Remote Tropical Island Mountaintop Measurements of Halogen Radicals

Theodore K. Koenig[1,2,†], Barbara Dix[1], Jérôme Brioude[3,4], Jean-Pierre Cammas[4], Winston Luke[5], Rainer Volkamer[1,2,*], and the TORERO and CONTRAST Science teams

[1]Dep. of Chemistry & Biochemistry, University of Colorado, Boulder, CO; [2]CIRES, University of Colorado, Boulder, CO; [3]University of La Réunion, St. Denis, France; [4]LACy, OSU-Réunion, St. Denis, France; [5]Air Resources Laboratory, NOAA, College Park, MD

† Theodore.Koenig@colorado.edu; *Rainer.Volkamer@colorado.edu

University of Colorado Boulder

http://ciresgroups.colorado.edu/volkamergroup

CIRES COOPERATIVE INSTITUTE FOR RESEARCH IN ENVIRONMENTAL SCIENCES

- Introduction -

Remote tropical island mountaintops offer access to the remote tropical free troposphere. The tropical free troposphere is important for regional and global transport, zonally and between the surface and stratosphere. Halogen chemistry plays an important role in this remote environment.

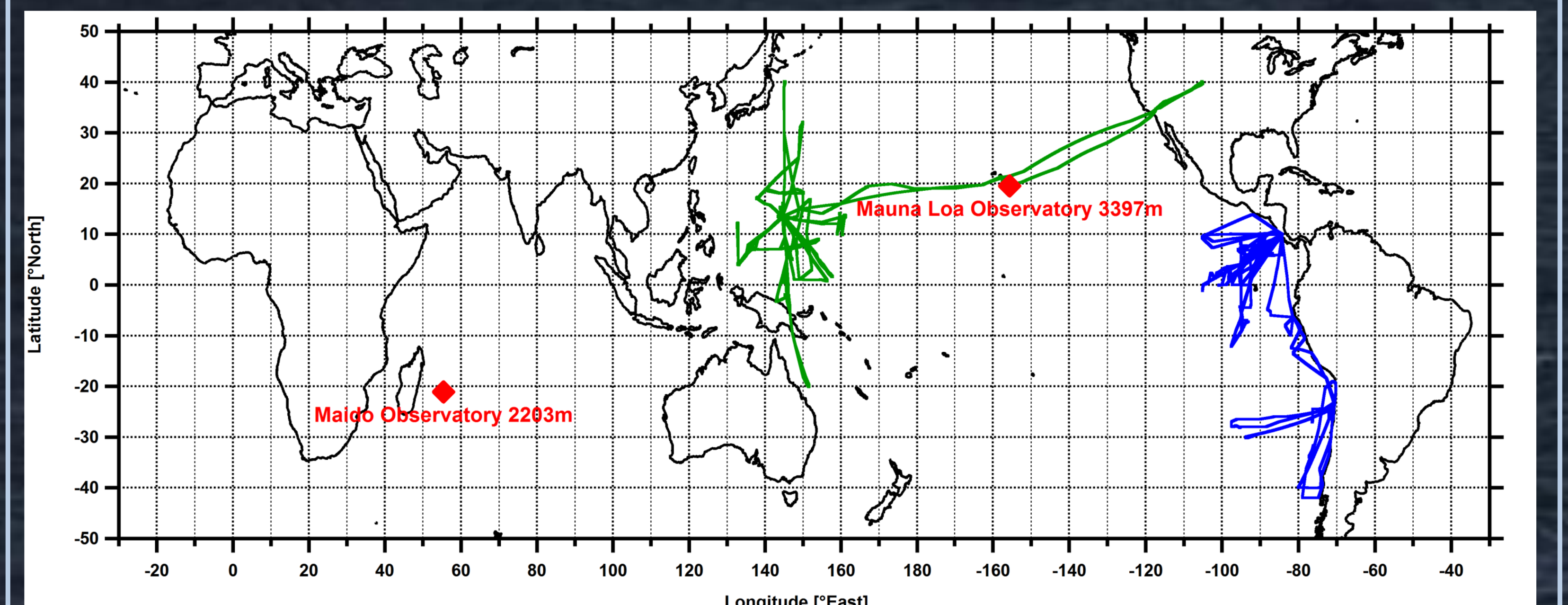


Fig. 1: Location of mountaintop sites set up in 2017. Also shown flight tracks from TORERO (Blue, 2012), and CONTRAST (Green, 2014)

Halogens destroy about 20% of tropospheric ozone, modify oxidizing capacity, atmospheric mercury, and aerosols. Long term measurements over remote oceans are generally scarce, and have traditionally been limited to very short lived organic species (VSLS). Long term measurements of inorganic halogen radicals provide insights into other sources (e.g., sea-salt) and are extremely limited in pristine air, yet help understand processes affecting preindustrial ozone, relative to which anthropogenic change needs to be evaluated.

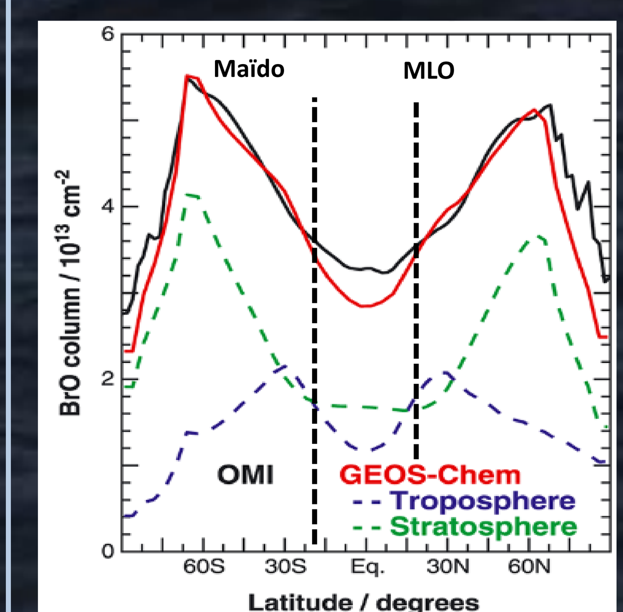


Fig. 2: Comparison of GEOS-Chem BrO VCDs to OMI measurements (Schmidt et al., 2016).

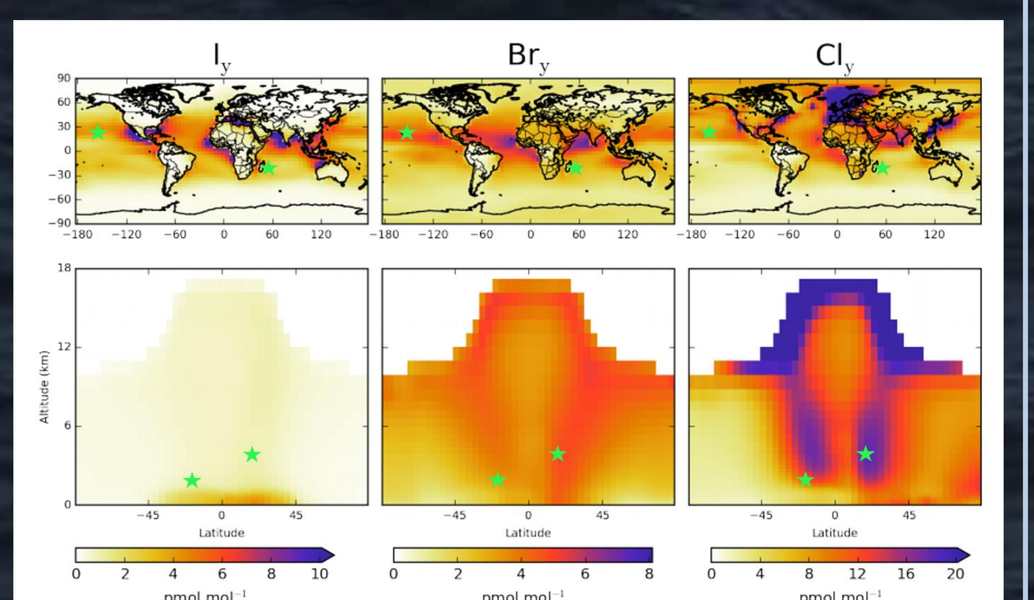


Fig. 3: Tropospheric annual average inorganic halogen concentrations from GEOS-Chem (Sherwen et al., 2016). Green stars indicate the locations of MLO and Maïdo.

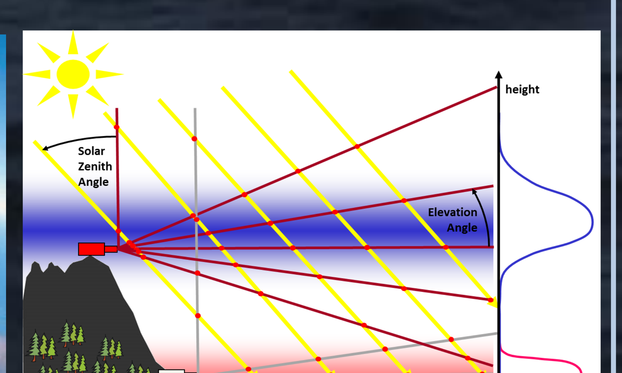


Fig. 4: La Réunion Island in the Eastern Indian Ocean (see Fig. 1) experiences SH tropical- and subtropical air. CU has a MAX-DOAS installed at Maïdo, and BIRA one at sea-level.

- Mountain top observations -

Methods

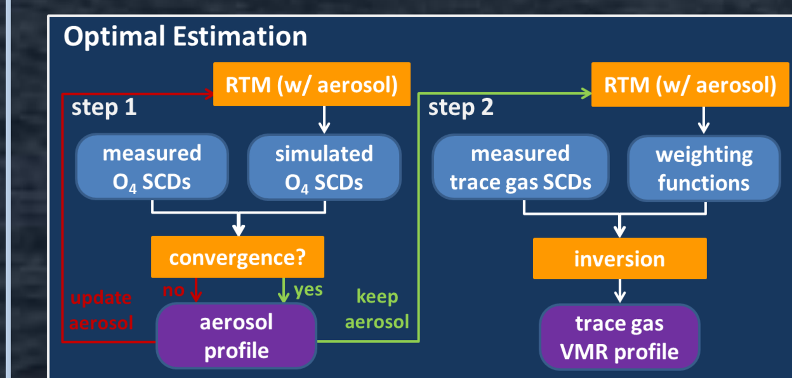


Fig. 5: MAX-DOAS observations are inherently calibrated by measurements of oxygen collision complexes (O_2-O_2), Raman scattering, and knowledge of the absorption cross-sections of molecules. Vertical profile retrievals use two steps: First, aerosol extinction is retrieved from O_2-O_2 measurements to constrain the radiation field, which is used in a second step to calculated weighting functions that serve as inversion input, together with vertically resolved trace gas SCDs .

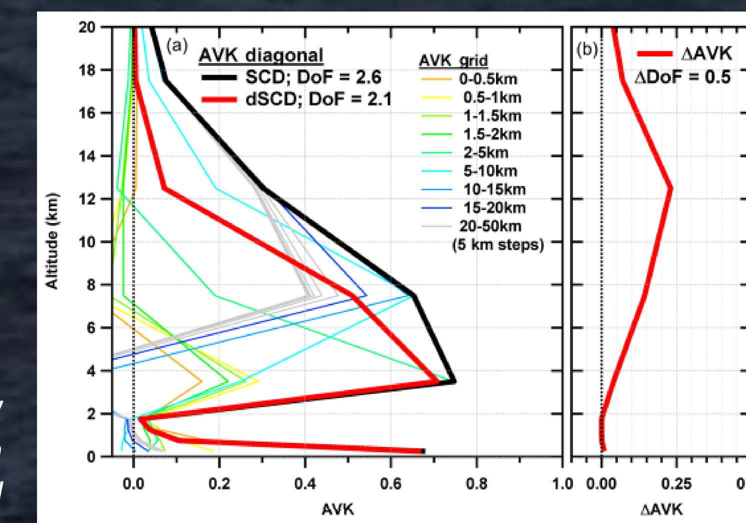
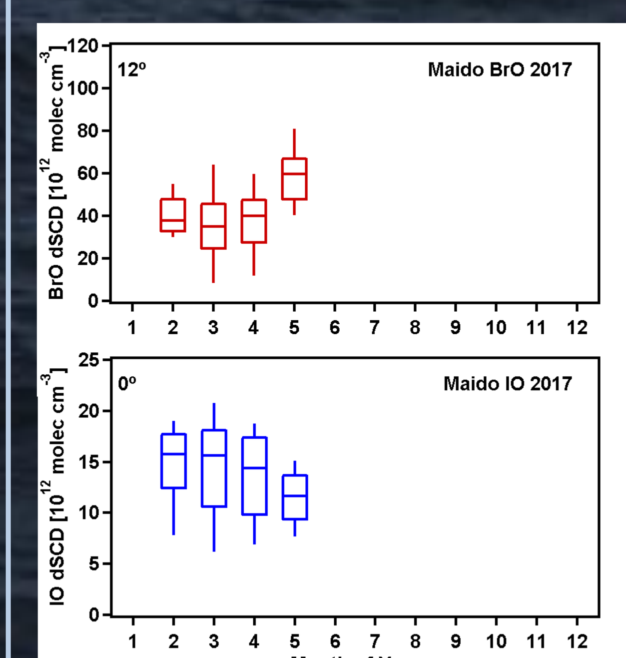


Fig. 6: Illustration of the benefits of the method outlined in Coburn et al., 2016. By maximizing the information about the SCD in the reference spectrum (SCD_{ref}) a further 0.5 Degrees of freedom are gained at altitudes distant from the instrument in the free troposphere.

Seasonal Changes at Maïdo Observatory



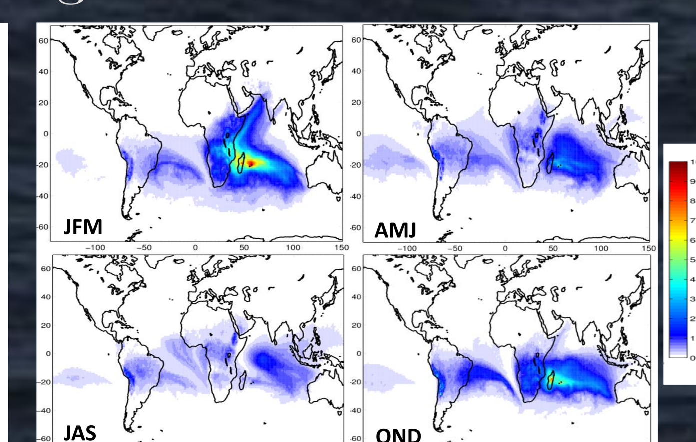


Fig. 7: Flexpart analysis of seasonal surface contributions to the air mass between 3-15 km above ground level, roughly the free troposphere above Maïdo.

Fig. 8 (left): BrO and IO dSCDs observed during the initial phase of our project at Maïdo Observatory. Measurements from two EA are shown to illustrate the potential to evaluate vertical profiles. BrO is mostly above, and IO near and below.

Halogens and Mercury at Mauna Loa Observatory

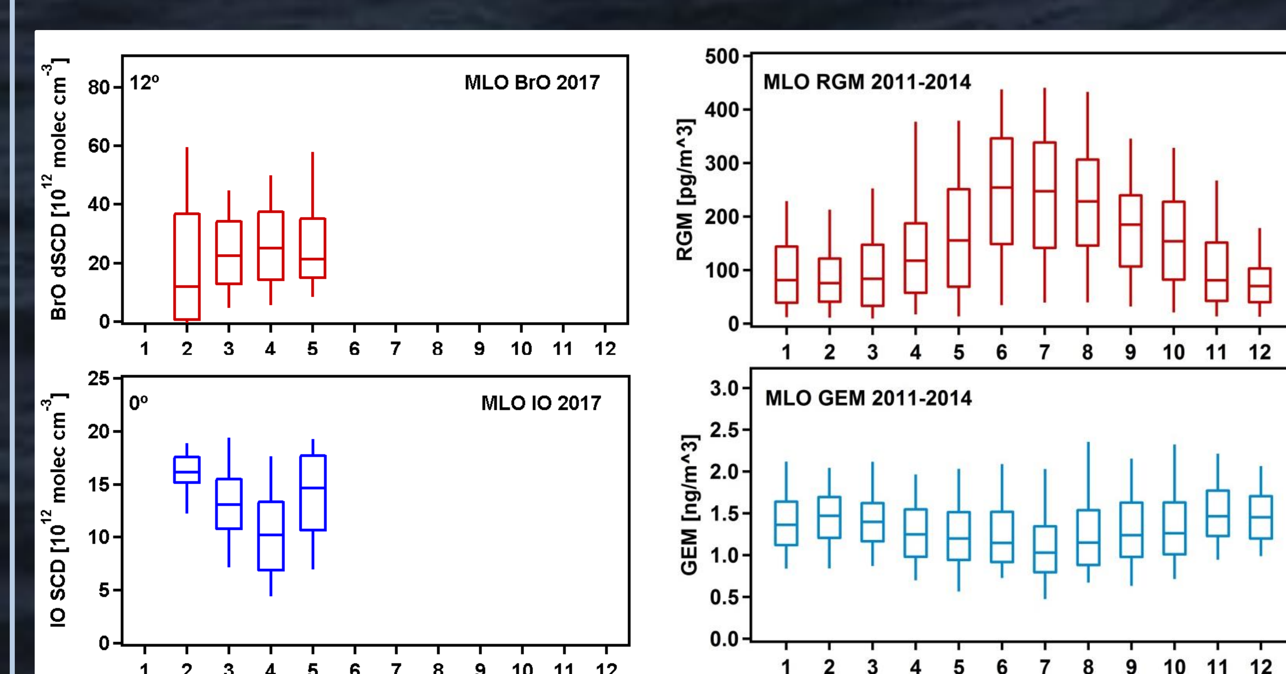


Fig. 9: Far Left- Measurements of BrO and IO from the mountaintop MAX-DOAS at MLO since February 2017.

Right panels- Seasonal cycle of Reactive Gaseous Mercury (RGM) and Gaseous Elemental Mercury (GEM) at MLO (2011-2014).

Bromine radicals oxidize GEM to form RGM. RGM is highly water soluble, and readily undergoes dry and wet deposition. The cause for the RGM maximum during JJA, and the minimum during DJF is unknown.

- Aircraft observations -

Br_y structure in the UTLS over the tWPO

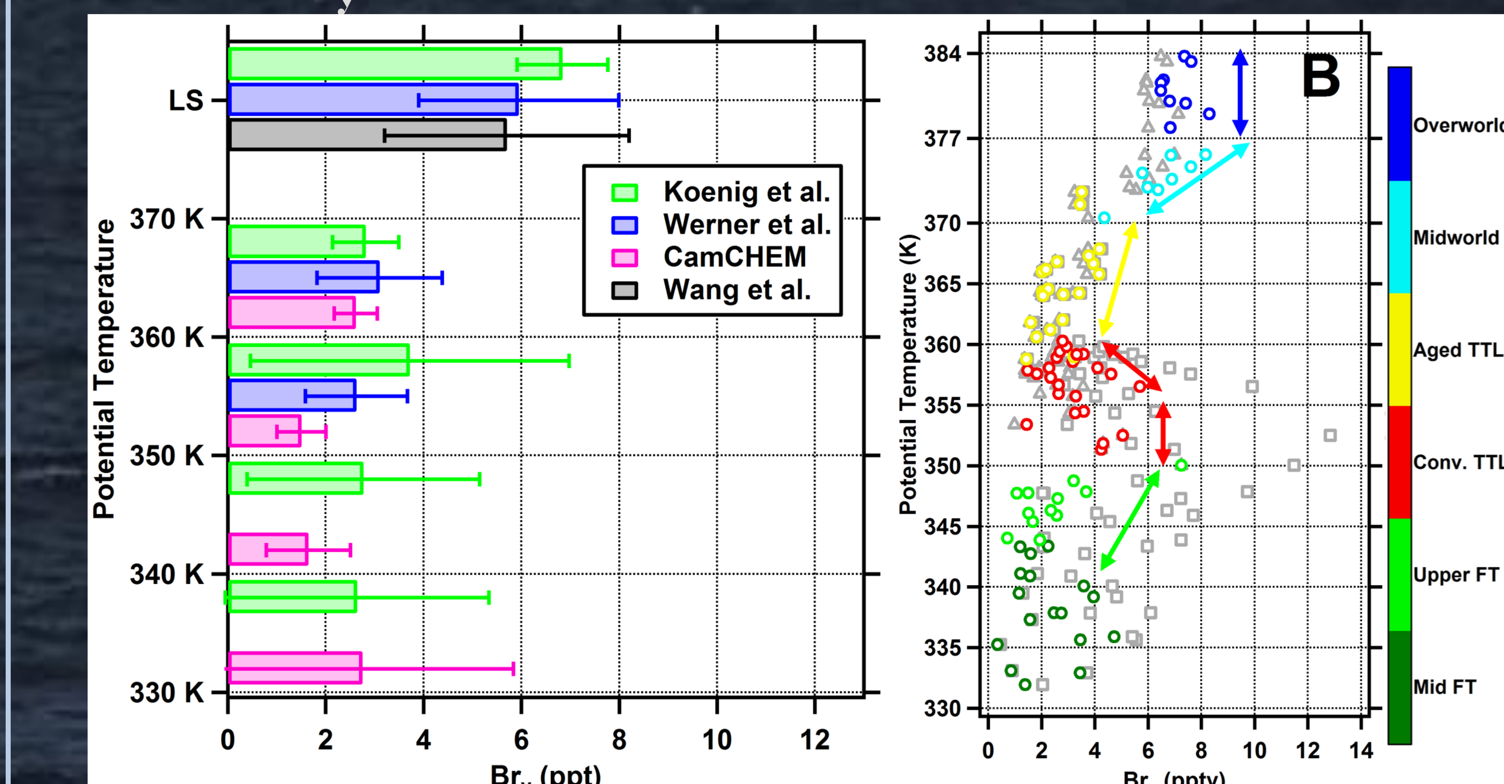


Fig. 10: Structure of gas-phase inorganic bromine, Br_y, in the UTLS constrained by CU AMAX-DOAS BrO and other observations during the CONTRAST campaign (Koenig et al., 2017). Carbon loss from VSLS is a source for increasing Br_y in the lower stratosphere. While other Br_y sources, presumably from sea-salt, are needed to explain elevated Br_y in the upper troposphere (Wang et al., 2015; Volkamer et al., 2015). The mechanism leading to the Br_y minimum is not currently understood. Decreasing BrO in the lower TTL (Dix et al., 2016), and increasing Br_y in the LS (Werner et al. 2017) had previously been observed, and are consistent with our observations of a Br_y minimum in the UTLS (Koenig et al., 2017).

Sea-salt influences on BrO distributions

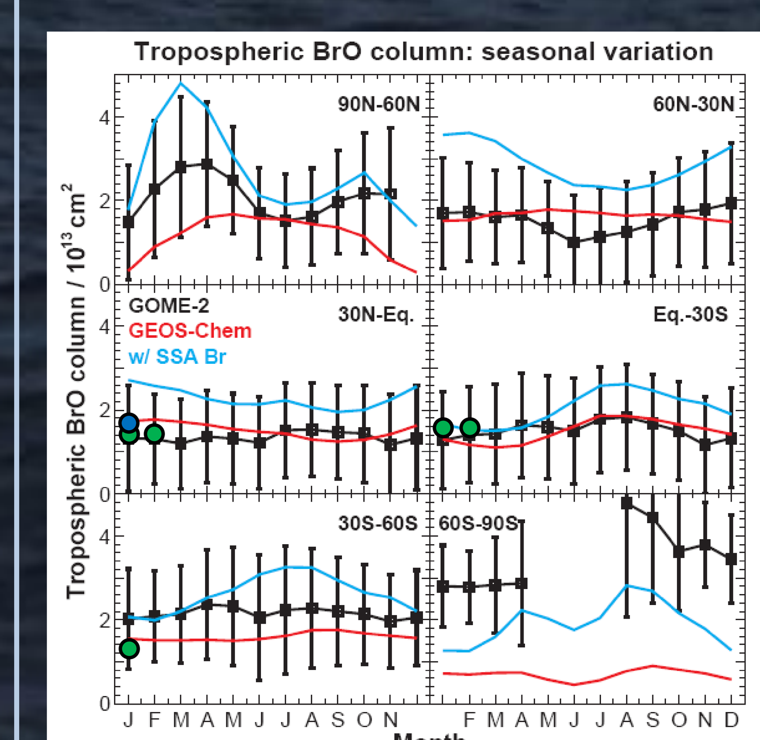


Fig. 11: GEOS-Chem tropospheric mean BrO VCD and GOME-2 2007 satellite observations (Schmidt et al., 2016). Green dots: TORERO, blue dots: CONTRAST

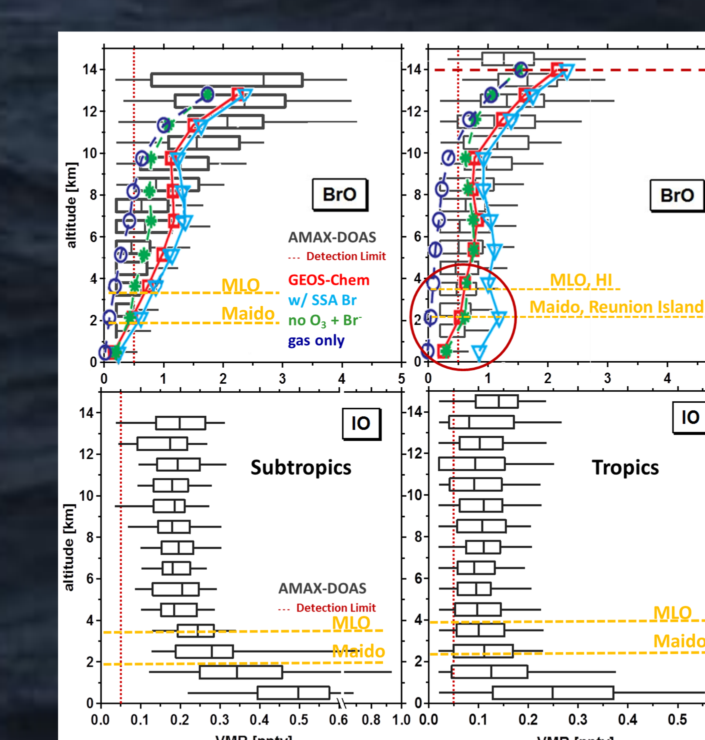
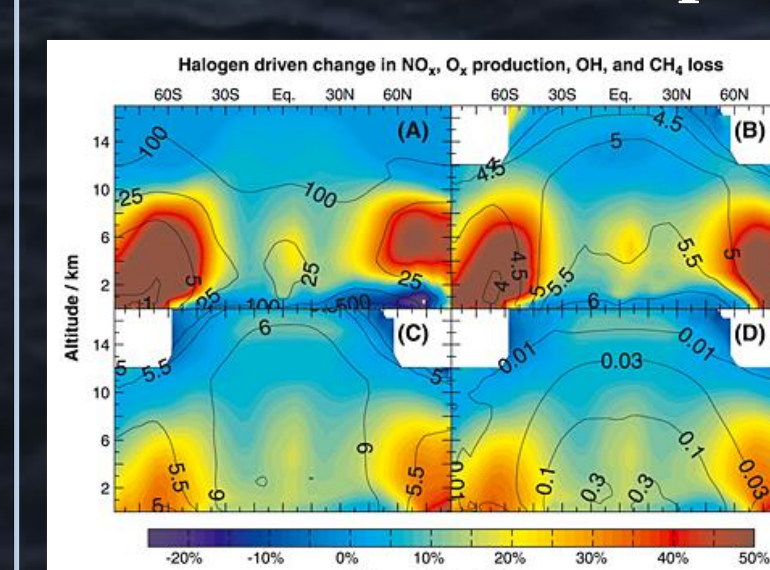


Fig. 12: GEOS-Chem tropospheric mean BrO and IO profiles, and comparison with observations over the tEPO (Schmidt et al., 2016).

Relevance of tropospheric halogen chemistry



Globally, tropospheric halogens:

- Reduce the tropospheric O_3 burden by 15-20%, O_3 lifetime from 26 days to 22 days.
- The sum of halogen driven O_x loss is 900 Tg O_x yr^{-1} (similar to the O_x loss from HO_2). NO_x oxidation is the most relevant process.
- Global mean OH is 4.5 % lower than in a simulation without halogens,
- Increase in the CH_4 lifetime (6.5 %) due to OH oxidation from 7.48 years to 7.96 years (Schmidt et al., 2016; Sherwen et al. 2016).

However, these model simulations currently do not represent a bromine source from sea salt aerosol de-bromination, which is needed to explain elevated Br_y in the upper FT. Including a sea salt source leads easily to overprediction in models (Schmidt et al., 2016). MBL aerosols are depleted in chlorine (Miyazaki et al., 2016) and bromine, but no BrO is observed in the MBL (Volkamer et al.,2015). A gas-phase process is missing that converts BrO_x into Br_y.

- Acknowledgements -

R.V. is grateful for NSF funding under CAREER award ATM-847793, AGS-1104104 (TORERO), AGS-1261740 (CONTRAST) and AGS-1620530 (this work). We thank the TORERO and CONTRAST Science teams, the staff at Maido Observatory, and Paul Fukumura and Preston Sato at the Mauna Loa Observatory. Future research at Maïdo will be coordinated with Michel van Roozendael's group at BIRA, Belgium.

References

Dix et al., Parameterization Retrieval of Trace Gas Volume Mixing Ratios from Airborne MAX-DOAS, AMT, doi:10.5194/amt-9-5655-2016, 2016.
Koenig et al., BrO and Br_y profiles over the Western Pacific: Relevance of Inorganic Bromine Sources and a Br_y Minimum in the Aged Tropical Tropopause Layer, in prep., 2017.
Miyazaki et al., Contribution of dissolved organic matter to submicron water-soluble organic aerosols in the marine boundary layer over the eastern equatorial Pacific, ACP, doi:10.5194/acp-16-7695-2016, 2016.
Schmidt et al., Modeling the observed tropospheric BrO background: Importance of multiphase chemistry and implications for ozone, OH, and mercury, JGR, doi: 10.1002/2015jd024229, 2016.
Sherwen et al., Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem, ACP, doi:10.5194/acp-2016-424, 2016.
Volkamer et al., Aircraft measurements of BrO, IO, glyoxal, NO_2, H_2O, O_2-O_2 and aerosol extinction profiles in the tropics: Comparison with aircraft-/ship-based in situ and lidar measurements , AMT, doi:10.5194/amt-8-2121-2015, 2015.
Wang et al., Active and Widespread Halogen Chemistry in the Tropical and Subtropical Free Troposphere , PNAS, doi:10.1073/pnas.1505142112, 2015.
Pan et al., The Convective Transport of Active Species in the Tropics (CONTRAST) Experiment , BAMS, doi:http://dx.doi.org/10.1175/BAMS-D-14-00272.1, 2016.