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Kaihui Tang and Zhengcheng Song contributed equally to this work.

Key Points:

- · Isotopic characteristics of gaseous elemental mercury in a typical transitional zone between two hemispheres were presented
- The observations indicate significant interhemispheric difference in gaseous elemental mercury concentrations and isotopic compositions
- Oceanic Hg⁰ emissions from Hg^{II} reduction were estimated to be below $2,250 \pm 891 \text{ Mg yr}^{-1} \text{ using a } \Delta^{200} \text{Hg}$ mass balance model

Supporting Information:

Supporting Information may be found in the online version of this article.

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An Interhemispheric Difference in Atmospheric Gaseous **Elemental Mercury Isotopes Reveals a New Insight in Oceanic Mercury Emissions**

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Abstract Oceanic emission of gaseous elemental mercury (Hg⁰ or GEM) is an important source for atmospheric mercury (Hg), but existing estimates of global gross oceanic Hg⁰ emissions are highly variable (800-7,220 Mg yr⁻¹). This study measured atmospheric GEM concentrations and isotopic compositions at two coastal sites in Terengganu, Malaysia, a region that receives air masses from both hemispheres, during 2019-2021 to diagnose the amount of oceanic Hg^0 emissions. Significantly lower mean (±1sd) concentration $(1.28 \pm 0.20 \text{ ng m}^{-3})$, Δ^{199} Hg (-0.23 $\pm 0.03\%$), and Δ^{200} Hg (-0.066 $\pm 0.018\%$) and significantly higher δ^{202} Hg (0.43 ± 0.12%) were observed during the wet season when air masses were predominantly from the Southern Hemisphere, compared with those (mean concentration, Δ^{199} Hg, Δ^{200} Hg, and δ^{202} Hg of 1.77 ± 0.09 ng m⁻³, $-0.17 \pm 0.03\%$, $-0.045 \pm 0.023\%$, and $0.25 \pm 0.11\%$, respectively) during the dry season when air masses were predominantly from the Northern Hemisphere, suggesting interhemispheric difference in GEM concentrations and its isotopic compositions. Using a Δ^{200} Hg mass balance model, we estimated that the oceanic Hg⁰ emissions from Hg^{II} reduction should be below 2,250 \pm 891 Mg yr⁻¹ (\pm 1sd), which is at the low-end range of the literature reported values. We then used the constrained value as emission input to a three-dimensional atmospheric Hg isotope model and reproduced well the global distributions and interhemispheric gradient of atmospheric GEM Δ^{200} Hg. The findings from the present study will help to better understand Hg⁰ emissions from global oceans and their roles in global atmospheric Hg cycling.

Plain Language Summary Oceanic Hg⁰ emission is one of the largest natural sources for atmospheric Hg. However, previous modeling estimates of global gross oceanic Hg⁰ emissions are highly variable (800-7,220 Mg yr⁻¹), making it a challenging task in predicting future trends of Hg levels in the atmosphere and earth's surface ecosystems under the implementation of Minamata Convention on Mercury. This study measures GEM concentrations and isotopic compositions at two coastal sites in Terengganu, Malaysia during 2019–2021. The results not only show the significant interhemispheric difference in GEM concentrations but also the difference in its isotopic compositions. This study constrains the estimates of oceanic Hg^0 emissions (<2,250 ± 891 Mg yr⁻¹) from Hg^{II} reduction using a mass balance model based on the interhemispheric gradient in GEM Δ^{200} Hg. The interhemispheric Δ^{200} Hg gradients are well reproduced using the constrained value of oceanic Hg⁰ emissions as input to the three-dimensional atmospheric Hg isotope model.

1. Introduction

Mercury (Hg) is a global pollutant with adverse health impacts on humans and wildlife. Atmospheric Hg is operationally defined in three forms: gaseous elemental mercury (Hg⁰ or GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM), with the sum of GEM and GOM also defined as total gaseous mercury (TGM). GEM is the dominant form of atmospheric Hg and can be transported globally because of its long lifetime, and thus plays an important role in global Hg cycling (Lindberg et al., 2007). GEM in the atmosphere can be deposited onto the earth's surfaces directly, or oxidized to GOM and PBM and subsequently deposit onto the earth's surfaces via dry and wet deposition (Driscoll et al., 2013). Following deposition, it can be

transformed into methylmercury and bioaccumulated in the food web in the aquatic ecosystems, posing humans and wildlife health risks (Driscoll et al., 2013; Obrist et al., 2018).

Atmospheric Hg comes from both anthropogenic and natural emissions (Pirrone et al., 2010; Streets et al., 2019a; Yue et al., 2023). During the last two decades, great advances have been achieved in the estimates of global anthropogenic Hg emissions, with the majority of existing estimates falling within a relatively small range (Outridge et al., 2018; Pacyna et al., 2010; Streets et al., 2019b). In contrast, the estimates of Hg (mainly in the form of GEM) emissions from natural sources are still subject to large uncertainties (Sonke et al., 2023). One of the largest natural sources is GEM emissions from oceans. Existing estimates of oceanic Hg⁰ emissions are highly variable, ranging from 800 to 7,220 Mg yr⁻¹ (Amos et al., 2013; L. Chen et al., 2014; Horowitz et al., 2017; Lamborg et al., 2002; Outridge et al., 2018; Shah et al., 2021; Soerensen et al., 2010; Y. X. Zhang et al., 2023). Such large uncertainties in oceanic Hg⁰ emissions hamper our understanding of the global Hg cycling and future trends of Hg levels in the atmosphere and earth's surface ecosystems under the implementation of Minamata Convention on Mercury.

GEM concentrations in the global atmosphere generally display strong interhemispheric gradient (Lamborg et al., 2002; Obrist et al., 2018; Slemr et al., 1995, 2011, 2018). Such interhemispheric GEM gradient is largely controlled by the prevailing spatial distributions of anthropogenic emissions in the NH, but is further enhanced by natural and secondary emissions (Travnikov et al., 2017; Yue et al., 2022). Compared to emission sources, atmospheric chemistry processes have limited effects on the interhemispheric GEM gradient (Travnikov et al., 2017). Consequently, it is anticipated that using this GEM gradient can clarify uncertainties in global oceanic Hg^0 emissions. The magnitudes of the interhemispheric GEM gradient simulated by several state-of-art chemical transport models are somewhat smaller than that obtained from observations, partly due to the uncertainties in emission input, especially the oceanic Hg^0 emissions (Shah et al., 2021). Thus, quantifying oceanic Hg^0 emissions is vital in improving our understanding of the observed interhemispheric GEM gradient and global Hg cycling.

Significant progress has been made in Hg isotopic compositions in geogenic and environmental samples during the last decades (Blum et al., 2014), which provide an effective tracer to understand the sources and transformations of Hg in natural environments. Previous studies showed that significant mass dependent fractionation (MDF) of Hg isotope (δ^{202} Hg signature) can be induced by many physical and chemical processes including reduction/oxidation, adsorption/desorption, and volatilization (Bergquist & Blum, 2007; Demers et al., 2013; Kritee et al., 2009; Yang & Sturgeon, 2009; Zheng et al., 2007). Mass independent fractionation (MIF) of odd-Hg isotopes (odd-MIF, Δ^{199} Hg, and Δ^{201} Hg signatures) is mainly observed during photochemical redox reactions (Bergquist & Blum, 2007; Sherman et al., 2010; G Y Sun et al., 2016a; Zheng & Hintelmann, 2009), whereas MIF of even Hg isotopes (even-MIF, Δ^{200} Hg, and Δ^{204} Hg signatures) is expected to be exclusively caused by atmospheric redox reactions at high altitudes (J B Chen et al., 2012; Fu, Jiskra, et al., 2021; Gratz et al., 2010). Therefore, Hg isotopes especially the even-MIF signatures could be used as a conservative tracer for tracking the biogeochemical cycling of Hg in natural environments (Blum et al., 2014; J B Chen et al., 2016; Jiskra et al., 2021; C X Li et al., 2023).

Existing studies on GEM isotopes mostly focused on the NH, and knowledge of GEM isotopes in the SH is limited (Song et al., 2022). Considering that the tropical region is the transitional zone and regularly receives air masses from the NH and SH in different seasons (Orbe et al., 2015), we chose two coastal sites in Terengganu, Malaysia, to continuously monitor GEM concentrations and isotope compositions for one whole year period. We then analyzed the observed data to identify the seasonality of GEM concentrations and isotopic compositions and explored the causes of interhemispheric GEM gradients by considering various factors, including interhemispheric exchange of air masses, anthropogenic and natural emissions, vegetation activities, and atmospheric oxidation processes. We further used a Δ^{200} Hg mass balance model and a global three-dimensional Δ^{200} Hg GEOS-Chem model to unveil the estimates of oceanic Hg⁰ emissions from photochemical and microbial reduction of Hg^{II}, results from which greatly improved our understanding of ocean emissions in global Hg cycling.



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Figure 1. The backward trajectories (a) and location of sampling sites (b) (M_1 and M_2 in Terengganu). The purple lines represent the air mass trajectories of May, June, July, August, September, and October. The green lines represent the air mass trajectories of January, February, March, April, November, and December.

2. Methods

2.1. Sample Collection

Two sampling sites, one inside the Universiti Malaysia Terengganu (M_1 , 103.088°E, 5.408°N, 0 m) and another inside the Polytechnic of Kuala Terengganu (M_2 , 103.136°E, 5.330°N, 0 m) were chosen for GEM sampling. Both sites are located in the tropics and close to ocean (Figure 1b). There are no large point Hg sources near these two sites (Figure S1 in Supporting Information S1) (Streets et al., 2019b). GEM samples were collected continuously using chlorine-impregnated activated carbon (CLC, 0.5 g) traps at a 10-day time resolution from December 2019 to January 2021 (Table S2 in Supporting Information S1), and a total of 49 GEM samples were collected at the sampling sites. The sampling inlets were connected sequentially to the Teflon filters, CLC traps, vacuum pumps, and air flow control systems using 1/4 in, following the procedure described in previous studies (Fu et al., 2014; Fu, Liu, et al., 2021). The height of Teflon tubing inlet was about 6 m, which was placed on the building roof. CLC traps collecting GEM were sealed with silicone stoppers and three successive polyethylene bags and kept in the field labs.

2.2. Preconcentration and Determination of GEM

GEM collected on CLC traps was thermally desorbed into 5 mL of mixed acid trapping solution (40%, 2HNO₃/ 1HCl, v/v) (K Li et al., 2019) and Hg concentration in the trapping solution was then measured using a cold vapor atomic fluorescence spectroscopy (CVAFS). GEM concentration in each GEM sample was calculated by dividing total Hg mass (ng) detected in the trapping solution by the sampling air volume. Blanks of CLC traps were determined using a DMA-80 automatic mercury analyzer and showed a mean value of 0.21 ± 0.03 ng g⁻¹ (±1sd, n = 5) (Table S3 in Supporting Information S1). Recoveries of CLC traps for GEM sampling were tested by injections of known amount of Hg⁰ vapor, which showed a mean value of 109.02 ± 12.19% (±1sd, n = 6) (Table S3 in Supporting Information S1). The SRM 2711 (contaminated soil) and BCR 482 (lichen CRM) were treated using the double-stage combustion method, which followed published protocols (R Y Sun et al., 2013). The mean recovery of SRM 2711 (contaminated soil) and BCR 482 (lichen CRM) were 91.06 ± 9.59% (±1sd, n = 6) and 95.03 ± 14.25% (±1sd, n = 3), respectively (Table S3 in Supporting Information S1).

2.3. Hg Isotope Analysis

Isotope ratios of GEM were measured by MC-ICPMS (Nu II, Instruments, U.K.) at the State key Laboratory of Environmental Geochemistry, CAS (Guiyang, China), following a previous study (Fu et al., 2019). MDF signatures of GEM are reported using delta notation (δ) and calculated as follows (Blum & Bergquist, 2007):

$$\delta^{\text{xxx}} \text{Hg}_{\text{GEM}} = \left[\left({^{\text{xxx}} \text{Hg}} \right)^{198} \text{Hg}_{\text{GEM}} / \left({^{\text{xxx}} \text{Hg}} \right)^{198} \text{Hg}_{\text{NIST 3133}} - 1 \right] \times 1000\%$$
(1)



where δ^{xxx} Hg_{GEM} represents the MDF signatures of GEM in per mil (% $_o$), and xxx refers to the mass number of Hg isotopes (199, 200, 201, 202, and 204). The MIF signatures of GEM are expressed using the capital delta notation (Δ) and calculated based on the Kinetic MDF law as follows (Blum & Bergquist, 2007):

$$\Delta^{\text{xxx}} \text{Hg}_{\text{GEM}} = \delta^{\text{xxx}} \text{Hg}_{\text{GEM}} - \beta^{\text{xxx}} \times \delta^{202} \text{Hg}_{\text{GEM}}$$
(2)

where Δ^{xxx} Hg_{GEM} represents the MIF signatures of GEM in per mil (‰), and β^{xxx} are 0.252, 0.5024, 0.752, and 1.493 for ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, and ²⁰⁴Hg, respectively.

Isotopic compositions of NIST RM 8610 (UM-Almaden), BCR 482 (lichen CRM), and SRM 2711 (contaminated soil) were repeatedly measured every three samples to assess the analytical uncertainties (2sd) of GEM isotopic compositions. The isotopic compositions of RM 8610 (δ^{202} Hg = $-0.51 \pm 0.06\%$, Δ^{199} Hg = $-0.02 \pm 0.04\%$, Δ^{200} Hg = $0.00 \pm 0.03\%$, ± 2 sd, n = 12), BCR 482 (δ^{202} Hg = $-1.59 \pm 0.15\%$, Δ^{199} Hg = $-0.58 \pm 0.09\%$, Δ^{200} Hg = $0.08 \pm 0.05\%$, ± 2 sd, n = 7), and SRM 2711 (δ^{202} Hg = $-0.12 \pm 0.05\%$, Δ^{199} Hg = $-0.21 \pm 0.04\%$, Δ^{200} Hg = $0.00 \pm 0.03\%$, ± 2 sd, n = 6) were all comparable with the literature data (Table S3 in Supporting Information S1) (Blum & Johnson, 2017). In this study, when the 2sd values of GEM isotopic compositions were lower than the procedural RM 8610, 2sd values of the procedural RM 8610 were used to represent the 2sd of GEM isotopic compositions.

2.4. Backward Air Mass Trajectory, Exposure to Anthropogenic Emissions, and Normalized Difference Vegetation Index

Seven-day air mass backward trajectories ended at M₁ and M₂ at a height of 100 m above sea level were calculated every 6 hr using the TrajStat Geographical Information System-based software (A plugin for MeteoInfo, version TrajStat 1.2.2.6) based on the Global Data Assimilation System (GDAS1) from the U.S. National Oceanic and Atmospheric Administration (NOAA) (Y Q Wang et al., 2009). Seven-day air mass backward trajectories at a different height (500 m) were also calculated (Figure S2 in Supporting Information S1), and a comparison of the two sets of trajectories (100 vs. 500 m) generally showed consistent results for the origins of the air masses. Thus, only one set of trajectories (arriving at 100 m) was used for analysis of air mass origins. The individual trajectories for each GEM sample were analyzed based on all endpoints corresponding to the sampling duration of the sample. Mean latitude of air masses for each GEM sample was calculated by averaging the latitudes of all endpoints associated with the sample. The total number of endpoints located in NH or SH for each GEM sample was calculated by summing the numbers of all endpoints associated with the sample in the respective hemisphere. Both the mean latitude of air masses and the total number of endpoints in each hemisphere for each GEM sample were used to identify whether its air masses were originated from the NH or SH. Mean cumulative anthropogenic Hg emission of each GEM sample, which represents the exposure of air masses to anthropogenic Hg emissions, was calculated by averaging the global gridded total Hg emissions ($0.25^{\circ} \times 0.25^{\circ}$ grid) in 2015 from all the sectors that matched all the endpoints associated with each sample (Streets et al., 2019b). To investigate the influence of vegetation activities on GEM isotopes, the mean value of normalized difference vegetation index (NDVI) for each month at local scale (e.g., $3^{\circ} \times 3^{\circ}$ grid) was calculated based on the global gridded NDVI data (from the National Aeronautic and Space Administration Earth Observation platform at 16 days temporal and 0.1° spatial resolution) using the ArcGIS (version 10.2).

2.5. Estimate of the Global Oceanic Hg⁰ Emissions Using a Δ^{200} Hg Mass Balance Model

As discussed in Section 3.3, the interhemispheric differences in GEM isotope compositions were mainly controlled by the different contributions of Hg emission sources between the NH and SH rather than the atmospheric chemistry processes. We therefore assume the interhemispheric difference in Hg emission sources is responsible for the interhemispheric gradient in the tropospheric GEM isotope compositions. The higher Δ^{200} Hg values in the NH are mainly caused by a higher integrated Δ^{200} Hg signature of the anthropogenic and natural emissions in the NH than SH. Soil (1,000–2,200 Mg yr⁻¹), anthropogenic (1,380–2,300 Mg yr⁻¹), geogenic (200–500 Mg yr⁻¹), and biomass burning (220–680 Mg yr⁻¹) Hg emissions were within a relatively small range, but this is not the case for the oceanic emissions (800–7,220 Mg yr⁻¹), suggesting the much larger uncertainties in the latter than former source sectors (Amos et al., 2013; L. Chen et al., 2014; Horowitz et al., 2017; Lamborg et al., 2002; Outridge et al., 2018; Shah et al., 2021; Soerensen et al., 2010; Y. X. Zhang et al., 2023). In this study,



the emission fluxes of the other source sectors (except for oceanic Hg⁰ emissions) reported by Shah et al. (2021) were used to calculate the contribution of oceanic Hg⁰ emissions using a Δ^{200} Hg mass balance model as follows:

$$F_{jN} = F_j \times \left(\frac{R_{j_{(N/S)}}}{1 + R_{j_{(N/S)}}} \times 100\%\right)$$
(3)

$$F_{jS} = F_j \times \left(1 - \frac{R_{j_{(N/S)}}}{1 + R_{j_{(N/S)}}} \times 100\% \right)$$
(4)

$$\frac{F_{1N}\Delta^{200}Hg_1 + F_{2N}\Delta^{200}Hg_2 + F_{3N}\Delta^{200}Hg_3 + F_{4N}\Delta^{200}Hg_4 + F_{5N}\Delta^{200}Hg_5 + F_{6N}\Delta^{200}Hg_6}{F_{1N} + F_{2N} + F_{3N} + F_{4N} + F_{5N} + F_{6N}} >$$

$$\frac{F_{1S}\Delta^{200}Hg_1 + F_{2S}\Delta^{200}Hg_2 + F_{3S}\Delta^{200}Hg_3 + F_{4S}\Delta^{200}Hg_4 + F_{5S}\Delta^{200}Hg_5 + F_{6S}\Delta^{200}Hg_6}{F_{1S} + F_{2S} + F_{3S} + F_{4S} + F_{5S} + F_{6S}}$$
(5)

where F₁ represents the Hg emission flux for source sector j (Shah et al., 2021). j represents the numbers from 1 to 6. F_{1N} to F_{6N} represent the Hg emission fluxes from different Hg emission sources in the NH and F_{1S} to F_{6S} represent those in the SH (1 = troposphere, 2 = soil, 3 = anthropogenic, 4 = geogenic, 5 = biomass burning, and6 = ocean). Briefly, F_{1N} to F_{6N} and F_{1S} to F_{6S} are calculated by multiplying the total emission fluxes from different Hg emission sources by their percentage (calculated from $R_{j(N/S)}$) in the NH and SH, respectively (Equations 3 and 4). R_{i(N/S)} represents the emission ratio of different Hg emission sources in the NH to those in the SH, and their calculation method is presented in Text S1 in Supporting Information S1 in SI. $R_{i(N/S)}$ used in Δ^{200} Hg mass balance model can largely affect the calculation results, especially the troposphere. We therefore compile the other published data that were closest to our sampling time to calculate $R_{i(N/S)}$. $\Delta^{200}Hg_1$ to $\Delta^{200}Hg_2$ represent the isotopic compositions of different Hg emission sources (Table S1 and Figure S3 in Supporting Information S1) (Fu, Jiskra, et al., 2021; Jiskra et al., 2015, 2021; Kurz et al., 2020; Obrist et al., 2017; Sherman et al., 2009; R Y Sun et al., 2019, 2016b; Tate et al., 2023; X Wang et al., 2020; Yu et al., 2016; Zambardi et al., 2009). We considered the precisions of Δ^{200} Hg signatures across all emission sources. Mean values and uncertainties of oceanic Hg⁰ emissions were calculated using Monte Carlo simulations. It is important to note that the standard deviation (sd) can vary significantly during these calculations due to the large number of isotopic composition variables from different Hg emission sources. Consequently, we achieved improved results by employing crystal ball fitting techniques (Figure S4 in Supporting Information S1).

Considering the Δ^{200} Hg value of most source sectors (soil, anthropogenic, geogenic, biomass burning, and ocean) ranges between -0.04 and 0.04, we changed the 1sd to 2sd of Δ^{200} Hg for each source sector separately in Δ^{200} Hg mass balance model to explore its effect on the oceanic Hg⁰ emissions. These changes only increased the standard deviations of oceanic Hg⁰ emissions, but maintained consistent mean values (Figure S5a in Supporting Information S1). We also conducted a sensitivity analysis for the Δ^{200} Hg mass balance model and found the variations in Δ^{200} Hg of anthropogenic and ocean can cause large uncertainties in oceanic Hg⁰ emissions (Figure S5b in Supporting Information S1). These results indicated that the small ranges of Δ^{200} Hg value for different source sector have minimal impact on the Δ^{200} Hg mass balance model results.

2.6. Global Three-Dimensional Δ^{200} Hg Model

To assess the accuracy of our estimates of the global oceanic Hg^0 emissions, we ran a recently developed threedimensional Δ^{200} Hg model within the GEOS-Chem (version 12.9.0) framework (Song et al., 2022), with additional updates of the model being described in a separate study (Song et al., 2024), to evaluate whether using our estimates as model input can better simulate the observed Δ^{200} Hg differences between the NH and SH. The isotopic model can simulate both the spatial variations of Hg isotope signatures and Hg concentrations in the global atmosphere, with uncertainties evaluated in previous studies (Song et al., 2022, 2024). This model employs the native MERRA-2 ($4^\circ \times 5^\circ$) meteorological reanalysis data from the NASA Global Modeling and Assimilation Office (GMAO). The model combines anthropogenic Hg inventories (in 2015) from Streets et al. (2019b) and natural emissions from ocean, soil, biomass, and geogenic sources following Shah et al. (2021). We excluded other potential oceanic mercury sources, such as hydrothermal emissions and river inputs, given that the hydrothermal mercury flux is minimal (Torres-Rodriguez et al., 2024) and that riverine mercury primarily influences coastal region (M D Liu et al., 2021). The model employs gridded ocean surface mercury concentrations as boundary conditions, which are developed from a global three-dimensional ocean model (Y. Zhang et al., 2015) and have been validated against oceanic observations.

All Δ^{200} Hg signatures of source emissions adhere to synthesized data in this study. The chemical mechanism follows the framework established by Shah et al. (2021), with the isotopic fractionation process implemented during the reduction of Hg^I species. This approach is based on the theory that even-MIF occurs during the photolysis of Hg^IBr (Fu, Jiskra, et al., 2021). Although this isotopic fractionation theory may not fully align with available observational data, we speculate the impact of source emissions on Δ^{200} Hg signatures based on the distribution trends of both modeled and observed Δ^{200} Hg signatures. In this study, we focus on the East Hemisphere.

The uncertainty of the isotope model in this study primarily stems from source emissions. As outlined in Table S1 in Supporting Information S1, the Δ^{200} Hg values of GEM emissions have standard deviations ranging from 0.02 to 0.03‰. To assess the impact of the upper and lower limits (maximum or minimum isotopic composition) of different emission sources on modeling results, we conducted two sensitivity simulations. The results, illustrated in Figure S6a in Supporting Information S1, reveal minimal differences compared with the 2,250 Mg y⁻¹ scenario, with simulated GEM Δ^{200} Hg differences ranging from ±0.03‰ to ±0.05‰. Another source of uncertainty arises from the enrichment factors that govern even-MIF during photo-chemical processes in the model. Fu, Jiskra, et al. (2021) proposed an enrichment factor of 0.26 ± 0.10‰ for atmospheric Hg redox processes. Two additional sensitivity simulations were conducted to explore the impact of the upper and lower limits of these enrichment factors on the results. As depicted in Figure S6b in Supporting Information S1, these simulations similarly show negligible differences in GEM Δ^{200} Hg, with variations ranging from ±0.01‰ to ±0.05‰. Although these uncertainties may lead to differences in the simulated GEM Δ^{200} Hg values, they do not change the trend of the results. This indicates that the uncertainties associated with source emissions and enrichment factors have minimal impact on the simulation results.

3. Results and Discussion

3.1. GEM Concentrations and Isotopic Compositions

Mean GEM concentrations at M_1 and M_2 in Terengganu, Malaysia during the whole study periods were 1.49 ± 0.27 ng m⁻³ (±1sd, n = 24) and 1.52 ± 0.31 ng m⁻³ (±1sd, n = 25), respectively (Table S4 in Supporting Information S1). These values were about 20% higher than the background mean value of 1.24 ± 0.10 ng m⁻³ in the tropical zone and comparable with the background mean value of 1.55 ± 0.06 ng m⁻³ in the NH in 2013 obtained from the Global Mercury Observation System (GMOS) (Sprovieri et al., 2016). The slightly higher GEM concentrations in Terengganu than at the other tropical sites should be attributed to the fact that the majority of air masses in Terengganu were originated from East and Southeast Asia (Figure 1), where located many anthropogenic Hg sources (Figure S1 in Supporting Information S1), which increased background GEM levels in Terengganu region (Streets et al., 2019b). Similar observations were also observed at Mt. Chacaltaya in Bolivia which showed that the transport of NH-influenced air masses elevated the GEM concentrations in the tropical South America (Koenig et al., 2022).

As illustrated in Figure 2, GEM samples collected at the M₁ and M₂ in Terengganu were characterized by positive δ^{202} Hg and negative Δ^{199} Hg and Δ^{200} Hg values (Table S2 in Supporting Information S1). The mean δ^{202} Hg values of GEM were 0.45 ± 0.12% (±1sd, n = 24) and 0.26 ± 0.10% (±1sd, n = 25), mean Δ^{199} Hg values were $-0.23 \pm 0.03\%$ (±1sd, n = 24) and $-0.17 \pm 0.04\%$ (±1sd, n = 25), and mean GEM Δ^{200} Hg values were $-0.062 \pm 0.017\%$ (±1sd, n = 24) and $-0.051 \pm 0.026\%$ (±1sd, n = 25) at M₁ and M₂, respectively (Table S4 in Supporting Information S1).

The annual mean δ^{202} Hg, Δ^{199} Hg, and Δ^{200} Hg values of GEM at M₁ and M₂ were similar to those observed at the NH background sites (δ^{202} Hg = 0.46 ± 0.44‰, Δ^{199} Hg = -0.18 ± 0.08‰, Δ^{200} Hg = -0.054 ± 0.039‰, ±1sd, n = 336, Figures 2a and 2b) (Demers et al., 2013, 2015; Enrico et al., 2016; Fu, Jiskra, et al., 2021; Fu et al., 2016, 2019; Gratz et al., 2010; Kurz et al., 2020; Nguyen et al., 2021; Obrist et al., 2017; X Wu et al., 2023; Yu et al., 2016). Comparing with data observed in free troposphere (δ^{202} Hg = 0.48 ± 0.16‰, Δ^{199} Hg = -0.32 ± 0.07‰, Δ^{200} Hg = -0.12 ± 0.03‰, ±1sd, n = 16, Figures 2a and 2b) (Fu, Jiskra, et al., 2021; Kurz et al., 2020; Tate et al., 2023), those observed at M₁ and M₂ in Terengganu were similar for δ^{202} Hg, but were





Figure 2. δ^{202} Hg, Δ^{199} Hg, and Δ^{200} Hg isotope signatures of GEM worldwide: free troposphere (Fu, Jiskra, et al., 2021; Kurz et al., 2020; Tate et al., 2023); the NH background (Demers et al., 2013, 2015; Enrico et al., 2016; Fu, Jiskra, et al., 2021; Fu et al., 2016, 2019; Gratz et al., 2010; Kurz et al., 2020; Nguyen et al., 2021; Obrist et al., 2017; X Wu et al., 2023; Yu et al., 2016); urban areas (Fu, Liu, et al., 2021; Yu et al., 2022); and M₁ and M₂ from the present study. Shaded ellipses indicate the range of the mean values of GEM isotope signatures worldwide.

higher for Δ^{199} Hg and Δ^{200} Hg. On the other hand, the mean values of δ^{202} Hg, Δ^{199} Hg, and Δ^{200} Hg at M₁ and M₂ were significantly different from those in the NH urban areas (δ^{202} Hg = $-0.23 \pm 0.69\%$, Δ^{199} Hg = $-0.09 \pm 0.08\%$, Δ^{200} Hg = $-0.022 \pm 0.040\%$, ± 1 sd, n = 203) (independent sample *t*-test, p < 0.001, Figure 2) (Fu, Liu, et al., 2021; Yu et al., 2022). Lower GEM δ^{202} Hg and higher Δ^{199} Hg and Δ^{200} Hg values in urban areas were caused by strong local anthropogenic emissions, which generally have negative δ^{202} Hg and near-zero MIF (Δ^{199} Hg and Δ^{200} Hg) signatures (R Y Sun et al., 2019, 2016b). The similar isotopic compositions between this study and previous background observations in the NH discussed above suggest very limited impact from local anthropogenic Hg emissions on our sampling sites. We can thus assume that our sites can overall represent the characteristics of regional background air in the planetary boundary layer in the Asian tropical region.

3.2. Seasonality of GEM Concentration and Isotope Compositions Driven by Interhemispheric Air Exchange

Significant seasonal variations were observed in both GEM concentrations and isotope compositions in Terengganu (data at M_1 and M_2 were aggregated together for discussion below), with consistent higher GEM concentrations and Δ^{199} Hg and Δ^{200} Hg values and lower δ^{202} Hg values during the dry season (November to April) than the wet season (May to October) (Figure 3) (Abtew et al., 2009). Mean GEM concentration in Terengganu was about 40% higher during dry (1.77 ± 0.09 ng m⁻³, ±1sd, n = 22) than wet season (1.28 ± 0.20 ng m⁻³, ±1sd, n = 27) (independent sample *t*-test, p < 0.001, Figures 3a and 3e and Table S4 in Supporting Information S1). Mean Δ^{199} Hg and Δ^{200} Hg values in Terengganu were 0.06 and 0.021‰, respectively, higher during dry (-0.17 ± 0.03‰ and -0.045 ± 0.023‰, ±1sd, n = 22) than wet season (-0.23 ± 0.03‰ and -0.066 ± 0.018‰, ±1sd, n = 27) (independent sample *t*-test, p < 0.001, Figures 3c and 3d, 3g, 3h and Table S4 in Supporting Information S1). In contrast, mean δ^{202} Hg_{GEM} in Terengganu was 0.18‰ lower during dry (0.25 ± 0.11‰, ±1sd, n = 22) than wet season (0.43 ± 0.12‰, ±1sd, n = 27) (independent sample *t*-test, p < 0.001, Figures 3b and 3f and Table S4 in Supporting Information S1).

Atmospheric oxidation processes, vegetation activities, anthropogenic emissions, and atmospheric pool can all cause the changes in GEM concentrations and isotope compositions (Fu et al., 2019; Horowitz et al., 2017; Jiskra et al., 2018; Lei et al., 2014; Slemr et al., 2011; Sprovieri et al., 2016; Q. R. Wu et al., 2020; X. Wu et al., 2023;



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Figure 3. Seasonal variations in GEM concentrations and isotope signatures at M_1 and M_2 (a, b, c, and d). Shaded gray areas represent monthly averages and ±1sd of the observations at M_1 and M_2 in Terengganu. The comparisons of GEM concentrations and isotope signatures between the dry season and wet season (e, f, g, and h).

Y. X. Zhang et al., 2016). The integrated Δ^{199} Hg/ Δ^{200} Hg ratio between GEM and Hg^{II} species can reflect the magnitude of atmospheric photochemical redox reactions (Fu, Jiskra, et al., 2021). A recent study at the free tropospheric Pic du Midi, France showed an integrated Δ^{199} Hg/ Δ^{200} Hg ratio of 3.3 in both GEM and Hg^{II} species, suggesting the dominant role of atmospheric photochemical redox reactions (Fu, Jiskra, et al., 2021). In contrast, the integrated Δ^{199} Hg/ Δ^{200} Hg ratio of 1.4 for GEM in this study and Hg^{II} species (AuYang et al., 2022) (Figure S7 in Supporting Information S1) would indicate the minor role atmospheric redox reactions played in our samples, which unlikely cause significant seasonal variations in oxidation of atmospheric GEM. Local mean NDVI (representing vegetation activities) varied little between dry and wet season and should not be the main driver of the significant seasonal variations observed in GEM concentrations and isotopic compositions (Table S4 in Supporting Information S1). There were no significant seasonal variations in mean cumulative anthropogenic Hg emission of each GEM sample collected in Terengganu during the study periods (Table S4 in Supporting Information S1) (Streets et al., 2019b), or in the mean net sea-air flux near the equator (Strode et al., 2007). Therefore, none of the above-mentioned factors, that is, atmospheric oxidation processes, vegetation activities, local anthropogenic Hg emissions, and local oceanic Hg emissions, was the main driver of the seasonal variations in GEM concentrations and isotope compositions in GEM concentrations processes, vegetation activities, local anthropogenic Hg emissions, and local oceanic Hg emissions, was the main driver of the seasonal variations in GEM concentrations and isotope compositions in GEM concentrations and isotope compositions at M₁ and M₂.

Backward air mass trajectory analysis at the sampling sites showed significant seasonal differences in the air mass origins, with the air masses mainly from the north of the sampling site during the dry season (~97.53%) and from the south of the sampling site during the wet season (~88.73%) (Figure 1a and Table S4 in Supporting Information S1). Variations in GEM concentrations, Δ^{199} Hg, and Δ^{200} Hg values at M₁ and M₂ were both significantly positively correlated with the mean latitude of air mass trajectories (r^2 was 0.68 for GEM concentrations, 0.32 for Δ^{199} Hg, and 0.19 for Δ^{200} Hg, Spearman test, p < 0.01 for all, Figure S8a, S8c, and S8d in Supporting Information S1), whereas variations in δ^{202} Hg were significantly negatively correlated with latitude ($r^2 = 0.40$, Spearman test, p < 0.01, Figure S8b in Supporting Information S1). Therefore, seasonal variations in GEM concentrations and isotope compositions at M₁ and M₂ were related to the transition of air masses originated from the NH in the dry season and from the SH in the wet season.

3.3. Interhemispheric Difference in GEM Isotope Compositions

According to the compilation of the published data, mean δ^{202} Hg, Δ^{199} Hg, and Δ^{200} Hg values of GEM were $0.50 \pm 0.23\%_{o}$, $-0.29 \pm 0.08\%_{o}$, and $-0.070 \pm 0.022\%_{o}$ (±1sd, n = 48), respectively, at the SH background sites (C X Li et al., 2023; Szponar et al., 2020; Yu et al., 2021), whereas lower mean δ^{202} Hg ($0.46 \pm 0.44\%_{o}$) and higher mean Δ^{199} Hg ($-0.18 \pm 0.08\%_{o}$) and Δ^{200} Hg ($-0.054 \pm 0.039\%_{o}$) were observed at the NH background sites (independent sample *t*-test, p < 0.001 for Δ^{199} Hg and Δ^{200} Hg, Figure 4, ±1sd, n = 336) (Demers et al., 2013, 2015; Enrico et al., 2016; Fu, Jiskra, et al., 2021; Fu et al., 2016, 2019; Gratz et al., 2010; Kurz et al., 2020;





Figure 4. Comparisons of isotopic compositions between the NH background sites (Demers et al., 2013, 2015; Enrico et al., 2016; Fu, Jiskra, et al., 2021; Fu et al., 2016, 2019; Gratz et al., 2010; Kurz et al., 2020; Nguyen et al., 2021; Obrist et al., 2017; X Wu et al., 2023; Yu et al., 2016) and SH background sites (C X Li et al., 2023; Szponar et al., 2020; Yu et al., 2021).

Nguyen et al., 2021; Obrist et al., 2017; X Wu et al., 2023; Yu et al., 2016). Mean δ^{202} Hg, Δ^{199} Hg, and Δ^{200} Hg values of GEM at M₁ and M₂ during the wet season (when the air masses mainly from the SH) were indeed similar to those observed at the SH background sites, and those during the dry season (when the air masses mainly from the NH) were mostly consistent with, although with slightly lower δ^{202} Hg value than the observed data at the NH background sites. Therefore, the GEM isotope compositions in the NH were likely characterized by less positive δ^{202} Hg and relatively higher Δ^{199} Hg and Δ^{200} Hg values than in the SH.

Atmospheric oxidation and deposition play crucial roles in the global GEM cycling (Selin et al., 2007). Positive odd-MIF (Δ^{199} Hg) could be induced in Hg⁰ because of oxidation initiated by Br atoms (G Y Sun et al., 2016a). The Hg + Br model simulation showed faster oxidation of Hg⁰ and greater Hg^{II} deposition in the SH than NH because of the oceanic source of bromo and the low temperatures over Antarctica (Holmes et al., 2010). The $Hg + OH/O_3$ model simulation (Holmes et al., 2010), however, suggest similar Hg^0 oxidation rates between the NH and SH and largest Hg^{II} deposition mainly occurring in the tropics. A recent model simulation combined Br and OH chemistry also showed no significant difference in the zonal net Hg⁰ oxidation rates in the planetary boundary layer between the NH and SH (Shah et al., 2021). A stronger oxidation by Br atoms in the SH than NH would likely cause the more positive Δ^{199} Hg values in the SH, which contradicts the more negative Δ^{199} Hg values observed in the SH, suggesting interhemispheric atmospheric redox reactions unlikely cause the difference in GEM isotope compositions between the NH and SH. The foliar uptake and re-emission of Hg⁰ would result in a positive shift in δ^{202} Hg and small negative shift in Δ^{199} Hg, respectively (Demers et al., 2013; Fu et al., 2019; X Wu et al., 2023; Yuan et al., 2019). The NH with higher vegetation cover (NOAA Earth Observations) would drive the δ^{202} Hg and Δ^{199} Hg toward more positive and negative values, respectively, which contradicts with existing observations. Therefore, less positive δ^{202} Hg and relatively higher Δ^{199} Hg and Δ^{200} Hg values in the NH than SH are unlikely explained by atmospheric redox reactions, atmospheric deposition, or vegetation activities.

Modern anthropogenic Hg emissions were higher in the NH than SH (Outridge et al., 2018; Streets et al., 2017). GEM affected by global anthropogenic sources were characterized by near-zero Δ^{199} Hg (-0.02%) and Δ^{200} Hg (0.00%) (R Y Sun et al., 2019, 2016b), which were significantly higher than the MIF values (Δ^{199} Hg = -0.32 ± 0.07%; Δ^{200} Hg = -0.12 ± 0.03%, ±1sd, *n* = 16) of GEM observed in the free troposphere (Fu, Jiskra, et al., 2021; Kurz et al., 2020; Tate et al., 2023). We speculate the larger anthropogenic emissions in the NH than SH has the potential to drive the GEM isotopic compositions toward higher Δ^{199} Hg and Δ^{200} Hg values in the NH. Natural emissions also play an important role in affecting the GEM isotope compositions. Δ^{200} Hg is a conservative tracer because it is mainly produced during the atmospheric Hg redox reactions at high-altitudes, therefore we use the Δ^{200} Hg values of different natural sources to explore their effects on GEM isotope compositions (J B Chen et al., 2012; Fu, Jiskra, et al., 2021; Gratz et al., 2021; Gratz et al., 2010). The isotope signatures of GEM



emitted from anthropogenic and natural sources (e.g., anthropogenic, oceanic, soil, geogenic, and biomass burning) were mostly characterized by near-zero to slightly positive Δ^{200} Hg, which are notably higher than that of the free tropospheric GEM (Table S1 and Figure S3 in Supporting Information S1). Therefore, the observed higher Δ^{200} Hg in atmospheric GEM in the NH than SH would likely reflect a relatively higher contribution of anthropogenic and natural emissions to atmospheric GEM in the NH.

 Δ^{200} Hg values of oceanic Hg⁰ emissions are expected to be positive (0.04 ± 0.02%) (Jiskra et al., 2021) and higher than those of the other emission sources that have close to zero or negative Δ^{200} Hg values (Figure S3 in Supporting Information S1) (Fu, Jiskra, et al., 2021; Jiskra et al., 2015, 2021; Kurz et al., 2020; Obrist et al., 2017; Sherman et al., 2009; R Y Sun et al., 2019, 2016b; Tate et al., 2023; X Wang et al., 2020; Yu et al., 2016; Zambardi et al., 2009). The contribution of oceanic emissions account for ~54% in the SH where the other sources (mainly anthropogenic and soil emissions) are relatively small (Strode et al., 2007). Earlier estimates of global gross oceanic Hg^0 emissions showed large range of variability and are mostly in the range of 4,000– 7,220 Mg yr⁻¹ (Amos et al., 2013; L. Chen et al., 2014; Horowitz et al., 2017; Lamborg et al., 2002; Outridge et al., 2018; Shah et al., 2021; Soerensen et al., 2010; Y. X. Zhang et al., 2023). Such large amounts of oceanic emissions, combined with high contribution ratios from this source sector, would result in higher Δ^{200} Hg values in the SH, contradicting to the observed data. We therefore conducted a global three-dimensional Δ^{200} Hg GEOS-Chem simulation to validate such a speculation. Using a representative oceanic Hg⁰ emission amount of 4,800 Mg yr⁻¹ as model input (Shah et al., 2021), the model produced higher Δ^{200} Hg_{GEM} values in the SH $(-0.042 \pm 0.006\%)$ than NH $(-0.052 \pm 0.004\%)$ (independent sample *t*-test, p < 0.001, Figures 5a and 5c), in contrast to previous observations (Araujo et al., 2022; Demers et al., 2013, 2015; Enrico et al., 2016; Fu, Jiskra, et al., 2021; Fu, Liu, et al., 2021; Fu et al., 2016, 2018, 2019; Gratz et al., 2010; Kurz et al., 2020; C X Li et al., 2023; Nguyen et al., 2021; Obrist et al., 2017; Szponar et al., 2020; X Wu et al., 2023; Yu et al., 2016, 2021, 2022). Thus, existing estimates of oceanic Hg^0 emissions and its relative contributions to total emissions need to be recalculated in global Hg transport models in order to reproduce the observed interhemispheric Δ^{200} Hg gradient.

Overall, considering the tropical Pacific upper troposphere is likely an important pathway of atmospheric Hg long-range transport (Koenig et al., 2022), we speculate that the lower Δ^{200} Hg values observed in the SH were caused by smaller total emission amounts from mixed natural and anthropogenic sources in the SH, which cannot derive higher Δ^{200} Hg value in the troposphere, opposite to the case in the NH. The interhemispheric difference in GEM isotope compositions were highly controlled by the different contributions of Hg emission sources between the NH and SH, in particular the differences in oceanic emissions.

3.4. Estimates of Oceanic Hg⁰ Emissions From Hg^{II} Reduction

Based on the assumption of higher Δ^{200} Hg signature in mixed natural and anthropogenic emissions in the NH, we estimated the gross oceanic Hg⁰ emissions using a mass balance model (Method 2.5 and Text S1). The result revealed that gross oceanic Hg⁰ emissions should below $2,250 \pm 891$ Mg yr⁻¹, which is at the low-end range of the literature reported values $(800-7,220 \text{ Mg yr}^{-1})$ (Amos et al., 2013; L. Chen et al., 2014; Horowitz et al., 2017; Lamborg et al., 2002; Outridge et al., 2018; Shah et al., 2021; Soerensen et al., 2010; Y. X. Zhang et al., 2023). To further validate our findings presented above, we used $2,250 \text{ Mg yr}^{-1}$ as model input of oceanic Hg⁰ emission and found that it could produce similar $\Delta^{200} Hg_{GEM}$ values between the NH (–0.060 \pm 0.006%) and SH $(-0.061 \pm 0.005\%)$ (independent sample *t*-test, p = 0.10, Figures 5b and 5d), and Δ^{200} Hg_{GEM} produced from model simulations was more comparable to the observations in the East Hemisphere (Figures 5b, 5d and 5f) (Araujo et al., 2022; Demers et al., 2013; Demers et al., 2015; Enrico et al., 2016; Fu, Jiskra, et al., 2021; Fu, Liu, et al., 2021; Fu et al., 2016, 2018, 2019; Gratz et al., 2010; Kurz et al., 2020; C X Li et al., 2023; Nguyen et al., 2021; Obrist et al., 2017; Szponar et al., 2020; X Wu et al., 2023; Yu et al., 2016, 2021, 2022). Furthermore, the model simulated GEM concentration ratio between NH and SH in the planetary boundary layer, representing the interhemispheric GEM concentration gradient, improves from 1.22 in the case of 4,800 Mg yr⁻¹ scenario to 1.47 in the case of $2,250 \text{ Mg yr}^{-1}$ scenario, the latter is more comparable to the observed GEM concentrations ratio of 1.41 (Diéguez et al., 2019; C X Li et al., 2023; X Wu et al., 2023; Yu et al., 2021) (AMNet: https://nadp.slh. wisc.edu/networks/atmospheric-mercury-network/, CAMNet: https://data-donnees.az.ec.gc.ca/data/air/monitor/ monitoring-of-atmospheric-gases, EMEP: https://ebas-data.nilu.no/) (Table S5 in Supporting Information S1). These results suggest that this estimate ($<2,250 \pm 891$ Mg yr⁻¹) for oceanic Hg⁰ emissions, based on which model can successfully reproduce the observed interhemispheric gradient and global spatial distribution in Δ^{200} Hg_{GEM},

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Figure 5. Annual output of mean Δ^{200} Hg_{GEM} (%) from two isotope model simulations and the mean Δ^{200} Hg_{GEM} (%) of GEM observations from Chinese cities and background in the East Hemisphere (a and b). Two model simulations and global background observations (mean value) (Demers et al., 2013, 2015; Enrico et al., 2016; Fu, Jiskra, et al., 2021; Fu et al., 2016, 2019; Gratz et al., 2010; Kurz et al., 2020; C X Li et al., 2023; Nguyen et al., 2021; Obrist et al., 2017; Szponar et al., 2020; X Wu et al., 2023; Yu et al., 2016, 2021) of latitude variation in Δ^{200} Hg_{GEM} (%) (c and d). The comparison of Δ^{200} Hg_{GEM} between model simulations and global background observations (mean value) in the East Hemisphere (e and f) (Araujo et al., 2022; Fu, Jiskra, et al., 2021; Fu, Liu, et al., 2021; Fu et al., 2018, 2019; C X Li et al., 2023; Nguyen et al., 2021; Szponar et al., 2021; Szponar et al., 2021; Yu et al., 2021; Fu et al., 2021; C X Li et al., 2021; Szponar et al., 2021; Fu, Liu, et al., 2021; Fu et al., 2018, 2019; C X Li et al., 2023; Nguyen et al., 2021; Szponar et al., 2021; Szponar et al., 2021; Fu, Liu, et al., 2021; Fu et al., 2018, 2019; C X Li et al., 2023; Nguyen et al., 2021; Szponar et al., 2020; X Wu et al., 2023; Yu et al., 2021; Fu et al., 2016, 2021).

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is more reasonable than most existing estimates reported in literature (e.g., 4,000–7,220 Mg yr⁻¹) (Figure 5). Furthermore, under the assumption that the contribution of other emission sources is constant, the proportion of oceanic Hg⁰ emissions in the global total Hg emissions would decrease to ~42% from the previous estimate of ~61% (Shah et al., 2021).

Previous modeling studies estimated the air-sea Hg⁰ flux using a thin film gas exchange model that depended on the gas transfer velocity (K_w) as well as the concentration gradient between dissolved gaseous mercury (DGM) in seawater and atmospheric GEM (Fu et al., 2010; McGillis et al., 2001; Nightingale et al., 2000; Strode et al., 2007; Wanninkhof, 1992). The current understanding of the K_w values under various environmental conditions is incomplete (Kuss et al., 2009; Osterwalder et al., 2021) due to its dependence on many environmental factors, such as water temperature and wind speed, which may yield uncertainties in the estimates of oceanic Hg⁰ emissions. In addition, aqueous photochemical and microbial reduction of Hg^{II} is generally regarded as the predominant source of DGM in surface seawater in these models. However, it should be noted that the air-sea Hg⁰ gas exchange is frequently bidirectional (Jiskra et al., 2021; Lamborg et al., 1999). Thus, previous model estimates of oceanic Hg⁰ emissions based on the DGM and atmospheric GEM concentration gradients likely included the emissions driven by aqueous Hg^{II} reductions as well as the fast re-emissions of atmospheric GEM that previously diffused into seawater (the portion that has not been oxidized and exists in the form of DGM in seawater). In the present study, our Hg isotope model only considers the GEM emissions driven by the seawater Hg^{II} reduction (Y. X. Zhang et al., 2014), which might be one of the reasons for our relatively lower estimate as compared with previous studies. Since most of the previous studies on air-sea Hg⁰ exchange are based on thin film gas exchange model, alternative and direct measurements of the air-sea Hg⁰ exchange fluxes are warranted in future to better constrain the global oceanic Hg⁰ emissions (Osterwalder et al., 2021).

4. Conclusions

Analysis of 1-year continuous data collected at two tropical sites revealed interhemispheric gradients in GEM concentration and isotopic composition, with higher GEM concentrations and MIF (Δ^{199} Hg and Δ^{200} Hg) values, alongside with lower δ^{202} Hg values, in the NH than SH. The divergences are highly related to differing contributions of Hg emission sources, especially oceanic emissions, between the NH and SH. Based on the difference in Δ^{200} Hg values of the integrated interhemispheric emission sources, gross oceanic Hg⁰ emissions from Hg^{II} reduction were constrained to be below 2,250 ± 891 Mg yr⁻¹. Using this revised value as input to a global three-dimensional Δ^{200} Hg GEOS-Chem simulation could produce more reasonable interhemispheric Δ^{200} Hg gradients.

Overall, our study provides a new Hg isotope approach to constrain the global oceanic Hg^0 emissions. Despite the potential uncertainties in our estimate, the relatively lower oceanic Hg⁰ emissions estimated in this study than most previously reported values have important implications in predicting future trends in Hg levels in the atmosphere and earth's surface ecosystems under the implementation of Minamata Convention on Mercury. Based on our new estimate of oceanic Hg⁰ emissions (e.g., $<2,250 \pm 891$ Mg yr⁻¹), the proportion of anthropogenic emissions in the global total Hg emissions would increase to \sim 35% from the previous estimate of \sim 20% (Shah et al., 2021; Y. X. Zhang et al., 2023). Therefore, a reduction of anthropogenic emissions could yield greater benefits in controlling atmospheric Hg pollution than traditional thought, a notion that can indeed be supported by many evidences of regional atmospheric GEM long-term trends. For instance, along with the abatements of anthropogenic Hg emissions over the past two decades, significant declines in atmospheric GEM concentrations have already been observed in North America, Europe, and Asia (Feng et al., 2024; K. Y. Liu et al., 2019; X. Wu et al., 2023; Y. X. Zhang et al., 2016; Y. Zhang et al., 2023). We caution that our knowledge of the Δ^{200} Hg signatures and Hg⁰ emission fluxes from various terrestrial sources are still very limited, which would cause significant uncertainties in our estimate. For better constraining the global oceanic Hg⁰ emissions using Hg isotopes, future studies on isotopic compositions of atmospheric Hg in the SH as well as the emission sources at the global scale are needed.

Data Availability Statement

Atmospheric Hg isotope and concentration data in Terengganu, Malaysia, measured in this study are available at ScienceDB (Tang et al., 2024). TrajStat-compatible meteorological data used in this study are available at the



NCEP Global Data Assimilation System (GDAS) (https://www.ready.noaa.gov/data/archives/gdas1), and the software (TrajStat 1.2.2.6) is obtained from Y Q Wang et al. (2009). Gridded anthropogenic Hg emissions data in 2015 are obtained from Streets et al. (2019b). The global gridded NDVI data are from the National Aeronautic and Space Administration Earth Observation platform at 16 days temporal and 0.1° spatial resolution (https://neo.gsfc.nasa.gov/). Details of Δ^{200} Hg mass balance model, additional tables, and figures supporting the results and discussion are available at Supporting Information S1.

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