

Underestimation of atmospheric oxidized mercury at a mountaintop site by the GEOS-Chem chemical transport model

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Abstract. An improved mechanistic model of mercury redox chemistry has recently been implemented in the GEOS-Chem model. In this study, GEOS-Chem simulations were compared to ambient measurements made during a high-oxidized mercury episode that originated in the free troposphere at a mountaintop site in Colorado, USA (40.455° N, -106.744° W, 3220 meters above sea level). Measurements were collected with a dual channel atmospheric oxidized mercury measurement system that has been shown to accurately quantify oxidized mercury compounds in ambient air. The model and observations showed similar temporal trends for elemental and oxidized mercury (R^2 of 0.54 to 0.79) and similar elemental mercury concentrations (normalized mean square error of 0.04 in the base model). However, the base model only produced 17% of the maximum oxidized mercury observed in the dual channel system. In sensitivity tests with increased oxidation rates, the model still only produced, at most, 23% of maximum observed oxidized mercury. In addition to underestimating net mercury oxidation, an analysis of elemental to oxidized mercury slopes indicated the model overestimated oxidized mercury deposition. An analysis of GEOS-Chem results from a separate study confirmed that while GEOS-Chem is able to simulate the range of measured oxidized mercury in low-oxidized mercury episodes and locations it consistently underestimates measured values during high-oxidized mercury periods at surface locations in western USA.

1 Introduction

30 Mercury (Hg) is a globally distributed toxicant that has the potential to harm ecosystem, wildlife, and human health (Mahbub et al., 2017; Rice et al., 2014). Mercury is found ubiquitously throughout the environment and exists in the atmosphere as elemental Hg (Hg^0) and oxidized Hg (denoted as Hg^{II} because almost all is believed to be in the +2-oxidation state (Shah et al., 2021)). Mercury is emitted into the atmosphere by natural (e.g., volcanic activity and biomass burning) and anthropogenic (e.g., coal fire power plants and artisanal gold mining) sources as either Hg^0 or Hg^{II} and can dynamically convert between the two forms (Jiao and Dibble, 2017a; Lam et al., 2019; Streets et al., 2019). Hg^0 is relatively inert, but it can deposit to soil and plant surfaces (Zhou and Obrist, 2021). Hg^{II} is soluble and only sparingly volatile, allowing it to be readily deposited to any surface (Lyman et al., 2020a).

Most previous measurements of atmospheric Hg^{II} were made with commercial systems that utilize a KCl-coated denuder; however, these are known to suffer from a low bias, the extent of which depends on atmospheric conditions (Lyman et al., 2010; McClure et al., 2014; Bu et al., 2018; Tang et al., 2022; Huang and Gustin, 2015). Cation exchange membrane-based systems have since been shown to avoid the low bias created by the KCl-coated denuder and have been deployed in locations around the globe (Tang et al., 2022; Luippold et al., 2020; Derry et al., 2024; Lyman et al., 2022; Gratz et al., 2015; Dunham-Cheatham et al., 2023). Although measurements of Hg^{II} are improving, current instrumentation is not compound specific; thus, many uncertainties surround the redox chemistry of atmospheric Hg (Jiao and Dibble, 2017b; Peng et al., 2021; Saiz-Lopez et al., 2019; Saiz-Lopez et al., 2020). Bromine (Br) and hydroxyl (OH) radicals are currently assumed to be the only primary oxidants of Hg^0 that are significant in the ambient atmosphere (Fu et al., 2024; Castro et al., 2022). Oxidation of Hg^0 is understood to occur via a two-step process by which Hg^0 is first oxidized by Br or OH to form Hg^{I} radicals and then further oxidized by O_3 and other atmospheric constituents to produce Hg^{II} compounds (Shah et al., 2021).

Previous work comparing GEOS-Chem model output against ambient measurements of Hg^{II} taken by a cation exchange membrane-based Hg^{II} measurement system concluded that although modeled total Hg ($\text{Hg}^0 + \text{Hg}^{\text{II}}$) concentrations matched well with observations, Hg^{II} was significantly lower in the model when compared to observations (Gratz et al., 2015; Shah et al., 2016). Later work included photoreduction of Hg^{I} and Hg^{II} to Hg^0 in the GLEMOS model which resulted in an overestimation of modeled Hg^0 and an underestimation of Hg^{II} , implying a missing oxidation pathway in the model (Saiz-Lopez et al., 2020).

An updated redox mechanism that includes photoreduction has been implemented in the GEOS-Chem model (Shah et al., 2021), but many aspects of the model are uncertain, including (but not limited to) atmospheric Br concentrations, rate coefficients for a number of the reactions in the chemical mechanism, gas-aerosol partitioning rates, and deposition processes. Shah et al. (2021) compared global annual average modeled Hg^{II} to KCl denuder-based Hg^{II} measurements, but because KCl denuder-based measurements are unreliable, the implications of these comparisons are unclear (See Fu et al. (2024) for a similar analysis with a different model platform). Gustin et al. (2023) compared direct cation exchange membrane samples collected over one- or two-week periods to GEOS-Chem with the Shah et al. (2021) chemistry and found that, while the model predicted Hg^{II} within the range of measurements at some locations, it drastically underestimated at other locations.

In this work, we compared GEOS-Chem results against Hg measurements at Storm Peak Laboratory in Colorado, USA, during a period with high Hg^{II} that has been shown to have originated from the free troposphere (Derry et al., 2024). These data were collected with a cation exchange membrane-based Hg measurement system that quantitatively recovered Hg^{II} halide compounds introduced from a calibrator traceable to International System of Units (SI) standards (Elgiar et al., 2024). We used a series of sensitivity analyses to attempt to improve model-measurement agreement, and we analyzed the measurement and model datasets to gain insight as to the causes of the discrepancy.

This work was part of a larger study investigating atmospheric Hg behavior at Storm Peak Laboratory. Elgiar et al. (2024) detailed the Hg measurement system for the study and showed it can accurately quantify Hg^0 and Hg^{II} . Derry et al. (2024) investigated the sources and behavior of Hg at Storm Peak over the entire measurement period (spring through fall 2021 and 2022). Lee et al. (2024) investigated the potential of iodine radical as a missing Hg^0 oxidant. Weiss-Penzias et al. (2025) explored the effects of precipitation on Hg^0 and Hg^{II} at Storm Peak and other locations.

2 Methods

2.1 Measurements of Hg

Ambient Hg^0 and Hg^{II} were measured using a dual channel measurement system developed by the Bingham Research Center at Utah State University. Details about the Hg measurement system were given by Elgiar et al. (2024). The dual channel system pulled air through a heated inlet (110°C) with an elutriator and impactor designed

to remove particles with an aerodynamic diameter greater than $2.5\ \mu\text{m}$ at a total flow rate of $9\ \text{L min}^{-1}$. Airflow from the inlet was routed sequentially through each of two channels to a Tekran 2537X Hg^0 analyzer. One channel contained a thermal converter heated to 650°C that converted all Hg in the sample to only Hg^0 , measuring total Hg. The other channel contained a series of two cation exchange membranes, which have been shown to quantitatively collect Hg^{II} while allowing Hg^0 to pass through (Miller et al., 2019), measuring Hg^0 only. Hg^{II} was calculated as the difference between the two channels. Hg^0 and Hg^{II} measurements were calibrated while sampling ambient air with an automated, SI-traceable permeation tube-based calibrator, also developed at the Bingham Research Center. Permeation tubes containing HgBr_2 or Hg^0 were housed in a temperature-controlled oven at 70°C . Ultra-high purity nitrogen was used to carry the gas emitted from the tubes out of heated lines and into the inlet of the dual channel system. Flow was controlled by a critical orifice downstream of the permeation tubes, and a multiport valve was used to select between different tubes.

This measurement and calibration system had a 1-hr detection limit for Hg^{II} of $6\text{--}12\ \text{pg m}^{-3}$ and recovered $97 \pm 4\%$ and $100 \pm 8\%$ ($\pm$ standard deviation) of Hg^0 and HgBr_2 , respectively. The expanded uncertainty (Elgiar et al., 2024; NIST, 2012) of Hg^0 and Hg^{II} were both 16%. More details about instrument performance were given by Elgiar et al. (2024).

2.2 Sampling Location and Period

The dual channel system and automated calibrator were deployed at Storm Peak Laboratory (SPL) in Steamboat Springs Colorado, USA, from March 2021 to September 2022. Measurement-model comparisons in this study focused on an elevated Hg^{II} episode in June 2021 that was characterized by Derry et al. (2024). Storm Peak Laboratory is a permanent mountaintop atmospheric monitoring station located at 40.455°N , -106.744°W and 3220 meters above sea level (Figure 1). Previous Hg^{II} measurements at Storm Peak showed elevated concentrations measured by a system that utilized a KCl-coated denuder (Fain et al., 2009). This is the first time that a cation exchange membrane-based system has been used to measure Hg^{II} at Storm Peak.



Figure 1. Location of Hg measurements at Storm Peak Laboratory, Colorado, USA.

2.3 GEOS-Chem Model

- 110 The GEOS-Chem 3D photochemical transport model (v12.8.0, DOI:[10.5281/zenodo.3784796](https://doi.org/10.5281/zenodo.3784796)), using Hg chemistry implemented by Shah et al. (2021), simulated Hg concentrations in the atmosphere. Simulations were performed for the period of 5 to 15 June 2021. Lee et al. (2024) conducted a comparison of measured and modeled ozone, temperature, and water vapor for the same base model used in this study.

- A total of five separate simulations were carried out (Table 1), including two base model simulations and three
 115 separate sensitivity analyses using modified reaction rates (Table 2). The first base model simulation (Base 0.25x0.3125) used boundary conditions generated by a global simulation with horizontal resolution of $2^{\circ} \times 2.5^{\circ}$ to run a North American (10° to 60° latitude, -130° to -60° longitude) nested grid simulation at $0.25^{\circ} \times 0.3125^{\circ}$ resolution. The second base model simulation (Base 2x2.5) was a $2^{\circ} \times 2.5^{\circ}$ resolution global simulation with no nested simulation. Sensitivity analyses (SA1, SA2, and SA3) were conducted using $2^{\circ} \times 2.5^{\circ}$ global resolution,

120 and comparisons were made only to the 2° x 2.5° resolution base model. Goddard Earth Observing System-
Forward Processing (GEOS-FP) meteorology was used as input for all simulations. The only change to default
Hg emissions used by Shah et al. was that Hg emissions from biomass burning events were updated to year 2021
using beta files produced by the Global Fire Emissions Database (Randerson et al., 2015). Daily oxidant files at
2° x 2.5° resolution were produced from a full chemistry simulation using GEOS-Chem version 13.2.1 (DOI:
125 [10.5281/zenodo.5500717](https://doi.org/10.5281/zenodo.5500717); Information about different versions is available from the GEOS-Chem wiki (GEOS-
Chem, 2025); See additional information about the full chemistry simulation in Lee et al. (2024)). Each simulation
was a reduced 47-layer simulation run with a spin-up time of one year. A spin-up time of three years was tested,
and average modeled Hg⁰ and Hg^{II} concentrations at SPL during the sampling period increased by only 60 and 1
pg m⁻³, respectively. Thus, it was determined that a spin-up time of one year was sufficient for the purposes of
130 this study.

Table 1. Descriptions of the different base model simulations and chemistry sensitivity analyses (SAs) using GEOS-Chem.

Simulation name	Description
Base 0.25x0.3125	0.25° x 0.3125° resolution base model run implementing the original <i>k</i> values used in Shah et al., 2021.
Base 2x2.5	2° x 2.5° resolution base model run implementing the original <i>k</i> values used in Shah et al., 2021.
SA1	Sensitivity analysis increasing <i>k</i> for (R1)
SA2	Sensitivity analysis decreasing <i>k</i> for (R2)
SA3	Sensitivity analysis increasing <i>k</i> for (R3) and (R4)

The reactions of focus in the sensitivity analyses were: (1) the three-body reaction involving the oxidation of Hg⁰
135 by Br (R1), (2) the three-body thermolysis reaction involving the dissociation of HgOH to produce Hg⁰ and OH
(R2), (3) the reaction of HgBr and O₃ to produce HgBrO and O₂ (R3) and (4) the reaction of HgOH and O₃ to
produce HgOHO and O₂ (R4) (Table 2). We also conducted additional sensitivity tests of the SA1 scenario
wherein the photoreduction frequency was increased iteratively to allow for Hg⁰ closer to observed values,
following Shah et al. (2021).

140 **Table 2. Summary of the rate coefficients (*k*) for the base model and modified *k* values for the sensitivity analyses. Units
are cm³ molec⁻¹ s⁻¹ for bimolecular reactions (R3 and R4) for cm⁶ molec⁻² s⁻¹ for *k*₀ of three-body reactions (R1
and R2).**

Reaction ID	Reaction	Base k	Modified k
(R1)	$\text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{BrHg}^{\text{I}} + \text{M}$	1.46×10^{-32}	1.46×10^{-31}
(R2)	$\text{Hg}^{\text{I}}\text{OH} + \text{M} \rightarrow \text{Hg}^0 + \text{OH} + \text{M}$	1.22×10^{-9}	1.22×10^{-10}
(R3)	$\text{Hg}^{\text{I}}\text{Br} + \text{O}_3 \rightarrow \text{Hg}^{\text{II}}\text{BrO} + \text{O}_2$	3×10^{-11}	7.5×10^{-11}
(R4)	$\text{Hg}^{\text{I}}\text{OH} + \text{O}_3 \rightarrow \text{Hg}^{\text{II}}\text{OHO} + \text{O}_2$	3×10^{-11}	7.5×10^{-11}

Experiments determining k for (R1) have ranged from $k = 1.46 \times 10^{-32} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Donohoue et al., 2006) to $k = 1.46 \times 10^{-31} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Ariya et al., 2002). We acknowledge that the Ariya et al. rate constant is unlikely to be representative of reality because of probable confounding effects from wall reactions (Donohoue et al., 2006). It is included in a sensitivity analysis here as a highest-case scenario. Rate coefficients for the reactions involving OH and Hg depend on calculations of the bond strength between OH and Hg, which has not yet been experimentally determined (Castro et al., 2022; Hewa Edirappulige et al., 2023). It was noted by Shah et al. (2021) that a minor change to this bond strength may have a substantial impact on Hg^{II} production in the model, which is important when considering k for (R2). Furthermore, Castro et al. (2022) recommended a $k = 7.5 \times 10^{-11}$ for (R3) and (R4), which is 2.4 times higher than the value for k used in the base model.

We performed sensitivity simulations with reduced dry and wet deposition rates using GEOS-Chem version 14.1 because the variables that drive deposition can be much more easily manipulated in this version. We used GEOS-FP meteorology and default Hg emissions and chemistry. Several updates and bug fixes related to Hg were implemented between versions 12.8 and 14.1 (GEOS-Chem, 2025). Hg^0 in our version 14.1 base model averaged 87% of concentrations in version 12.8, and Hg^{II} was 91% of concentrations in version 12.8. To reduce Hg^{II} deposition in version 14.1, we manipulated variables for Hg_CHEM_PROP, which determines deposition for Hg^{II} species, in the species_database.yml file. We reduced dry deposition by changing the DD_Hstar variable from 1.0×10^{14} to 1.0×10^5 . We reduced wet deposition by changing the Henry_K0 variable from 1.40×10^6 to 1.40×10^4 .

2.4 Data Processing and Analysis

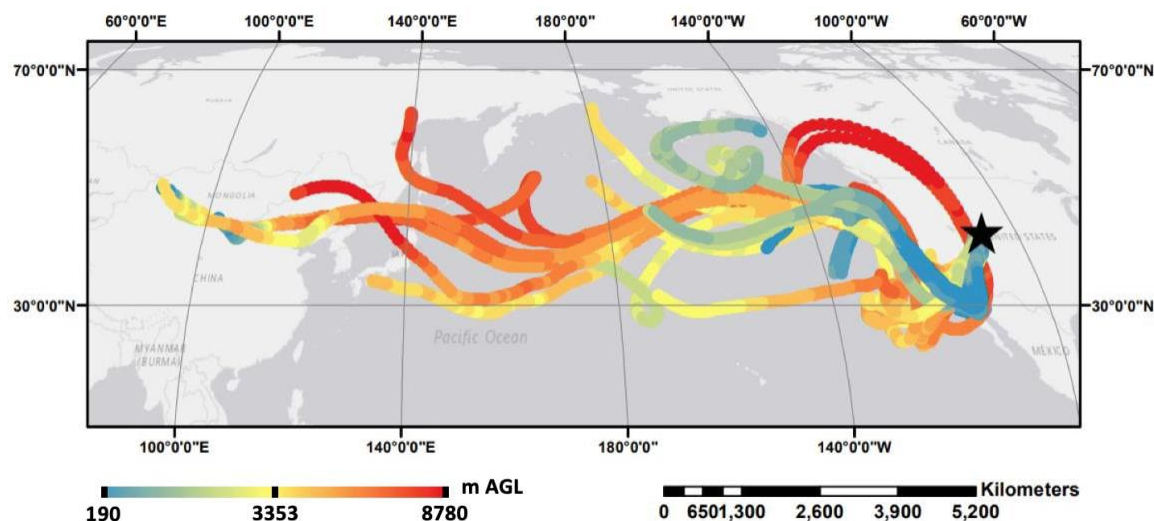
Daily average Hg concentrations were extracted from GEOS-Chem model output at the latitude and longitude of Storm Peak Laboratory and the corresponding vertical level in the model closest to Storm Peak Laboratory's elevation above sea level (The model terrain height was lower than the actual elevation because of the model's coarse horizontal resolution). The sum of all Hg^{I} and Hg^{II} species in the model (gas and particle phases) was used for comparison with Hg^{II} measurements made by the dual-channel system. Only the Hg mass of oxidized Hg

species was used, since only Hg mass is measured by the dual-channel analyzer. Model performance was evaluated using methods recommended by Chang and Hanna (2004). Processing of model outputs was performed with Python version 3.11, including with the GCPy toolkit. Statistical analyses were performed using Microsoft Excel, except that RMA regression was performed in Python with the pylr2 package. All data are reported as daily values $\pm$ the 95% confidence interval, unless otherwise specified.

3 Results and Discussion

3.1 Observations of Hg

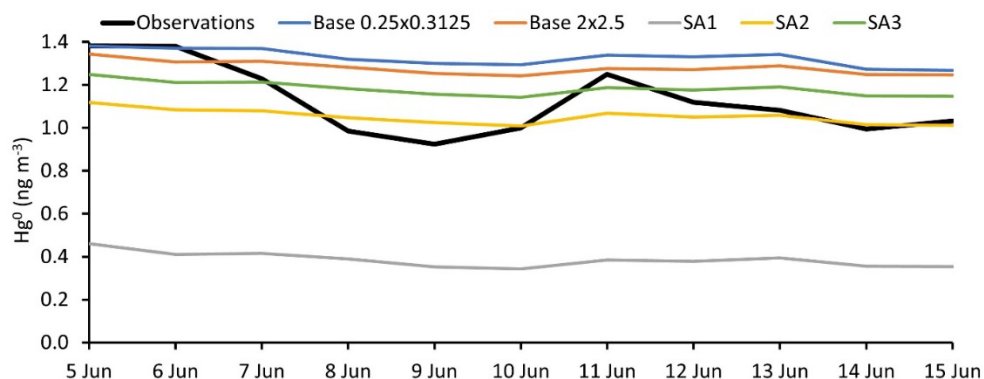
The time period of interest for this study, 7 to 11 June 2021, was an episode of elevated Hg^{II} . Hg^{II} reached a maximum of 212 pg m^{-3} on 9 June and was 23% of the measured Hg^0 at that time. An $\text{Hg}^{\text{II}}/\text{Hg}^0$ ratio of 0.18 is considered high and indicative of in-situ oxidation (Timonen et al., 2013). Ten-day HYSPLIT backwards trajectories with GDAS input meteorology (Draxler and Rolph, 2003) for this day showed a mix of air originating high in the troposphere above the Pacific Ocean off the East Asian coast and lower in the troposphere near the Western coast of Mexico (Figure 2). Average observed Hg^{II} and Hg^0 concentrations during the episode were $151 \pm 74 \text{ pg m}^{-3}$ and $1.08 \pm 0.19 \text{ ng m}^{-3}$, respectively. Observed Hg^{II} and Hg^0 exhibited a strong anti-correlation ($r^2 = 0.91$), a phenomenon also observed by others who have measured Hg at SPL (Fain et al., 2009). More details concerning this and other elevated Hg^{II} episodes at Storm Peak can be found in Derry et al. (2024).



185 **Figure 2. 10-day HYSPLIT backwards trajectories ending on 9 June 2021. The black star represents the location of Storm Peak Laboratory.**

3.2 Temporal Trends and Magnitude of Hg^{II} and Hg^0

All simulations captured the observed temporal trends of Hg^{II} and Hg^0 , which indicates that GEOS-Chem accurately simulated the air mass transport event observed during the episode (Figures 3 and 4; Figures S2 and S3 show the same data on different scales to emphasize temporal trends in modeled data). Regression analysis comparing observed and modeled Hg^0 and Hg^{II} showed moderate to strong correlations with measurements, ranging from $R^2 = 0.54$ to 0.79 (Figures 5 and S1; Table 3). Despite these temporal correlations, none of the simulations was able to accurately capture the magnitude of the episode. Measured Hg^{II} reached a maximum of 19% of total Hg compared with 14% for SA1 and much lower values in the other simulations.



195 **Figure 3. Observed and simulated daily average Hg^0 from 5 to 15 June 2021.**

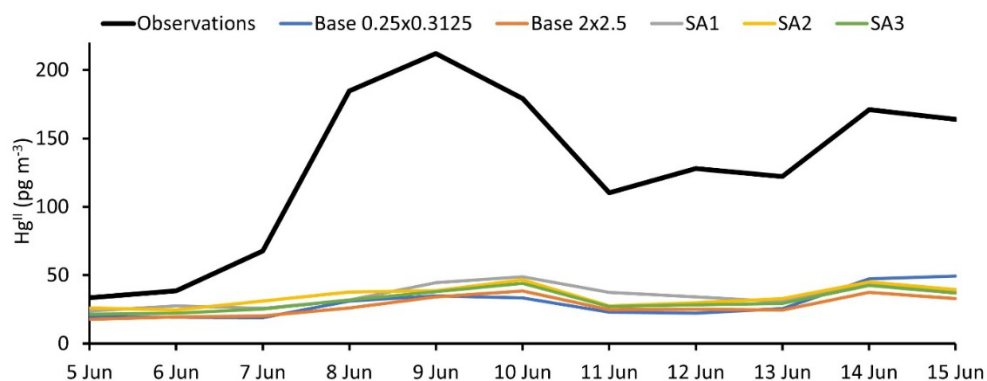


Figure 4. Observed and simulated daily average Hg^{II} from 5 to 15 June 2021.

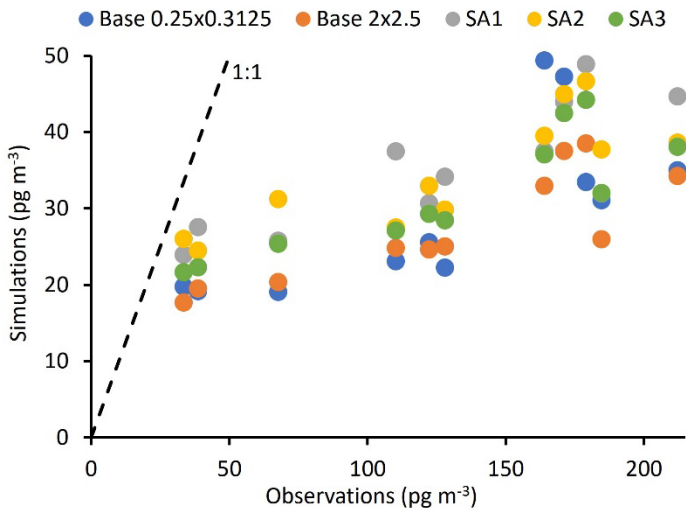


Figure 5. Observed versus simulated daily average Hg^{II}. A 1:1 slope is shown as a black dashed line.

Table 3 and comprehensive statistical analyses in Table S1 show that simulated Hg⁰ was within the range of observations, except for SA1. Simulated Hg^{II}, however, was consistently much lower than observations. Simulations underpredicted average observed Hg^{II} by between 3.2 and 4.2 times.

Table 3. Summary of observed and modeled daily average Hg concentrations from 7 to 11 June 2021, and correlation between observed and simulated Hg. Averages are shown as average ± 95% confidence interval. Slopes and intercepts were calculated using RMA regression. The Hg^{II}:Hg⁰ intercept is the Hg^{II} concentration at 0 ng m⁻³ Hg⁰.

	Avg. Hg ⁰ (ng m ⁻³)	Avg. Hg ^{II} (pg m ⁻³)	Min. Hg ⁰ (ng m ⁻³)	Max. Hg ^{II} (pg m ⁻³)	Max. Hg ^{II} / Hg ⁰	Obs. vs. Sim. Hg ⁰ (r ²)	Obs. vs. Sim. Hg ^{II} (r ²)	Hg ^{II} : Hg ⁰ slope	Hg ^{II} :Hg ⁰ intercept (pg m ⁻³)	Hg ^{II} : Hg ⁰ (r ²)
Observations	1.08 ± 0.19	150 ± 74	0.92	212	0.23	--	--	-0.38	552	0.95
Base 0.25x0.3125	1.32 ± 0.04	28 ± 9	1.27	35	0.03	0.71	0.54	-0.28	397	0.89
Base 2x2.5	1.27 ± 0.03	29 ± 9	1.24	39	0.03	0.68	0.74	-0.23	323	0.86
SA1	0.38 ± 0.04	38 ± 12	0.34	49	0.14	0.69	0.67	-0.23	125	0.83
SA2	1.05 ± 0.04	36 ± 9	1.01	47	0.05	0.79	0.69	-0.22	261	0.79
SA3	1.18 ± 0.03	33 ± 10	1.14	44	0.04	0.73	0.75	-0.23	309	0.85

210 The highest average modeled Hg^{II} occurred in SA1 and was $38 \pm 12 \text{ pg m}^{-3}$ (Table 3). A GEOS-Chem sensitivity analysis with the same change in the $\text{Hg}+\text{Br}$ rate constant as SA1 was performed by Shah et al. (2016) and Gratz et al. (2015). They showed that increasing the rate constant led to an approximate two-fold increase in Hg^{II} , but the model continued to underestimate Hg^{II} measurements by up to three times. In this study, SA1 resulted in only a 30% increase in Hg^{II} . Unlike the current study, Shah et al. (2016) increased rates of in-cloud reduction of Hg^{II} to Hg^0 to maintain the burden of total Hg in the simulated atmosphere. Hg^{II} likely did not increase as much in 215 SA1 compared to Shah et al. because total Hg decreased substantially in SA1.

Overall, modifying k values in SA1, SA2, and SA3 did not have a large impact on Hg^{II} concentrations in the model, only increasing average Hg^{II} concentrations by 9, 8, and 5 pg m^{-3} , respectively, when compared to the base model. The largest impact on modeled Hg^{II} was stratospheric Hg^{II} production in SA1, reaching a maximum of $\sim 900 \text{ pg m}^{-3}$, compared to $\sim 600 \text{ pg m}^{-3}$ in the base simulation, likely due to the abundance of Br in the stratosphere 220 (Salawitch et al., 2005). Maximum stratospheric Hg^{II} values in SA2 and SA3 remained similar to the base simulation (Figure 6). Others have shown evidence that the stratosphere is important to the overall atmospheric Hg^{II} load (Lyman and Jaffe, 2012; Murphy et al., 2006; Saiz-Lopez et al., 2025). Derry et al. (2024) did not find evidence that the air mass in this study originated in the stratosphere, though it is possible that a more generalized influence from the stratosphere did influence Hg^{II} concentrations.

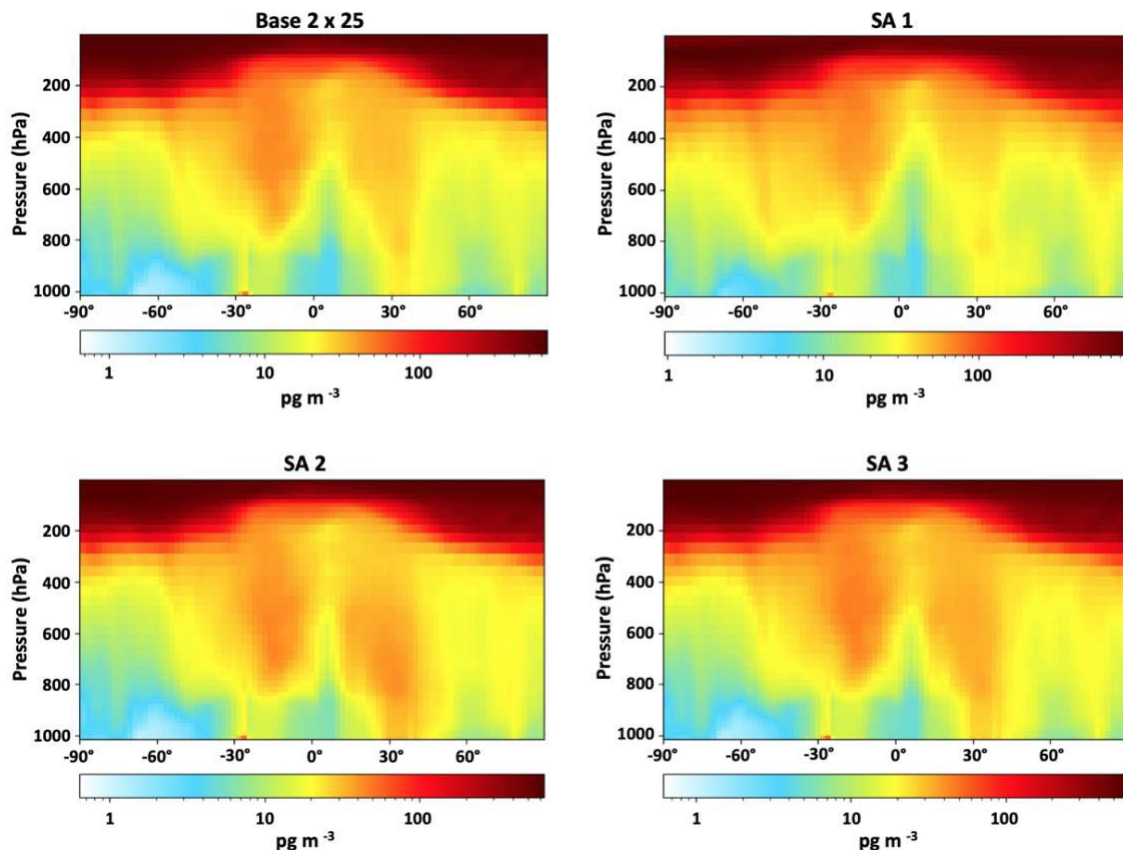


Figure 6. Global zonal mean plots for four of the GEOS-Chem simulations Hg^{II} on 9 June 2021.

GEOS-Chem users typically adjust the photoreduction frequency of organic particulate Hg^{II} to match observed global Hg^0 (Shah et al., 2021; Horowitz et al., 2017). Since SA1 resulted in Hg^0 much lower than measurements, we conducted a set of sensitivity analyses that had the same modified $\text{Hg}^0 + \text{Br}$ reaction rate as SA1, but wherein the photoreduction frequency was increased to allow for more Hg^0 , with a maximum increase of 2000 times above than the default value. Hg^0 increased in these sensitivity analyses, but Hg^{II} stayed within the same range (Figure S4). We hypothesize that the decrease in total Hg^{II} caused by the increase in photoreduction frequency was balanced by an increase in Hg^{II} because more Hg^0 was available for oxidation.

3.3 Relationship between Hg^{II} and Hg^0

235 While all simulations resulted in a negative $\text{Hg}^{\text{II}}:\text{Hg}^0$ slope, simulated slopes were less negative than observations (Table 3; Figure 7). An $\text{Hg}^{\text{II}}:\text{Hg}^0$ slope of -1 can be expected for a well-mixed air mass in which no addition or loss of Hg occurs (since Hg mass is conserved). Reduction of Hg^{II} back to Hg^0 or uptake of Hg^{II} by aerosols would maintain the -1 slope (assuming our instrument accurately measures aerosol-phase Hg). Assuming no addition or loss of Hg^0 , a slope greater than -1 (i.e., less negative) should indicate that a portion of Hg^{II} was lost from the air mass via dry or wet deposition after it was produced (Swartzendruber et al., 2006; Lyman and Jaffe, 2012). Since all the simulations resulted in a greater $\text{Hg}^{\text{II}}:\text{Hg}^0$ slope than the observations, we hypothesized that Hg^{II} depositional processes are overestimated in GEOS-Chem. To test this, we performed additional sensitivity tests with GEOS-Chem version 14.1 wherein Hg^{II} dry and wet deposition rates in GEOS-Chem were reduced, but we found an increase, rather than a decrease, in slope (from -0.28 to -0.18; see Figure S5). Further sensitivity tests to probe this issue are warranted but are beyond the scope of the current study.

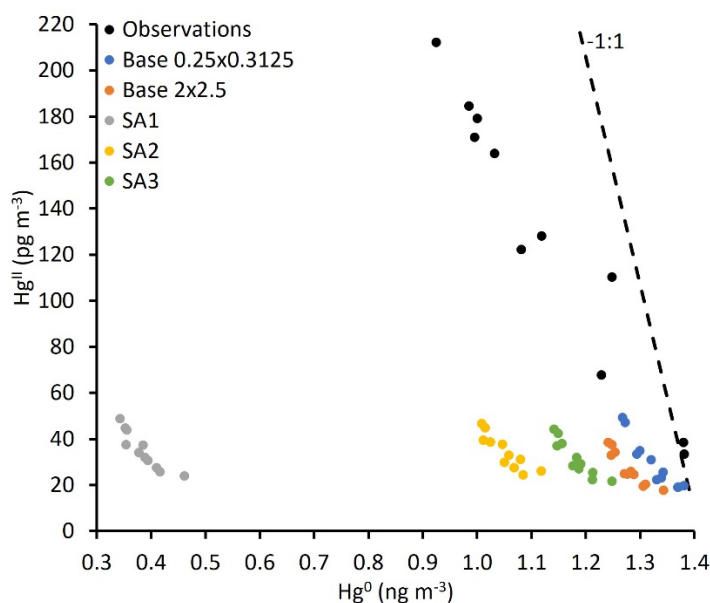


Figure 7. Relationship between daily average Hg^0 and Hg^{II} in observations and simulations. A -1:1 slope (shown as the black dashed line) indicates no addition or loss of Hg from the air mass. A slope greater than -1 (as shown in the measurement and model data) likely indicates depositional loss of Hg^{II} from the air mass.

250 The sensitivity simulations did not result in any meaningful changes in the slope relative to the Base 2x2.5 simulation, which is expected because depositional processes were not changed. This was the case even for SA1, wherein the rate of the $\text{Hg} + \text{Br}$ reaction was increased by 10 times. The $\text{Hg}^{\text{II}}:\text{Hg}^0$ slope of the higher-resolution Base 0.25x0.3125 simulation was the most similar to observations. It is possible that cloud and precipitation processes were simulated more accurately in Base 0.25x0.3125, leading to more realistic deposition rates. Since
255 Hg^{II} and Hg^0 values were extracted from simulations at the elevation of Storm Peak Laboratory rather than at the model surface level, interaction with the surface (and dry deposition) may have been less in the simulated versus observed air mass. Also, it is possible that the observed and simulated slopes greater than -1 were due to the confounding influence of a separate low- Hg^0 air mass that increasingly impacted the measurement location as Hg^{II} increased. This could be the case if the air mass was affected by the stratosphere, though Derry et al. (2024)
260 did not find evidence for this.

While $\text{Hg}^{\text{II}}:\text{Hg}^0$ slopes close to -1 have been observed (Swartzendruber et al., 2006; Lyman and Jaffe, 2012), slopes greater than -1, as found in this study, have been more commonly found in other studies (Lyman and Jaffe, 2012; Fu et al., 2021). Derry et al. (2024) classified the period modeled in this work as two separate high Hg^{II} events: one from 7 through 11 June (their Event 4) and another from 13 through 15 June 2021 (their Event 5).
265 They found $\text{Hg}^{\text{II}}:\text{Hg}^0$ slopes of -0.35 and -0.52, respectively, for the two periods. They identified a total of 18 high Hg^{II} events for the 2021-2022 measurement campaign with slopes ranging from -0.76 to -0.16, showing that $\text{Hg}^{\text{II}}:\text{Hg}^0$ slopes greater than -1 are common at Storm Peak Laboratory.

3.4 Magnitude of Changes in Hg^{II} and Hg^0

The magnitude of the increase in Hg^{II} was calculated as the difference between the observed maximum Hg^{II}
270 concentration during the high- Hg^{II} episode and the Hg^{II} concentration for 5 and 6 June, which were prior to the episode. The magnitude of the decrease in Hg^0 was calculated as the difference between the observed minimum Hg^0 concentration during the episode and the Hg^0 concentration for the days prior to the episode. The observed change in magnitude for Hg^{II} and Hg^0 was 176 pg m^{-3} and -0.46 ng m^{-3} , respectively. The modeled change in magnitude for Hg^{II} and Hg^0 , in contrast, ranged from 16 to 23 pg m^{-3} and -0.08 to -0.11, respectively.

275 Since Hg^{II} concentrations are influenced both by net oxidation and depositional loss, the change in magnitude of Hg^0 is a better indicator to net oxidation during the episode (though we concede that Hg^0 variability is also impacted by emissions, deposition, and transport phenomena, confounding the accuracy of this indicator). By

this measure, observed net oxidation during the episode was about four times higher than simulations, including sensitivity simulations that increased oxidation reaction rates. Similarly, correlation between simulated and observed Hg^0 is likely a more useful metric for model evaluation of redox processes than Hg^{II} correlations. By this measure, SA2 performed better than any of the other simulations, with an r^2 of 0.79. This better correlation could indicate that the reaction rate change employed in SA2 led to an oxidation environment that better matched reality.

3.5 Global Distribution of Hg

Maps showing global modeled Hg^{II} concentrations at the surface for Base 2x2.5, SA1, SA2, and SA3 are presented in Figure 8. Surface Hg^{II} was higher in SA1, especially in the arctic and mid-latitude oceans. SA2 and SA3 showed only small increases in global Hg^{II} . Average modeled Hg^0 and total Hg concentrations for all simulations except SA1 were within 23% or better of observations. SA1 showed a decrease in average Hg^0 of 65% when compared to the base model. Shah et al. (2016) did not show a decrease in Hg^0 when performing a similar sensitivity analysis. This is because they increased rates of in-cloud reduction of Hg^{II} to Hg^0 to maintain the burden of total Hg in the simulated atmosphere, which was not performed here. Figures 9 and S6 show increases to average dry and wet deposition for Hg^{II} in the base model and SA1 across the globe on 9 June 2021. This increased deposition likely explains the lower total Hg in the model. Further, natural and anthropogenic emissions of Hg are highly uncertain (Selin and Jacob, 2008; Zhu et al., 2016). It is also possible that emissions are too low in the model and that this is the cause of unrealistically low total Hg when Hg oxidation rates were adjusted in the sensitivity analyses.

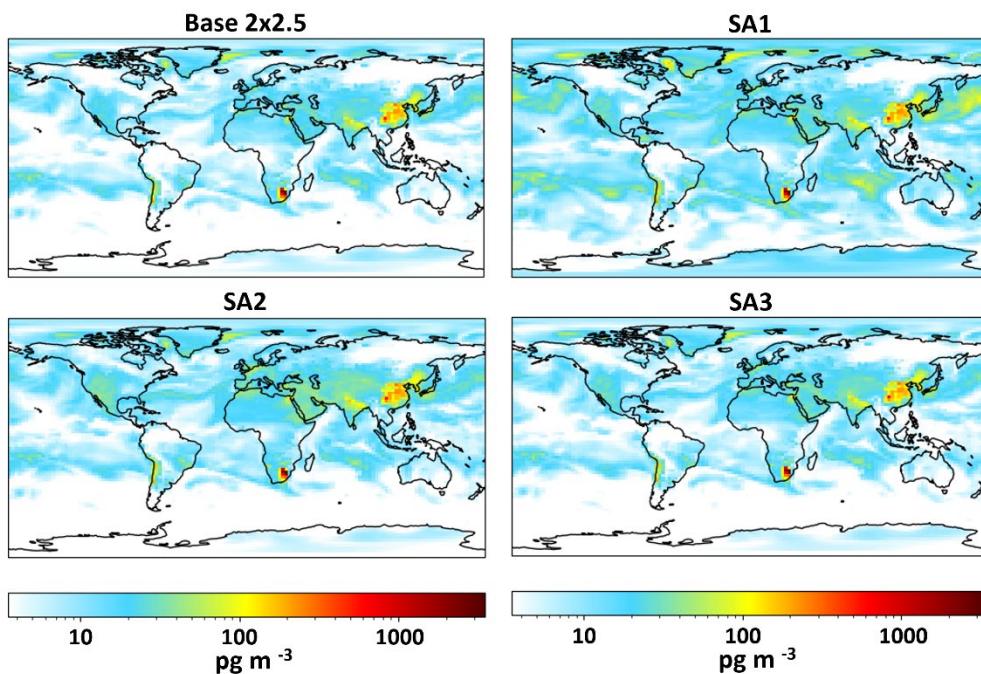
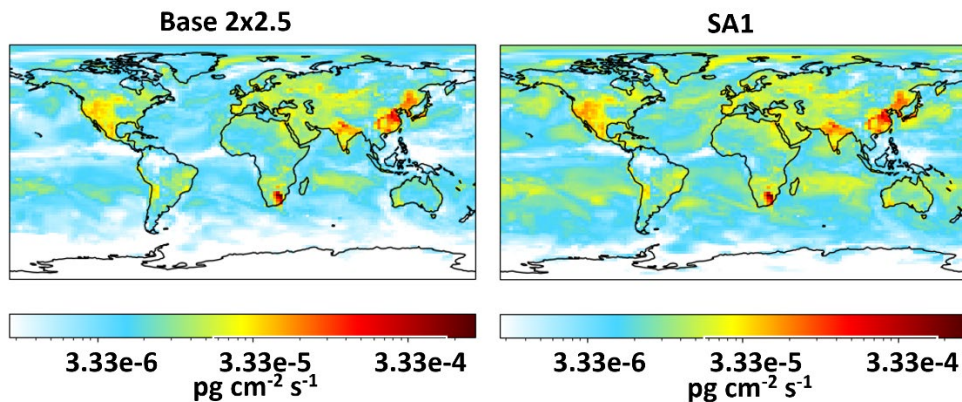


Figure 8. Average Hg^{II} concentrations at the surface on 9 June 2021 for four of the model simulations.



300 Figure 9. Average dry deposition for the Base 2x25 and SA1 simulations on 9 June 2021.

3.5 Speciation of Hg^{II}

Of the 20 Hg^{II} species simulated at the measurement location (Figure S7) in the Base 2x2.5 GEOS-Chem simulation, more than 99% were comprised of aerosol-phase Hg^{II} (24%) or gas-phase HgCl_2 (72%), $\text{Hg}(\text{OH})_2$

(3%), and HgBrOH (1%). Speciation was very similar in the sensitivity analyses. In SA1, for example, even though the rate of the Hg + Br reaction was increased by 10 times, HgCl₂ still comprised 73% of Hg^{II}, with HgBrOH, HgOH₂, and aerosol Hg^{II} comprising 2%, 1%, and 24%, respectively. In the model's chemical mechanism, any Hg^{II} sorbed to and subsequently volatilized from particles becomes HgCl₂, which makes it the dominant Hg^{II} species in the model. Luippold et al. (2020) used an indirect thermal desorption method to show that nitrogen- and sulfur-containing Hg compounds may make up a large fraction (up to 61 and 69.7%, respectively) of Hg^{II} compounds in ambient air, though primary oxidation of Hg⁰ by nitrogen- and sulfur-containing oxidants is not known to occur (Lyman et al., 2020b; Edirappulige et al., 2024). Nevertheless, one or more missing oxidation pathways could also help explain the underestimation of Hg^{II} in the model. Compound specific Hg^{II} measurement methods may help resolve this discrepancy (Khalizov et al., 2020; Lyman et al., 2020a).

3.6 Comparison with Others' Work

Shah et al. (2021) acknowledge a low Hg^{II} bias in their simulations of atmospheric Hg, especially in the free troposphere, and note that (1) higher model Br does not solve the problem, and (2) modifications to aqueous Hg^{II} photoreduction and organic particulate Hg^{II} helps but requires unrealistic organic particulate Hg^{II} photoreduction rates. Similarly, our work shows a low Hg^{II} bias that is unresolvable with the current chemical mechanism. While Shah et al. focus on global mean conditions, however, the current work focuses on the dynamics of a specific high-Hg^{II} episode. We show that GEOS-Chem predicts Hg^{II} similar to measurements prior to the episode, and that the model simulates the timing and nature of the episode reasonably, but that the model's low bias for Hg^{II} appears to be driven by failure to adequately simulate the amount of Hg^{II} produced during the episode.

Gustin et al. (2023) collected 1- or 2-week samples of Hg^{II} by direct capture on cation exchange membranes at locations in Nevada, Texas, Utah, and Georgia, USA, and at Reunion Island in the Indian Ocean. They used the same GEOS-Chem model setup as this study to compare GEOS-chem against their measurements. Table 4 shows the results of their comparison, along with a summary from this study. The simulation underpredicted the magnitude of Hg^{II} at all sites in the Gustin et al. study, except Utah, though model bias is relatively low for Georgia and the Indian Ocean. For Nevada and western Texas, observations were several times higher than model output, similar to the findings of this study. In some studies, high Hg^{II} has been measured in Utah (Lyman et al., 2022; Lan et al., 2012), and we expect that low Utah Hg^{II} in the Gustin et al. study was due to winter conditions at the site, though we acknowledge measurements in western Texas were also made during winter months. Simulated

Hg^{II} at the Nevada location, which had the highest observed Hg^{II} in the Gustin et al. study, was in the same range as Utah, which had the lowest observed Hg^{II}.

In agreement with the current study, the Gustin et al. results show relatively low model bias at low-Hg^{II} locations and much higher bias at locations with high Hg^{II}. The relationship between measured Hg^{II} and the observed:modeled Hg^{II} ratio is linear and significant ($p < 0.01$; $r^2 = 0.82$; Figure S8), showing that the GEOS-Chem low bias is predictable. **Table 4. Observed and modeled Hg^{II} from this study and from Gustin et al. (2023). All observations shown in the table, except those from this study, are from the RMAS direct Hg^{II} capture method. Model results from both studies used GEOS-Chem simulations with similar chemistry and other parameters. For this study, model output from the Base 2x25 simulation is shown. P values are from t-tests.**

	Observed Hg ^{II} (pg m ⁻³)	Modeled Hg ^{II} (pg m ⁻³)	Observed:modeled ratio	p value
Storm Peak Laboratory (low Hg ^{II} ; 5-7 Jun 2021)	47 ± 46	19 ± 3	2.4	0.12
Storm Peak Laboratory (high Hg ^{II} ; 8-15 Jun 2021)	159 ± 30	30 ± 5	5.2	<0.01
Utah (October-December 2021)	12 ± 12	19 ± 5	0.6	0.13
Western Texas (October- December 2021)	93 ± 28	24 ± 5	3.8	<0.01
Georgia (October- December 2021)	16 ± 4	9 ± 3	1.8	0.01
Indian Ocean (October- December 2021)	15 ± 6	8 ± 3	1.9	0.04
Nevada (June-July 2020)	133 ± 47	18 ± 4	7.4	<0.01

4 Conclusions

The purpose of this study was to investigate the ability of the GEOS-Chem 3D photochemical transport model to simulate a high-Hg^{II} episode observed at Storm Peak Laboratory in Colorado. The base GEOS-Chem reproduced

- (1) Hg⁰ concentrations to within 20% of observations
- (2) Hg^{II} concentrations prior to the start of the high-Hg^{II} episode to within 50%
- (3) The timing of changes in Hg⁰ and Hg^{II} (R^2 of 0.54 to 0.79) which implies the model correctly simulated the transport of air masses that influenced the measurement site.

The model failed to reproduce:

- 350 (1) The magnitude of temporal variability in Hg^0 and Hg^{II} observed by the measurement system. Measured Hg^{II} and the measured decrease in Hg^0 were both several times greater than simulations during the episode, including simulations with increased Hg^0 oxidation rates. Under-simulation of the decrease in Hg^0 is an indicator of underestimated net oxidation during the episode. Under-simulation of the increase in Hg^{II} is an indicator of underestimated net oxidation and/or overestimated Hg^{II} deposition.
- 355 (2) The slope of the $\text{Hg}^0:\text{Hg}^{\text{II}}$ relationship during the episode. All simulations showed an inverse relationship, but the slope was more negative in the measurements than in the simulations. We infer from this that the model overestimated Hg^{II} deposition, though our measurements are inadequate to determine whether dry or wet deposition (or both) in the model led to the overestimate. Weiss-Penzias et al. (2025) investigated washout of Hg^{II} during precipitation events in the area of the study.
- 360 The results from Gustin et al. (2023) corroborated our findings, showing that the low bias of GEOS-Chem is worse when Hg^{II} is higher. Gratz et al. (2015) and Shah et al. (2016) both had similar findings, but they used a much simpler Hg chemical mechanism that only included oxidation of Hg^0 by halogens. Our work provides evidence that the much more comprehensive Shah et al. (2021) still underrepresents Hg^{II} in some conditions, as acknowledged by Shah et al.
- 365 This study shows that the general causes of the model's low bias during high- Hg^{II} episodes are underestimation of net Hg^0 oxidation and overestimation of Hg^{II} deposition. Some of this presumed bias could be due to intrusion of low- Hg^0 stratospheric air into the studied air mass, but Derry et al. (2024) found no evidence for stratospheric influence in this or other high- Hg^{II} air masses at Storm Peak Laboratory. Additional work is needed to elucidate the exact causes of the low bias.

370 **5 Code/Data Availability**

Measurement data collected during this project are publicly available at <https://doi.org/10.5281/zenodo.10699270> (Gratz et al., 2024). GEOS-Chem model code is available at <https://geoschem.github.io/index.html>.

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inputs and provided guidance and mentoring for the GEOS-Chem simulations.

7 Author Contributions

380 The primary contributor to the work is listed as the first author. The project lead is listed as the last author. Other
authors are listed alphabetically. LEG, SNL, AGH, and RV planned the campaign. TRE, SNL, and LEG were
responsible for Hg measurements. SNL and TRE developed and improved the dual-channel Hg measurement
system. TRE and LD conducted GEOS-Chem modelling and analysis. TRE and SNL wrote the manuscript. TRE,
SNL, LD, LEG, AGH, and RV reviewed and edited the manuscript.

385 8 Competing Interests

The authors declare no competing interests.

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