Detection of IO radicals over the continental U.S.: Implications for gaseous mercury oxidation from the troposphere into the stratosphere

Christopher F. Lee[1,2], Margarita Reza[1,2], Kyle Zarzana[1], Tyler Elgiar[3], Liji David[4], Seth Lyman[3], Lynne Gratz[5], Noah Hirshorn[6], Ian McCubbin[6], Gannet Hallar[6], Alessandro Franchin[7], Teresa Campos[7], Florian Obersteiner[8], Andreas Zahn[8], Cory Wolff[7], NSF/NCAR GV Team[7], and Rainer Volkamer[1,2]

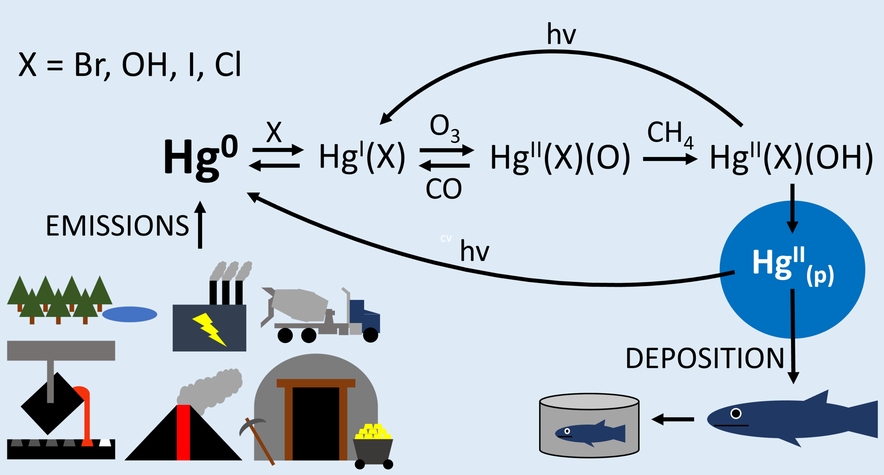
[1]Department of Chemistry, University of Colorado Boulder, Boulder, CO; [2]Cooperative Institute for Research in Environmental Sciences, Boulder, CO; [3]Department of Chemistry & Biochemistry, Utah State University, Logan, UT; [4]Bingham Research Center, Utah State University, Vernal, UT; [5]Environmental Program, Colorado College, Colorado Springs, UT; [6]Department of Atmospheric Sciences, University of Utah, Salt Lake City, UT; [7]National Center for Atmospheric Research, Boulder, CO; [8]Karlsruhe Institute of Technology, Karlsruhe, Germany
Contact: christopher.f.lee@colorado.edu, rainer.volkamer@colorado.edu

Introduction

Mercury is a neurotoxin and pollutant emitted to the atmosphere in gaseous elemental form (Hg^0) from both natural (5207 Mg yr^{-1}) and anthropogenic sources (2320 Mg yr^{-1})[1].

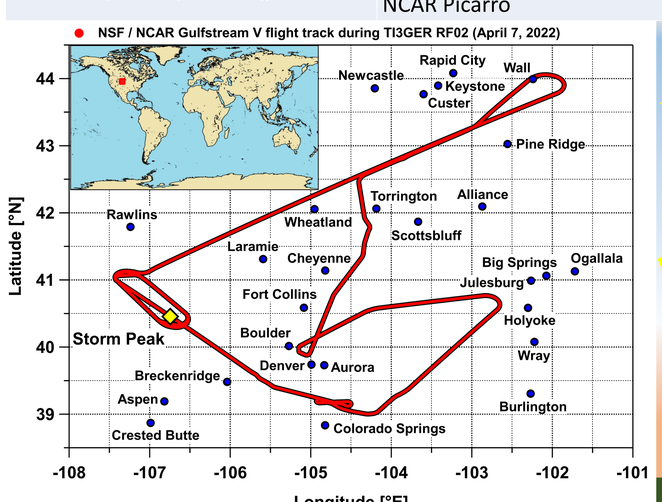
In the most recent GEOS-Chem implementation of global atmospheric mercury chemistry[2], bromine (Br) and hydroxyl radical (OH) equally contribute to the oxidation of gaseous Hg^0 to Hg^I. Short-lived gaseous Hg^I species undergo sequential oxidation by ozone (O_3) and methane (CH_4) to form stable gaseous Hg^{II} species, which partition to the particle phase.

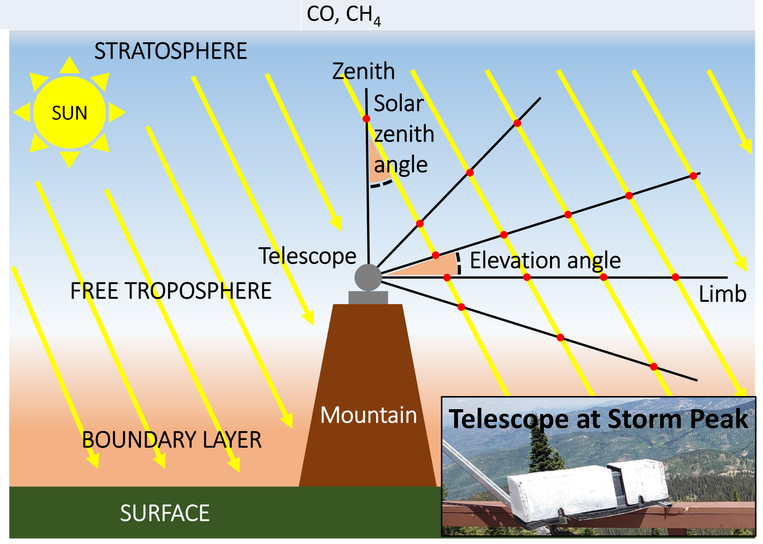
Outside of polar regions, the role of iodine (I) as an oxidant of Hg^0 to Hg^I has been disregarded due to its relatively low atmospheric concentrations and the fast thermal decomposition of the Hg-I bond. This study revisits iodine as an oxidant of Hg^0 to Hg^I in light of recent observations of iodine over the continental U.S.



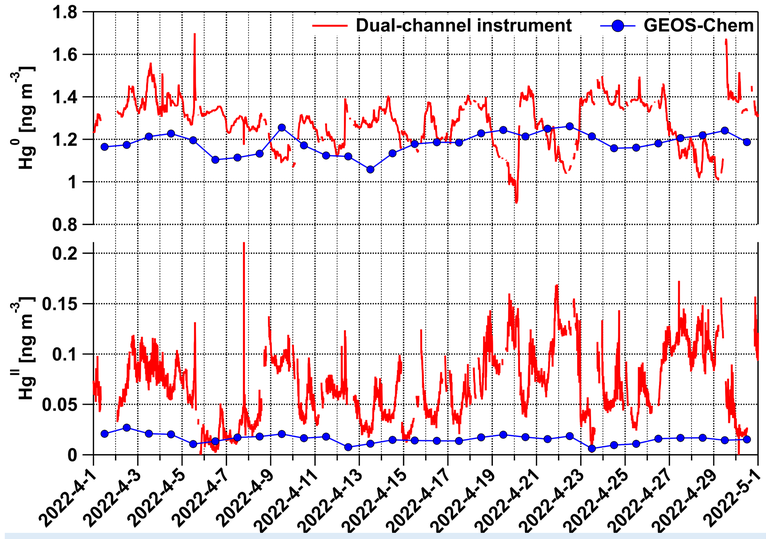
Methods

Platform	Instrument	Gas-phase species measured
Storm Peak Laboratory (SPL), CO 40.455 °N, 106.744 °W 3209 masl	University of Colorado Multi-AXis Differential Optical Absorption Spectroscopy (CU MAX-DOAS)[3]	IO, BrO, NO_2, O_3, HCHO, CHOCHO, H_2O, O_2-O_2
	Dual-channel mercury instrument[4]	Hg^0, Hg^{II}
NSF/NCAR Gulfstream V Technological Innovation Into Iodine and GV-Aircraft Environmental Research (TI^3GER) campaign	University of Colorado Airborne MAX-DOAS[5]	IO, BrO, NO_2, O_3, HCHO, CHOCHO, H_2O, O_2-O_2
	NCAR fast chemiluminescence	NO, NO_2, NO_y, O_3
	KIT FAIRO	O_3
	NCAR Picarro	CO, CH_4



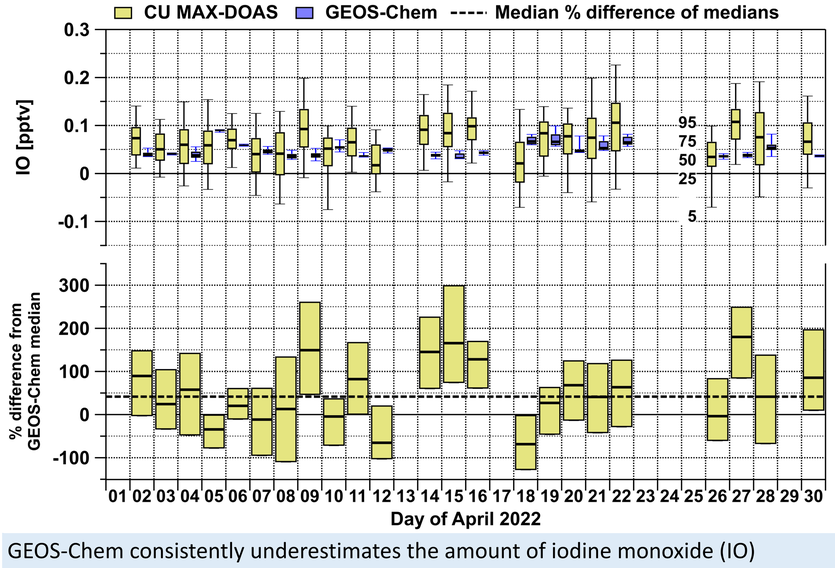


April 2022 Hg^0 & Hg^{II} measurements at SPL



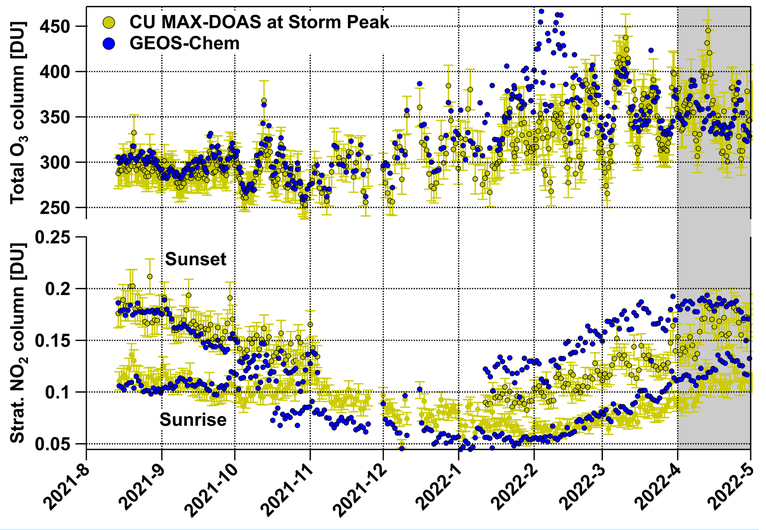
GEOS-Chem consistently underestimates the amount of gaseous oxidized mercury measured at Storm Peak Laboratory.

April 2022 IO measurements at SPL



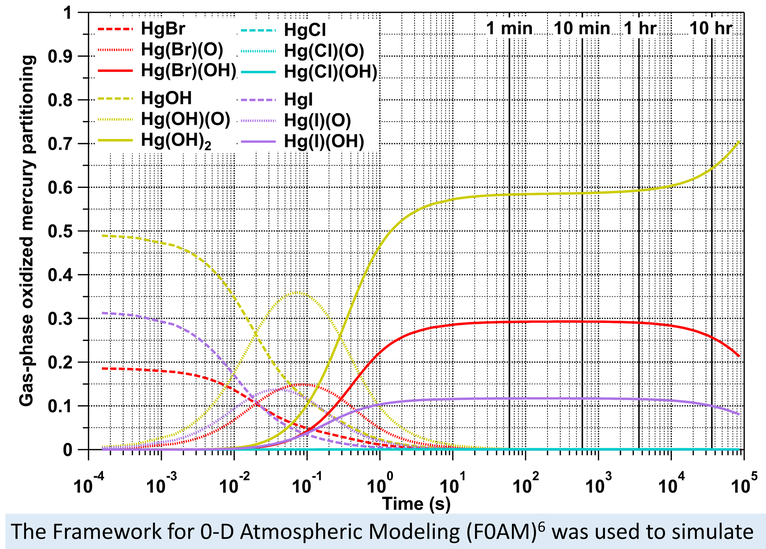
GEOS-Chem consistently underestimates the amount of iodine monoxide (IO) radicals measured at Storm Peak Laboratory.

Long-term stratospheric observations at SPL



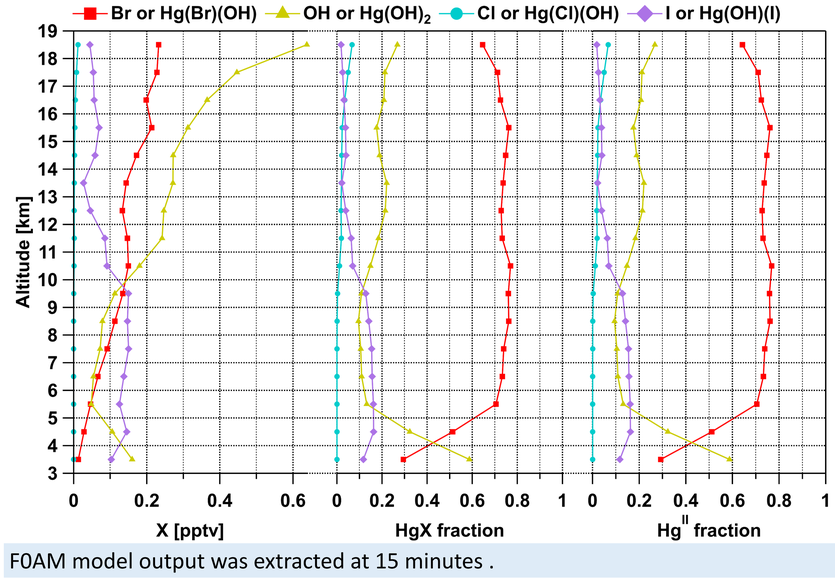
CU MAX-DOAS measurements of the total O_3 and stratospheric NO_2 columns capture long-term stratospheric variability above Storm Peak Laboratory.

Time evolution of gas-phase Hg partitioning at SPL



The Framework for 0-D Atmospheric Modeling (F0AM)[6] was used to simulate atmospheric mercury chemistry at SPL, as constrained by a combination of measurements and GEOS-Chem model output.

Profile of gas-phase Hg^I & Hg^{II} partitioning above SPL



F0AM model output was extracted at 15 minutes .

Conclusions

- Measurements of iodine monoxide (IO) radicals at Storm Peak Laboratory indicate higher levels of iodine than predicted by GEOS-Chem.
- Ours are the first measurements of IO in the lower free troposphere over the continental U.S., far from marine sources.
- Iodine oxidation of Hg^0 to Hg^I adds a minor yet non-negligible pathway for mercury oxidation that is currently missing in atmospheric models.
- Iodine reduces the consistent underestimation of oxidized mercury measurements by GEOS-Chem in the middle of the continental U.S.

References & Acknowledgements

(1) Pirrone et al. (2010) - doi:10.5194/acp-10-5951-2010
(2) Shah et al. (2021) - doi:10.1021/acs.est.1c03160
(3) Coburn et al. (2011) - doi:10.5194/amt-4-2421-2011
(4) Lyman et al. (2020) - doi.org:10.1021/acs.est.0c02747
(5) Baidar et al. (2013) - doi:10.5194/amt-6-719-2013
(6) Wolfe et al. (2016) - doi:10.5194/gmd-9-3309-2016

Measurements at Storm Peak Laboratory were funded by U.S. NSF awards AGS-1951513/1951514/1951515/1951632. The TI3GER project is funded by NSF award AGS-2027252.