Elevated Tropospheric Iodine over the Central Continental United States: Is Iodine a Major Oxidant of Atmospheric Mercury?

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Abstract

Previous efforts to measure atmospheric iodine have focused on marine and coastal regions. We report the first ground-based tropospheric iodine monoxide (IO) radical observations over the central continental United States. Throughout April 2022, IO columns above Storm Peak Laboratory, Colorado (3220 m.a.s.l.) ranged from 0.7±0.5 to 3.6±0.5×1012 (average: 1.9×1012 molec cm-2). IO was consistently elevated in air masses transported from over the Pacific Ocean. The observed IO columns were up to three times higher and the range was larger than predicted by a global model, which warrants further investigation into iodine sources, sinks, ozone loss, and particle formation. IO mixing ratios increased with altitude. At the observed levels, iodine may be competitive with bromine as an oxidant of elemental mercury at cold temperatures typical of the free troposphere (4–12km; <260K). Iodine-induced mercury oxidation is missing in atmospheric models, understudied, and helps explain model underestimation of oxidized mercury measurements.

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Key Points:

- Measurements of iodine monoxide radicals at Storm Peak Laboratory are up to three times higher than predicted by GEOS-Chem.
- IO tropospheric column variability is significant and highlights a need to better understand sources and sinks of free tropospheric iodine.
- Iodine rivals bromine as an oxidant of mercury in the upper troposphere; iodine-mercury chemistry is understudied and missing in atmospheric models.

Abstract

Previous efforts to measure atmospheric iodine have focused on marine and coastal regions. We report the first ground-based tropospheric iodine monoxide (IO) radical observations over the central continental United States. Throughout April 2022, IO columns above Storm Peak Laboratory, Colorado (3220 m.a.s.l.) ranged from 0.7±0.5 to 3.6±0.5×10^{12} (average: 1.9×10^{12} molec cm^{-2}). IO was consistently elevated in air masses transported from over the Pacific Ocean. The observed IO columns were up to three times higher and the range was larger than predicted by a global model, which warrants further investigation into iodine sources, sinks, ozone loss, and particle formation. IO mixing ratios increased with altitude. At the observed levels, iodine may be competitive with bromine as an oxidant of elemental mercury at cold temperatures typical of the free troposphere (4–12km; <260K). Iodine-induced mercury oxidation is missing in atmospheric models, understudied, and helps explain model underestimation of oxidized mercury measurements.

Plain Language Summary

Halogens such as chlorine, bromine, and iodine are highly reactive gases that participate in atmospheric chemistry, including ozone destruction, particle formation, modification of greenhouse gas lifetime (i.e. methane, dimethylsulfide), and the oxidation of elemental mercury. Iodine mainly enters the atmosphere from oceans; therefore, past measurements of atmospheric iodine have focused on marine and polar regions. This study describes the first lower atmospheric measurements of iodine monoxide (IO) radicals at a remote mountaintop site in the central continental United States. These measurements indicate that the concentration of IO radicals showed a large range over the course of one month and reached levels up to three times higher than predicted by a global atmospheric chemistry model. These observations suggest that our understanding of the iodine sources and sinks to the free troposphere may be incomplete. Moreover, we suggest that iodine's contribution to ozone destruction and mercury chemistry may be underestimated; in particular, iodine may be competitive with bromine in the oxidation of elemental mercury in the free troposphere.

1 Introduction

Atmospheric iodine destroys ozone (Read et al., 2008; Saiz-Lopez et al., 2012, 2014; Sherwen et al., 2017; Koenig et al., 2020, 2021), forms new particles (O'Dowd et al. 2002; Sipilä et al., 2016; Baccarini et al., 2020; He et al., 2021; Gómez Martín et al., 2022; Finkenzeller et al., 2023), and modifies atmospheric oxidative capacity (Sherwen et al., 2016a, 2016b). Iodine mainly enters the atmosphere in inorganic gaseous form (HOI, I_2) through reaction with ozone at the ocean surface (Carpenter et al., 2013; MacDonald et al., 2014; Wang et al., 2021), with smaller sources from organic iodine species (Bell et al, 2002; Sive et al., 2007; Jones et al., 2010; Ordóñez et al., 2012; Wang et al., 2021), windblown dust (Williams et al., 2007; Koenig et al., 2021), and volcanic eruptions (Schönhardt et al., 2017). Tree ring and ice core records indicate that atmospheric iodine has increased threefold since 1950, which is attributed to increased anthropogenic surface ozone pollution resulting in increased marine iodine emissions (Legrand et al., 2018; Cuevas et al., 2018; Zhao et al. 2019).

Most of our knowledge about the global distribution of atmospheric iodine is from measurements of iodine monoxide (IO) radicals in the marine boundary layer (Alicke et al., 1999; Allan et al., 2000; Whalley et al., 2007; Furneaux et al., 2010; Coburn et al., 2011;

Mahajan et al., 2012; Gómez Martín et al., 2013; Großmann et al., 2013; Prados-Roman et al., 2015; Inamdar et al., 2020; Takashima et al., 2022) and at high latitudes (Wittrock et al., 2000; Frieß et al., 2010; Mahajan et al., 2010; Schönhardt et al., 2012, 2017). Recent evidence of IO in the free troposphere is limited to measurements over oceans (Puentedura et al., 2012; Dix et al., 2013; Wang et al., 2015; Volkamer et al., 2015; Koenig et al., 2021). IO in the tropical transition layer (Volkamer et al., 2015) and lower stratosphere (Koenig et al., 2020) suggests that iodine is globally distributed. To our knowledge, there is no previous ground-based measurement of tropospheric IO over the continental United States. The only previous attempt to measure IO from the continental U.S. was by Wennberg et al. (1997), who measured IO slant column densities (SCDs) during three sunrises at Kitt Peak, Arizona, with a solar geometry that maximized sensitivity to stratospheric IO but minimized sensitivity to tropospheric IO; they did not attempt to quantify tropospheric IO. Therefore, tropospheric IO over the center of the continental U.S. is unconstrained by ground-based measurements.

Mountaintop Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) is well-suited for tropospheric IO measurements because it maximizes measurement sensitivity by minimizing aerosol scattering effects, provides access to the free troposphere due to the extended spatial scale (tens of kilometers) of the measurement light path, and enables cost-effective long-term measurements compared to airborne campaigns. Mountaintop MAX-DOAS has been successfully employed for IO measurements in the marine free troposphere (Puentedura et al., 2012).

The role of iodine radicals as oxidants of atmospheric mercury is understudied. Mercury enters the atmosphere mainly in gaseous elemental form, $Hg^0_{(g)}$, where it is oxidized into short-lived $Hg^I(X)_{(g)}$ species (X = Br, OH, Cl) and subsequently reacts with ozone or other secondary oxidants to form $Hg^{II}_{(g)}$ species (Dibble et al., 2020; Shah et al., 2021; Castro et al., 2022). The oxidation of $Hg^0_{(g)}$ by atmospheric iodine radicals has been deemed unimportant due to the low amounts of tropospheric iodine and the much faster thermal decomposition of $Hg^I(I)_{(g)}$ compared to $Hg^I(Br)_{(g)}$ (Goodsite et al., 2004; Shepler et al., 2005; Cremer et al., 2008). Accordingly, the latest implementation of atmospheric mercury chemistry in the GEOS-Chem model does not include reactions involving iodine (Shah et al., 2021). However, mercury measurements in aerosols are empirically correlated with iodine (Murphy et al., 2006). Additionally, the fast, barrierless reaction of Hg^I species with ozone (Saiz-Lopez et al., 2020) can compete with the thermal decomposition of $Hg^I(I)_{(g)}$, prompting us to re-evaluate the importance of iodine as an $Hg^0_{(g)}$ oxidant.

Here we present one month (April 1–30, 2022) of MAX-DOAS measurements of IO, H_2O, NO_2, and HCHO tropospheric vertical column densities (VCD_{trop}) and volume mixing ratios at instrument altitude (VMR_{instr}) alongside co-located in-situ measurements of $Hg^0_{(g)}$ and Hg^{II} at a remote mountaintop observatory in the central continental U.S. Section 2 describes the measurement site and methods. Section 3 presents the first ground-based observational constraint on tropospheric IO over the central continental U.S., explores correlations, and compares observations with a global model. Section 4 uses the observations to constrain a box model of gas-phase mercury chemistry to investigate the relevance of iodine radicals for $Hg^0_{(g)}$ oxidation and discusses atmospheric implications.

2 Methods

2.1 Storm Peak Laboratory

Storm Peak Laboratory (SPL) is a mountaintop observatory on top of the continental divide in the Rocky Mountains in northwestern Colorado (3220 m.a.s.l, 40.455°N, 106.745°W). SPL has been an atmospheric research station since the 1980's (Borys & Wetzel, 1997; Hallar et al., 2016) and has been previously used for atmospheric mercury measurements (Obrist et al., 2008; Fain et al., 2009). All measurements presented here were conducted at SPL from April 1–30, 2022.

2.1.1 CU MAX-DOAS

The University of Colorado MAX-DOAS (CU MAX-DOAS) instrument (Coburn et al., 2011, 2016) measured ultraviolet-visible scattered-light solar spectra at different elevation angles in a single azimuthal viewing direction. Trace gas differential slant column densities (dSCDs) were retrieved from solar spectra using the DOAS method (Platt & Stutz, 2008; Van Roozendael, 2021). A cloud-free zenith reference spectrum (Gielen et al., 2014; Wagner et al., 2014) on April 6, 2022 at 18:00 UTC was used for all DOAS retrievals; fit settings are in Tables S1 & S2. IO, H_2O, HCHO, and O_2-O_2 dSCDs were converted into SCDs by adding the trace gas SCD in the reference spectrum (SCD_{ref}); past studies have shown that accounting for SCD_{ref} maximizes sensitivity in the free troposphere (Hendrick et al., 2007; Coburn et al., 2016) and avoids bias in the retrieval of columns and profiles (Volkamer et al., 2015). For NO_2, the stratospheric signal was removed by subtracting the zenith dSCDs from the off-axis dSCDs. A linear optimal estimation algorithm (Rodgers, 2004) was used to retrieve IO, NO_2, H_2O, and HCHO VCD_{trop} and VMR_{instr} from the measured SCDs (zenith-subtracted dSCDs for NO_2). Instrument and retrieval details are in Text S1.

2.1.2 Dual-channel mercury system

A cation-exchange membrane-based dual-channel system to measure $Hg^0_{(g)}$ and Hg^{II} (Lyman et al., 2020; Elgiar et al., submitted) pulled sample air through a heated PTFE Teflon-coated inlet with an elutriator and particle impactor (2.5 µm cut point), 50 cm of heated PFA Teflon line, to two separate measurement channels. A Tekran 2537X Hg vapor analyzer sampled from each channel sequentially. One channel included a series of two in-series cation exchange-membranes that have been shown to pass $Hg^0_{(g)}$ and retain Hg^{II} (Miller et al., 2019); the other channel included a thermal converter that converted total atmospheric Hg to $Hg^0_{(g)}$. Hg^{II} was calculated as the difference between the two channels every ten minutes.. The dual-channel system had a 1-hour Hg^{II} detection limit less than 15 pg m^{-3}; total Hg and $Hg^0_{(g)}$ are assumed to be similar. A NIST-traceable permeation tube-based calibrator was used to add $Hg^0_{(g)}$ and $HgBr_2$ to the inlet of the dual-channel system while it sampled ambient air, and the system recovered 97±4% and 100±9%, respectively (mean ± standard deviation). The dual-channel system is described in detail in Elgiar et al. (submitted).

2.2 Model tools

2.2.1 GEOS-Chem

The GEOS-Chem 3-D atmospheric chemistry model was used to simulate (1) oxidant fields and (2) mercury chemistry as described in Shah et al. (2021). Details are in Text S2. April 2022 daytime averages of GEOS-Chem oxidant fields and Hg^0 were used to constrain the gas-phase mercury box model described in Section 2.2.3.

2.2.2 HYSPLIT-STILT

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model coupled to the Stochastic Time-Inverted Lagrangian Transport Model (STILT; Lin et al., 2003; Loughner et al., 2021) was used to simulate air mass origin at SPL. One thousand 24-hour back trajectories were initiated at each of multiple altitudes (5 m, 2 km, 4 km, 6 km, 10 km above ground level) at SPL every 3 hours from April 1–30, 2022. At each initial altitude, the one thousand back-trajectories were averaged in three dimensions (latitude, longitude, altitude) to calculate a single back trajectory every three hours (Figure 1). Details are in Text S4.

2.2.3 Mercury box model

The Framework for 0-D Atmospheric Modeling (F0AM; Wolfe et al, 2016) version 4.2.2 was used to simulate gas-phase mercury chemistry in 1 km layers from the surface at 2 km to 12 km. GEOS-Chem April 2022 daytime averages were used to constrain oxidant fields and Hg^0; iodine radicals were scaled to the average observed IO column (Text S3). The reaction mechanism used is based on Shah et al. (2021) with three significant differences; first, reactions involving I & IO were added analogously to reactions involving Br & BrO (Saiz-Lopez et al., 2018); second, the reaction coefficient used for $Hg^IX + O_3 \rightarrow Hg^{II}(X)(O) + O_2$ was the value for a barrierless reaction reported in Saiz-Lopez et al. (2020); third, only gas-phase reactions are treated here, as the goal is to examine the relative contributions of Br, OH, and I to $Hg^0_{(g)}$ oxidation rates. $Hg^{II}_{(g)}$ deposition and particle-phase partitioning is not the focus of this study and deemed independent of $Hg^{II}_{(g)}$ chemical identity (Shah et al., 2021). Sensitivity studies were performed varying the rate for $Hg^0 + I + M \rightarrow Hg^I(I) + M$, where a) $Hg^I(I)$ forms at the same rate as $Hg^I(Br)$ and b) $Hg^I(I)$ forms at the rate calculated by Goodsite et al. (2004). The bond strength of $Hg^I(I)$ is uncertain (Goodsite et al., 2004; Shepler et al., 2005; Cremer et al., 2008), and sensitivity studies were performed varying the decomposition rate for $Hg^I(I) + M \rightarrow Hg^0 + I + M$, where a) $Hg^I(I)$ dissociates at the same rate as $Hg^I(OH)$, b) 10 times faster, and c) 100 times faster. Box model output was extracted at fifteen minutes, after gas-phase equilibrium was reached (Figure S3). The complete reaction mechanism is in Tables S5 and S6.

2.2.4 Radiative transfer model

The 3D Monte Carlo Atmospheric Radiative Transfer Inversion Model (McArtim3; Deutschmann et al., 2011) was used to calculate weighting functions for trace gas profile inversions. Model settings are in Table S2. Weighting functions were calculated in a Rayleigh atmosphere using April 2022 average daytime temperature and pressure profiles from ECMWF CAMS reanalysis (Inness et al., 2019) and empirically scaled to match the measured O_2-O_2 SCD for each spectrum. This approach uses the known O_2-O_2 vertical profile to account for the effects of terrain and temporal atmospheric state variability (temperature, pressure, weak aerosols) on the measured photon path distribution (Spinei et al., 2015; Ortega et al., 2016; Wagner et al., 2019; Tirpitz et al., 2021; see Text S1).

3 Results

Here, IO observations are described, compared with GEOS-Chem simulations, and examined alongside co-located observations of air mass tracers for atmospheric dynamics (H_2O), pollution (NO_2), total oxidative capacity (HCHO), and mercury oxidation ($Hg^0_{(g)}$, Hg^{II}). Pearson correlation coefficients (R) of less than 0.20 are referred to as having no correlation; R is reported alongside its standard error. Averages are reported alongside standard deviations.

3.1 Detection of IO in the continental free troposphere

IO concentrations above the detection limit were consistently observed throughout the month; spectral proofs are shown in Figure 1. On April 16, the day with the highest IO signal, IO dSCDs of up to $(2.2\pm0.4)\times10^{13}$ and $(1.6\pm0.1)\times10^{13}$ molec cm^{-2} were observed in the limb (EA=0°) and zenith (EA=90°) geometries, respectively. On April 6, the day with the lowest IO signal, IO dSCDs of up to $(1.4\pm0.4)\times10^{13}$ and $(0.6\pm0.1)\times10^{13}$ molec cm^{-2} were observed in the limb and zenith geometries, respectively.

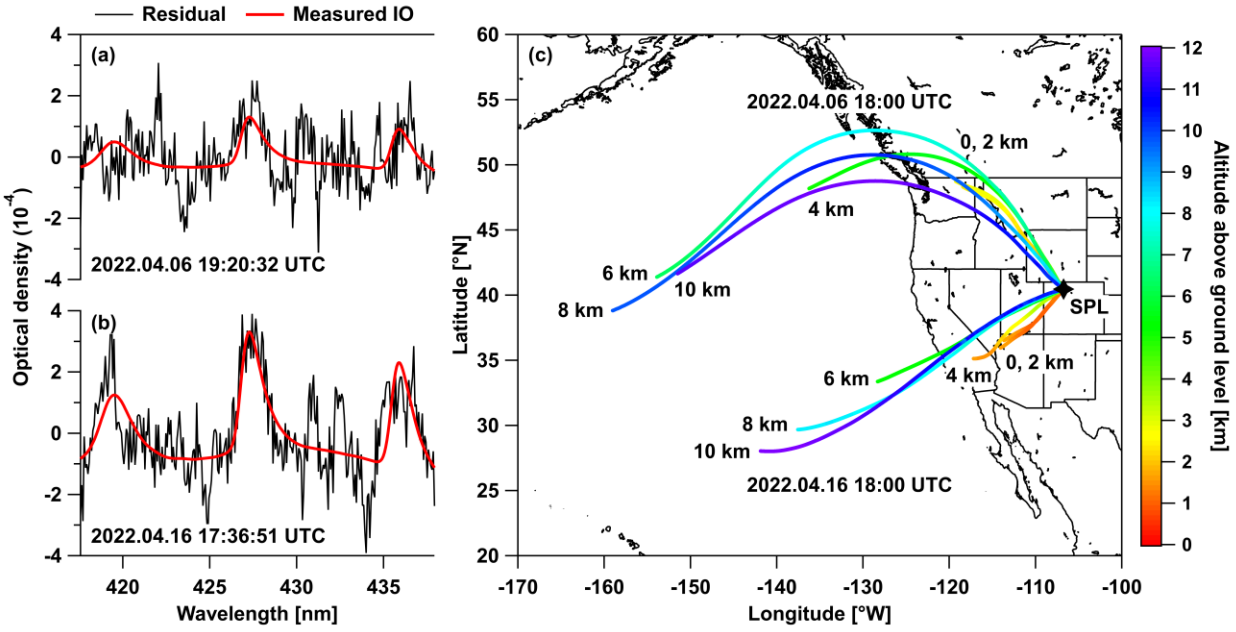

Figure 1. Detection of IO radicals above Storm Peak Laboratory during April 2022. (a) IO spectral proof for a "low IO" case on April 6 at 19:20:32 UTC corresponding to $(0.6\pm0.1)\times10^{13}$ molec cm^{-2} IO dSCD. (b) IO spectral proof for a "high IO" case on April 16 at 17:36:51 UTC corresponding to $(1.6\pm0.1)\times10^{13}$ molec cm^{-2} IO dSCD. (c) Average STILT 24-hour back trajectories for April 6 at 18:00 UTC and April 16 at 18:00 UTC.

Sensitivity studies varying the a priori profile used for the IO column retrieval indicate that IO VMR increased with altitude. Two a priori profiles were tested: a "flat" profile with a constant 0.10 pptv IO throughout the atmosphere, and the GEOS-Chem April 2022 daytime average IO profile. The GEOS-Chem profile, in which IO VMR increases with altitude, consistently resulted in better agreement between measured and a posteriori simulated IO SCDs than the "flat" profile (Figure S2). Therefore, the GEOS-Chem profile was used in the IO retrieval as it is more physically representative of the measurements.

IO VCD_{trop} (VMR_{instr}) was 0.7–3.6×10^{12} molec cm^{-2} (0.00–0.16 pptv), averaging (1.9±0.6)×10^{12} molec cm^{-2} (0.08±0.03 pptv). IO VCD_{trop} (IO VMR_{instr}) error is 0.5×10^{12} molec cm^{-2} (0.03 pptv), with contributions from choice of a priori settings (0.3×10^{12} molec cm^{-2}; 0.01 pptv), uncertainty in SCD_{ref} (0.1×10^{12} molec cm^{-2}; <0.01 pptv), and method error (spectral fitting, radiative transfer modeling, optimal estimation; 0.1×10^{12} molec cm^{-2}; 0.02 pptv). Uncertainty in the IO absorption cross section is 2%, and negligible (Spietz et al., 2005).

24-hour STILT back trajectories indicated that the observed air masses consistently originated from over the Pacific Ocean. The air mass observed during the day with the highest IO signal (April 16) originated from the southwest, towards the tropics (Figure 1c). The air mass observed during the day with the lowest IO signal (April 6) originated from the northwest, towards mid-latitudes. However, not all tropical air masses contained higher IO; on April 28, for example, the back-trajectories indicated an air mass originating even further south than on April 16, yet the IO VCD was significantly larger on April 16 than on April 28. While air mass origin alone cannot account for the observed IO variability, we consistently found higher IO in air masses with less than 24-hour transport time from the Pacific Ocean. This indicated that IO variability also depended on the strength of IO sinks along the transport path, which are not constrained in our analysis.

IO VCD_{trop} and VMR_{instr} were up to three times larger, and the range of IO VCD_{trop} and VMR_{instr} was larger than predicted by GEOS-Chem (Figure 2). GEOS-Chem daytime IO VCD_{trop} (VMR_{instr}) was 0.3–1.5×10^{12} molec cm^{-2} (0.0007–0.10 pptv), averaging 0.8±0.2×10^{12} molec cm^{-2} (0.04±0.02 pptv), two times smaller than observed. There was no correlation between measured and modeled IO VCD_{trop}. There was a very weak but statistically significant anti-correlation between measured and modeled IO VMR_{instr} (R: -0.20±0.05; $p<1\times10^{-4}$). The two days with the lowest IO VCD_{trop}, April 6 and 26, showed reasonable agreement with GEOS-Chem. However, on all other days, IO VCD_{trop} was significantly larger than predicted. The GEOS-Chem horizontal grid cell size (0.5°×0.625°) is comparable to the tens of kilometers sampled by the MAX-DOAS light path. The similar magnitude of underestimation of IO VCD_{trop} and VMR_{instr} by GEOS-Chem provides evidence that IO VMR increased with altitude, since GEOS-Chem consistently simulated increasing IO VMR with altitude. One would expect the GEOS-Chem underestimation to be different between IO VCD_{trop} and VMR_{instr} if the measured profile shape was very different than modeled.

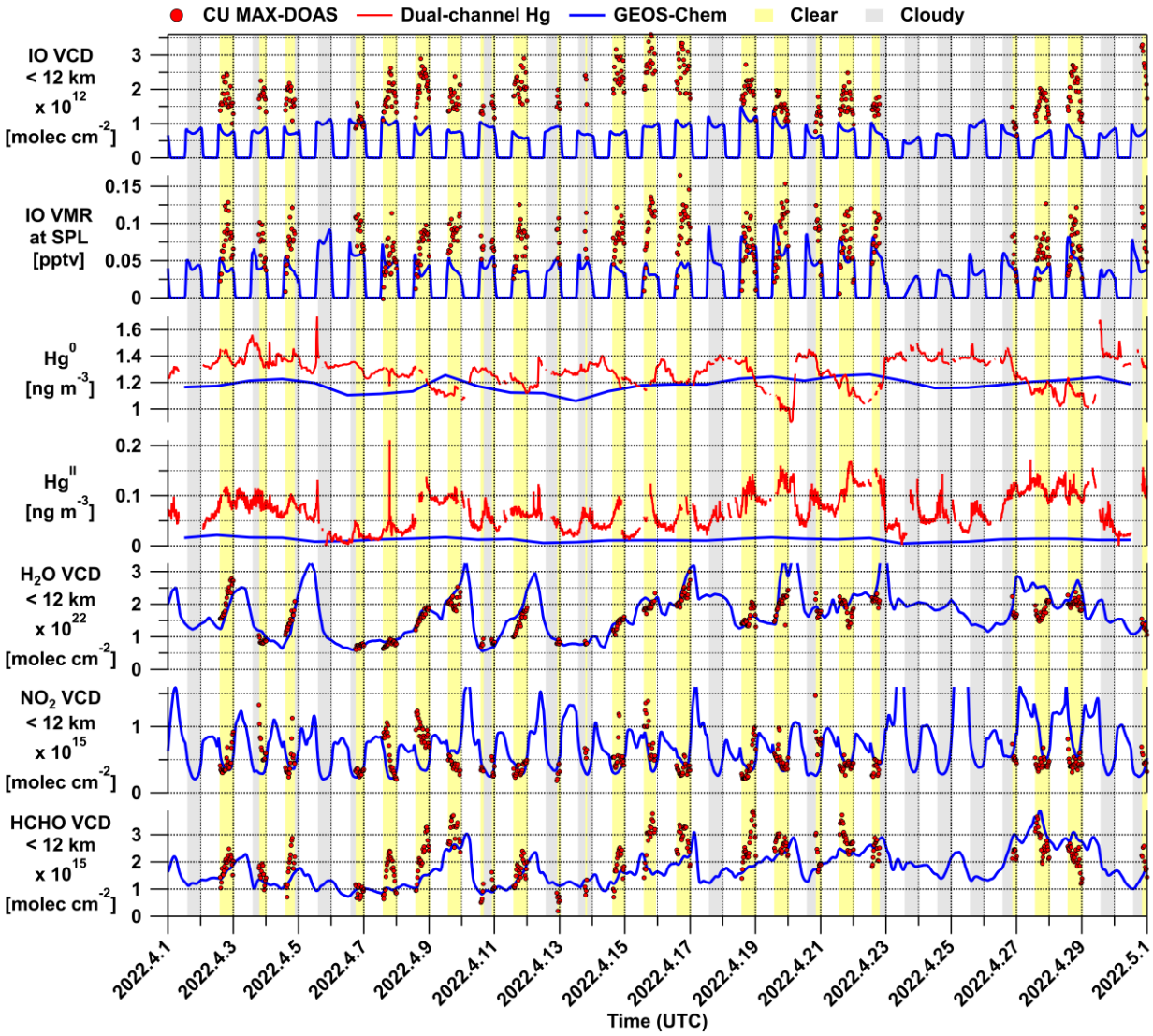

Figure 2. Measurements of IO, Hg^0, Hg^{II}, H_2O, NO_2, and HCHO at Storm Peak Laboratory are compared with GEOS-Chem during April 2022.

3.2 Measurements of other gases at SPL

During April 1–30, 2022 at SPL, GEOS-Chem very accurately simulated both H_2O magnitude and temporal variability; very accurately simulated NO_2 magnitude but failed to simulate NO_2 temporal variability; and accurately simulated HCHO magnitude but had only moderate success in simulating HCHO temporal variability.

3.2.1 H_2O

H_2O VCD_{trop} (VMR_{instr}) was 0.6–3.0×10^{22} molec cm^{-2} (0.4–2.8‰), averaging 1.6±0.5×10^{22} molec cm^{-2} (1.5±0.5 ‰). Total error for H_2O VCD_{trop} (VMR_{instr}) is 0.2×10^{22} molec cm^{-2} (0.1‰). There was no correlation between H_2O VCD_{trop} and IO VCD_{trop}, and a weak correlation between H_2O VMR_{instr} and IO VMR_{instr} (R: 0.35±0.05; $p<1\times10^{-5}$).

GEOS-Chem daytime H_2O VCD_{trop} (VMR_{instr}) is from the MERRA-2 reanalysis and was 0.6–3.8×10^{22} molec cm^{-2} (0.7–6.8‰), averaging 1.7±0.7×10^{22} molec cm^{-2} (3.1±1.2 ‰). The measured and modeled H_2O VCD_{trop} variations were strongly correlated (R: 0.76±0.03; $p<1\times10^{-5}$) and agreed well (Figure 2), indicating model skill in simulating atmospheric H_2O column variability due to passing frontal systems, consistent with earlier observations (Bosilovich et al. 2017). This agreement corroborates control over radiative transfer in the column retrieval method that applies to all trace gas columns presented here.

3.2.2 NO_2

NO_2 VCD_{trop} (VMR_{instr}) was 0.2–1.5×10^{15} molec cm^{-2} (0.01–0.26 ppbv), averaging 0.5±0.2×10^{15} molec cm^{-2} (0.08±0.05 ppbv). Total error for NO_2 VCD_{trop} (VMR_{instr}) is 0.4×10^{15} molec cm^{-2} (0.01 ppbv). There was no correlation between the NO_2 VCD_{trop} and IO VCD_{trop} or between NO_2 VMR_{instr} and IO VMR_{instr}, which is expected due to different sources.

GEOS-Chem daytime NO_2 VCD_{trop} (VMR_{instr}) was 0.2–1.6×10^{15} molec cm^{-2} (0.01–0.24 ppbv), averaging 0.5±0.2×10^{15} molec cm^{-2} (0.07±0.03 ppbv). GEOS-Chem struggled to accurately simulate tropospheric NO_2 at SPL; this is consistent with previously observed model-measurement disagreement in tropospheric NO_2 (Shah et al., 2023). While the range and average for the columns and concentrations closely agree with those observed, there was no correlation between measured and modeled NO_2 VCD_{trop} or VMR_{instr}.

3.2.3 HCHO

HCHO VCD_{trop} (VMR_{instr}) was 0.2–3.9×10^{15} molec cm^{-2} (-0.02–0.67 ppbv), averaging 2.2±0.8×10^{15} molec cm^{-2} (0.36±0.15 ppbv). Total error for HCHO VCD_{trop} (VMR_{instr}) is 0.2×10^{15} molec cm^{-2} (0.03 ppbv). There was no correlation between HCHO VCD_{trop} and IO VCD_{trop}, and a weak correlation between HCHO VMR_{instr} and IO VMR_{instr} (R: 0.31±0.05; $p<1\times10^{-5}$).

GEOS-Chem daytime HCHO VCD_{trop} (VMR_{instr}) was 0.7–3.9×10^{15} molec cm^{-2} (0.0–0.7 ppbv), averaging 1.7±0.6×10^{15} molec cm^{-2} (0.3±0.1 ppbv). The observed HCHO was systematically higher than predicted. The correlation between measured and modeled HCHO VCD_{trop} was moderate (R: 0.57±0.04; $p<1\times10^{-5}$), and a strong correlation was found between measured and modeled HCHO VMR_{instr} (R: 0.66±0.04; $p<1\times10^{-5}$). Overall, the range and average for HCHO VCD_{trop} and VMR_{instr} agree closely with those observed, and the model had better skill in predicting HCHO variability than NO_2 or IO variability at SPL.

3.2.4 BrO

A measurement constraint on bromine was not possible during the study period. The amount of tropospheric BrO observed at SPL was consistently below the detection limit of ~0.5 pptv VMR_{instr}. The GEOS-Chem April 2022 daytime average BrO VMR_{instr} at SPL was 0.15 pptv, consistent with the observations and too low to be observable even with the state-of-the-art MAX-DOAS instrument used here. We therefore used the GEOS-Chem BrO profile without modifications to constrain the mercury box model.

3.3 Mercury

$Hg^0_{(g)}$ (Hg^{II}) was 0.90–1.70 ng m^{-3} (0–211 pg m^{-3}), averaging 1.28±0.11 ng m^{-3} (68±34 pg m^{-3}). Interestingly, there was a weak anti-correlation between $Hg^0_{(g)}$ and HCHO VMR_{instr} (R: -0.35±0.05; $p<1\times10^{-5}$), and a moderately strong correlation between Hg^{II} and HCHO VMR_{instr}

(R: 0.64±0.04; $p<1\times10^{-5}$), indicating a possible connection between mercury oxidation and total atmospheric oxidative capacity.

Oxidized mercury at SPL coincided with warm air masses at low relative humidity, consistent with past work (Fain et al., 2009), but also at high absolute humidity. There was a weak anti-correlation between $Hg^0_{(g)}$ and measured temperature (R: -0.37±0.02; $p<1\times10^{-5}$), a strong correlation between Hg^{II} and measured temperature (R: 0.70±0.01; $p<1\times10^{-5}$), a weak correlation between $Hg^0_{(g)}$ and measured relative humidity (R: 0.39±0.02; $p<1\times10^{-5}$), a moderate anti-correlation between Hg^{II} and measured relative humidity (R: -0.43±0.01; $p<1\times10^{-5}$), and a weak correlation between Hg^{II} and H_2O VMR_{instr} (R: 0.37±0.04; $p<1\times10^{-5}$). This is consistent with the idea that mercury survives longer in air masses with less wet deposition, providing more time for oxidation to occur.

GEOS-Chem $Hg^0_{(g)}$ (Hg^{II}) was 1.06–1.26 ng m^{-3} (4–22 pg m^{-3}), averaging 1.18±0.05 ng m^{-3} (12±4 pg m^{-3}). While measured and modeled Hg^0 concentrations agreed reasonably well, there was no correlation in Hg^0 temporal variability. Moreover, the measured Hg^{II} concentration was up to ten times larger and more variable (i.e., a six times larger standard deviation) than modeled (Figure 2). Despite these differences, measured and modeled Hg^{II} were moderately correlated (R: 0.47±0.01; $p<1\times10^{-5}$), indicating that GEOS-Chem had some skill in predicting Hg^{II} variability at SPL but not the magnitude. Increased Hg^{II} sources (i.e., iodine-induced oxidation) and/or decreased Hg^{II} sinks in the model are needed to explain this model-measurement disagreement.

4 Discussion

4.1 Literature comparison

The observed IO VCD_{trop} monthly average of $1.9\pm0.6\times10^{12}$ molec cm^{-2} over the central continental U.S. is consistent with the few previous airborne measurements. Dix et al. (2013) reported an IO VCD_{trop} of 2.49 to 2.91×10^{12} molec cm^{-2} over the central Pacific and Volkamer et al. (2015) found 2.1 to 2.5×10^{12} molec cm^{-2} over the eastern Pacific; both studies probed tropical air in the northern hemisphere winter. The average IO VCD_{trop} above SPL demonstrates that iodine is widespread in the free troposphere, including over continents.

The significant day-to-day temporal variability in IO VCD_{trop} over the central continental U.S. (0.7±0.5 to $3.6\pm0.5\times10^{12}$ molec cm^{-2}) has not been previously observed. Our measurements also characterize IO VCD_{trop} for the first time in the spring. Information about iodine spatiotemporal variability in the free troposphere is extremely scarce. Two sources affecting free tropospheric IO variability are marine convection (Dix et al., 2013) and dust (Puentedura et al., 2012; Koenig et al., 2021). Regional-scale IO variability over the Eastern Pacific Ocean was systematically probed by Wang et al. (2015), who reported IO VCD_{trop} of 2.6 to 3.5×10^{12} molec cm^{-2} and 5.1×10^{12} molec cm^{-2} in the southern hemisphere tropical and subtropical Pacific, respectively, during Austral summer. Some of this variability could be attributed to dust sources of iodine from the Sechura and Atacama deserts (Koenig et al., 2021), with regional impacts on ozone in the marine boundary layer and free troposphere. Puentedura et al. (2012) reported variability in IO dSCDs related to Saharan dust impacts in the free troposphere over Tenerife Island in the Eastern Atlantic; they did not attempt to retrieve IO VCD_{trop}. Elevated IO VCD_{trop} over SPL is related to rapid transport from the Pacific Ocean, consistent with marine convection upwind, and unrelated to immediate dust impacts.

Schönhardt et al. (2008) reported global satellite measurements of IO SCDs. Their analysis used a reference spectrum over the tropical Pacific, where airborne measurements indicate that there is a significant IO VCD_{trop} (Dix et al., 2013; Volkamer et al., 2015). Therefore, the satellite IO SCDs are lower limits and not directly comparable to our measurements.

4.2 Ozone relevance

Iodine is responsible for a ~9% reduction in the total tropospheric ozone burden, and model-measurement agreement for IO profiles over the eastern tropical Pacific indicates that marine sources for IO are reasonably well-constrained (Wang et al., 2021). The consistent low bias in modeled IO compared to our observations suggests that iodine's contribution to tropospheric ozone destruction may be higher than currently estimated over continents. In particular, GEOS-Chem iodine chemistry has not been significantly updated since version 11-02-rc, with the implementation of Wang et al. (2021) in version 12.9 leaving the mechanism of Sherwen et al. (2016b) largely unchanged.

4.3 Implications for atmospheric mercury oxidation

Iodine oxidation of mercury is deemed unimportant, and is therefore missing in atmospheric models, in part due to the lower Hg-I bond strength (8.3–10.9 kcal mol^{-1}) compared to Hg-Br (14.4–17.9 kcal mol^{-1}) and Hg-OH (9.4–12.4 kcal mol^{-1}) (Goodsite et al., 2004; Shepler et al., 2005; Cremer et al., 2008; Dibble et al., 2020). The Hg-OH bond strength was previously thought to be too weak to lead to Hg^{II} formation, but the discovery that the reaction of Hg^{I} species with ozone is kinetically barrierless (Saiz-Lopez et al., 2020) has resulted in a re-evaluation of the global relevance of OH radicals to $Hg^{0}_{(g)}$ oxidation (Shah et al., 2021; Castro et al., 2022; Hewa Edirappulige et al., 2023). There is evidence suggesting that the reaction of $Hg^{0}_{(g)}$ with I atom proceeds faster than with Br atom (Goodsite et al., 2004). In light of the larger than predicted amounts of tropospheric iodine over continents, the Hg-I bond strength and $Hg^{I}(I)_{(g)}$ dissociation rate warrant re-evaluation.

Our box model results (Figure 3) show that I atoms may oxidize Hg^{0} at rates rivaling Br atoms at cold temperatures typical of the free troposphere (4–12 km; <260K). Above 9 km, this finding is independent of the assumed Hg-I bond strength, as $Hg^{I}(I)_{(g)}$ dissociation is slow at cold temperatures. Below 9 km, iodine-induced Hg oxidation may rival Br depending on the assumed Hg-I bond strength, which is highly uncertain. Our most conservative estimate, which uses the Hg+Br kinetics measured by Donohoue et al. (2006) for the Hg+I reaction and assumes that $Hg^{I}(I)$ dissociates 100 times faster than $Hg^{I}(OH)$, places iodine atoms at a contribution of 1.2%–42.1% to $Hg^{II}_{(g)}$ formation below 12 km (Br: 17.4–68.3%; OH: 7.6–81.1%; Cl: <0.5%). Our least conservative estimate, which uses the bimolecular rate constant calculated by Goodsite et al. (2004) for the Hg+I reaction and assumes that $Hg^{I}(I)$ dissociates at the same rate as $Hg^{I}(OH)$, places iodine atoms at a contribution of 40.1–78.7% to $Hg^{II}_{(g)}$ formation below 12 km (Br: 12.4–46.9%; OH: 6.4–57.8%; Cl: <0.5%). These results are consistent with the observed correlation between mercury and iodine in aerosols in the lower stratosphere (Murphy et al., 2006), and suggest these correlations might have a mechanistic causal relationship. The inclusion of iodine radical oxidation of $Hg^{0}_{(g)}$ to Hg^{II} in atmospheric models is desirable and will benefit from better knowledge of the chemical kinetics, from laboratory experiments and calculations, and better constraints on the tropospheric iodine distribution.

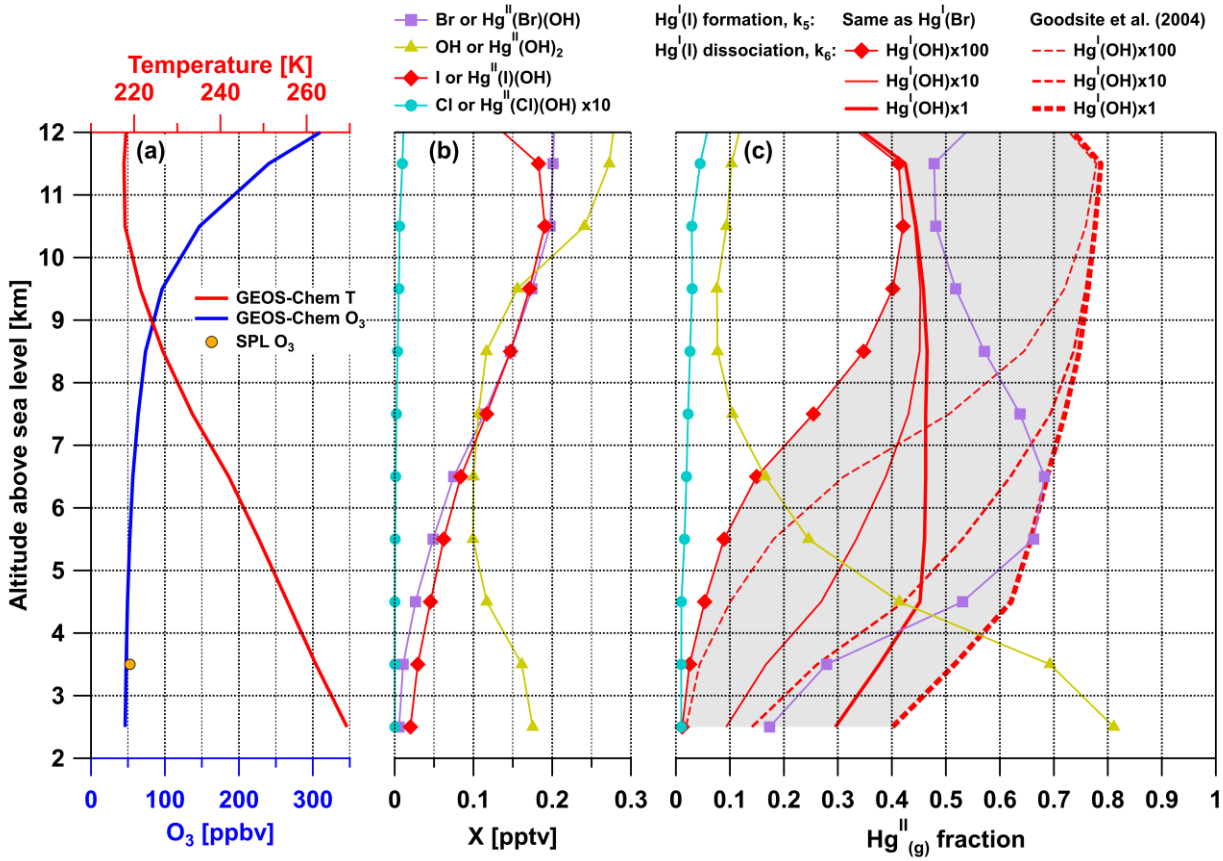

Figure 3. Iodine-initiated Hg^0 oxidation compared with other radical pathways above Storm Peak Laboratory. Iodine appears to be a competitive oxidant throughout the troposphere and becomes more relevant at colder temperatures in the upper free troposphere. See Section 2.2.3, Section 4.3, Text S3, Table S5, and Table S6 for details.

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Data availability statement

All CU MAX-DOAS and dual-channel mercury system measurement data at Storm Peak Laboratory during April 2022 (measured and GEOS-Chem simulated trace gas SCD, VCD_{trop},

VMR_{instr}; measured and GEOS-Chem simulated Hg^0 & Hg^{II}) as well as the gas-phase mercury chemical box model constraints & output described in this study are publicly available at zenodo via https://zenodo.org/doi/10.5281/zenodo.10805549 with a Creative Commons Attribution 4.0 license. The HYSPLIT-STILT back trajectory simulations at Storm Peak Laboratory during April 2022 described in this study are publicly available at zenodo via https://doi.org/10.5281/zenodo.10806478 with a Creative Commons Attribution 4.0 license. The long-term measurements of Hg^0, Hg^{II}, trace gases, and meteorology at Storm Peak Laboratory, a subset of which are used in this study, are publicly available at zenodo via https://doi.org/10.5281/zenodo.10699270 with a Creative Commons Attribution 4.0 license. Version 13.2.1 of the GEOS-Chem model was used to simulate atmospheric oxidant fields, is preserved at https://doi.org/10.5281/zenodo.5500717, is available via an MIT license, and is developed openly at https://github.com/geoschem/GCClassic/tree/13.2.1. Version 12.8.0 of the GEOS-Chem model was used to simulate atmospheric mercury chemistry, is preserved at https://doi.org/10.5281/zenodo.3784796, is available via an MIT license, and is developed openly at https://github.com/geoschem/geos-chem/tree/12.8.0. Version 3.4.5 of the QDOAS spectral analysis software developed by the DOAS UV-VIS team at the Royal Belgian Institute for Space Aeronomy (BIRA-IASB) was used for all DOAS spectral analysis, is available via a BSD 3-clause type license, and is developed openly at https://github.com/UVVIS-BIRA-IASB/qdoas. Version 8.0.4.2 of the IGOR Pro software developed by WaveMetrics, Inc. was used for data analysis and is available via a commercial license at https://www.wavemetrics.com/products/igorpro. Vector map data of coastlines and state borders used in Panel (c) of Figure 1 are available at Natural Earth via https://www.naturalearthdata.com/ with a public domain license.

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