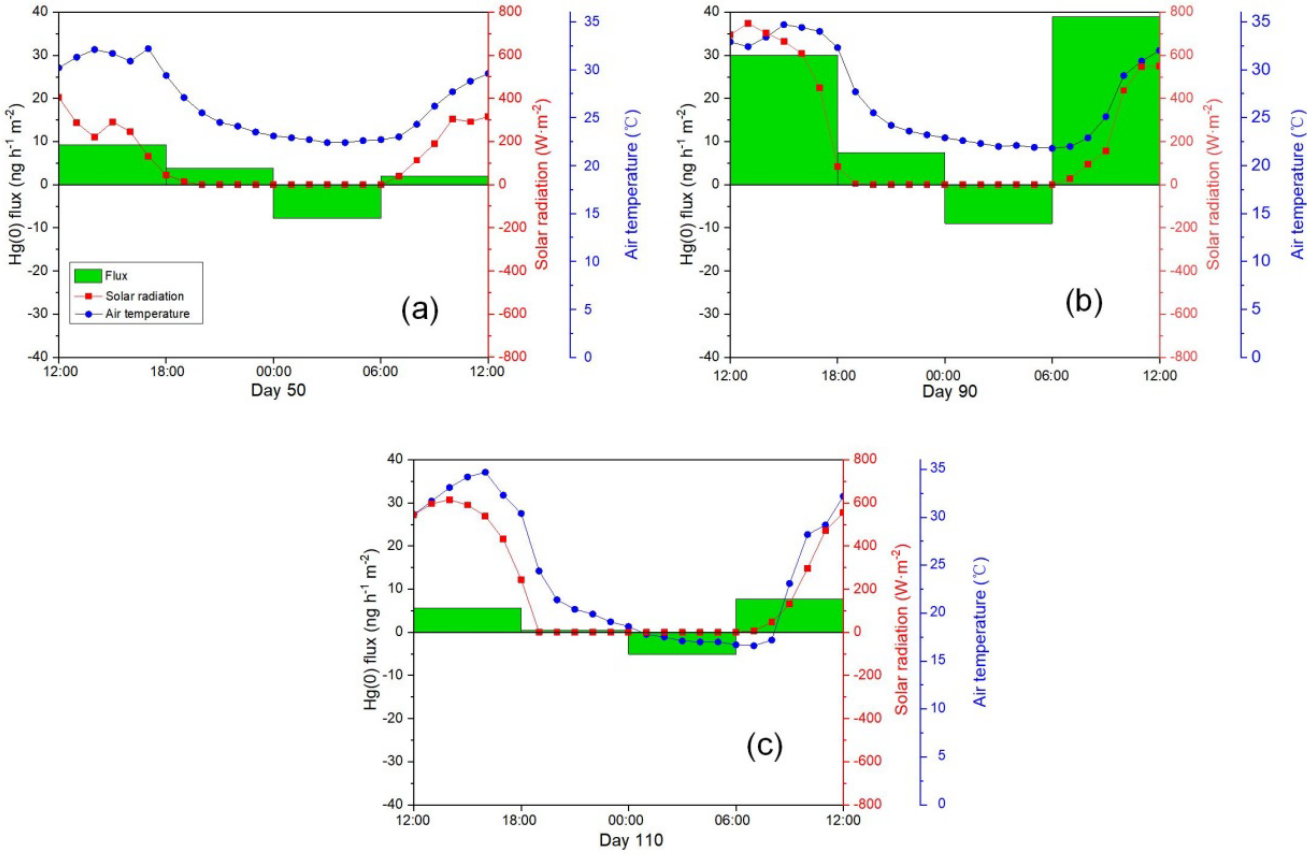
- During the night: $\delta^{202}Hg = -0.79 \pm 0.57‰$;

  $\Delta^{199}Hg = -0.32 \pm 0.32‰$ （2SD, n=8

)Hg(0) collected during the night may be a mixture of a small amount of abiotic dark reduction product Hg(0) and a delayed release of Hg(0) was previously produced during the day. Therefore, in this study, the enrichment factor for **abiotic dark reduction** was obtained from Zheng and Hintelmann (2010) (**$\varepsilon^{202}Hg = -1.77 \sim -1.52‰$, $E^{199}Hg = 0.17 \sim 0.26‰$**).

Results and discussion

3. The Atmosphere–paddy soil Hg(0) exchange fluxes



Diurnal variations of atmosphere–paddy soil Hg(0) exchange fluxes and meteorological parameters.

- Soil Hg(0) emission fluxes were significantly higher on the 90th than the 50th and 110th day ($p < 0.01$)
- **Solar radiation** and **aerobic/anaerobic conditions** mainly affect the release of soil Hg(0).
- The isotopic compositions of the Hg(0) emitted from the paddy soil:

Day 50: $\delta^{202}Hg_{ex} = -1.22 \pm 0.46‰$,

$\Delta^{199}Hg_{ex} = -0.08 \pm 0.20‰$;

Day 90: $\delta^{202}Hg_{ex} = -0.81 \pm 0.65‰$,

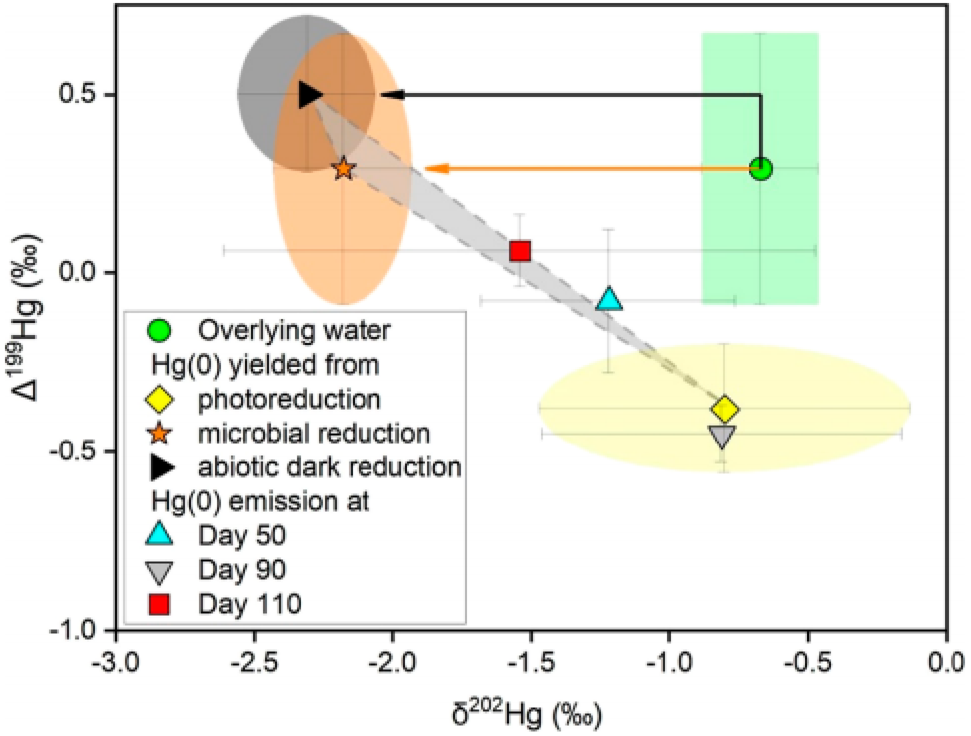
$\Delta^{199}Hg_{ex} = -0.45 \pm 0.08‰$;

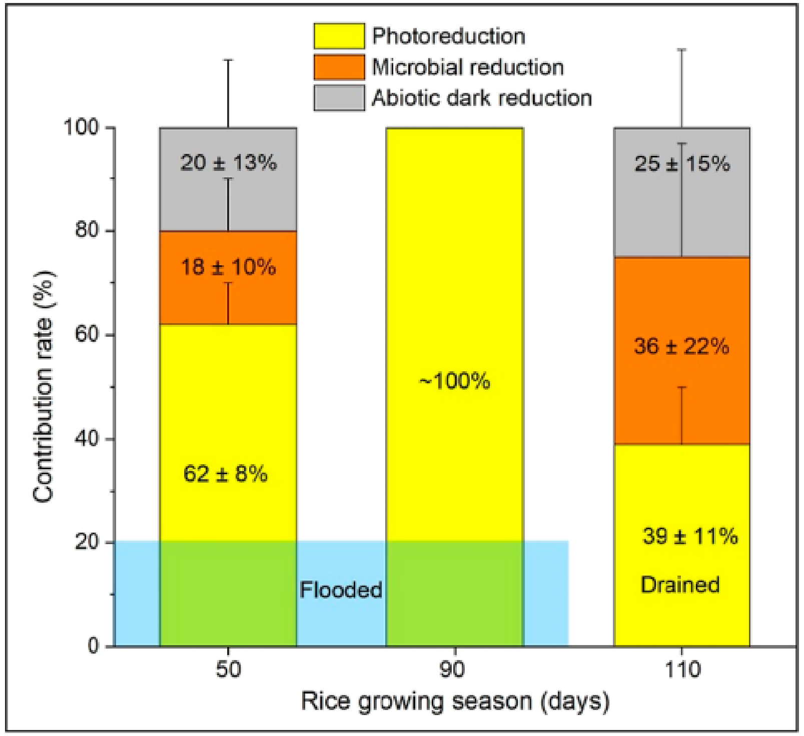
Day 110: $\delta^{202}Hg_{ex} = -1.54 \pm 1.07‰$,

$\Delta^{199}Hg_{ex} = 0.06 \pm 0.10‰$.

Results and discussion

4. The contributions of different reduction processes to Hg(0) emissions from paddy soils





◀ **Ternary mixing model and the contribution rates of three Hg(II) reduction processes to Hg(0) emissions from paddy soils at different sampling times.**

Photoreduction, microbial reduction, and abiotic dark reduction contributed 62 ± 8, 18 ± 10, and 20 ± 13% respectively, to the total Hg(0) emission from the rice paddy soil on the 50th day, and were 39 ± 11, 36 ± 22, and 25 ± 15%, respectively, on the 110th day. On the 90th day, photoreduction contributed almost 100%.

Outline

Conclusions

◆Hg(0) exchange fluxes between the atmosphere and the paddy soils were dominated by emissions during different sampling periods.

◆Photoreduction is the most important contributor to Hg(0) emissions from paddy soils; however, the contributions of microbial reduction and abiotic dark reduction during other periods cannot be ignored.

These novel findings can help improve future estimation of soil Hg(0) emissions from rice paddy ecosystems, which involve complex biotic-, abiotic-, and photoreduction processes.

(Zhang et al., 2024 *ES&T*)

Thanks for your attention!

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