BrO and inferred Br\textsubscript{y} profiles over the western Pacific: relevance of inorganic bromine sources and a Br\textsubscript{y} minimum in the aged tropical tropopause layer

Theodore K. Koenig\textsuperscript{1,2}, Rainer Volkamer\textsuperscript{1,2}, Sunil Baidar\textsuperscript{1,2,a}, Barbara Dix\textsuperscript{1}, Siyuan Wang\textsuperscript{2,3,b}, Daniel C. Anderson\textsuperscript{4,c}, Ross J. Salawitch\textsuperscript{1,5,6}, Pamela A. Wales\textsuperscript{5}, Carlos A. Cuevas\textsuperscript{7}, Rafael P. Fernandez\textsuperscript{7,8}, Alfonso Saiz-Lopez\textsuperscript{7}, Mathew J. Evans\textsuperscript{9}, Tomás Sherwen\textsuperscript{9}, Daniel J. Jacob\textsuperscript{10,11}, Johan Schmidt\textsuperscript{12}, Douglas Kinnison\textsuperscript{13}, Jean-François Lamarque\textsuperscript{13}, Eric C. Apel\textsuperscript{13}, James C. Bresch\textsuperscript{13}, Teresa Campos\textsuperscript{13}, Frank M. Flocke\textsuperscript{13}, Samuel R. Hall\textsuperscript{13}, Shawn B. Honomichl\textsuperscript{13}, Rebecca Hornbrook\textsuperscript{13}, Jørgen B. Jensen\textsuperscript{13}, Richard Lueb\textsuperscript{13}, Denise D. Montzka\textsuperscript{13}, Laura L. Pan\textsuperscript{13}, J. Michael Reeves\textsuperscript{13}, Sue M. Schauffler\textsuperscript{13}, Kirk Ullmann\textsuperscript{13}, Andrew J. Weinheimer\textsuperscript{13}, Elliot L. Atlas\textsuperscript{14}, Valeria Donets\textsuperscript{14}, Maria A. Navarro\textsuperscript{14}, Daniel Riemer\textsuperscript{14}, Nicola J. Blake\textsuperscript{15}, Dexiong Chen\textsuperscript{16,d}, L. Gregory Huey\textsuperscript{16}, David J. Tanner\textsuperscript{16}, Thomas F. Hanisco\textsuperscript{17}, and Glenn M. Wolfe\textsuperscript{17,18}

\textsuperscript{1}Department of Chemistry & Biochemistry, University of Colorado, Boulder, CO, USA
\textsuperscript{2}Cooperative Institute for Research in Environmental Sciences (CIRES), Boulder, CO, USA
\textsuperscript{3}Department of Chemistry, University of Michigan, Ann Arbor, MI, USA
\textsuperscript{4}Department of Atmospheric & Oceanic Science, University of Maryland, College Park, MD, USA
\textsuperscript{5}Department of Chemistry & Biochemistry, University of Maryland, College Park, MD, USA
\textsuperscript{6}Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD, USA
\textsuperscript{7}Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, Spanish National Research Council (CSIC), Madrid, Spain
\textsuperscript{8}Argentine National Research Council (CONICET), FCEN-UNCuyo, UNT-FRM, Mendoza, Argentina
\textsuperscript{9}Wolfson Atmospheric Chemistry Laboratories (WACL), Department of Chemistry, University of York, York, UK
\textsuperscript{10}John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA
\textsuperscript{11}Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
\textsuperscript{12}Department of Chemistry, Copenhagen University, Copenhagen, Denmark
\textsuperscript{13}National Center for Atmospheric Research (NCAR), Boulder, CO, USA
\textsuperscript{14}Department of Atmospheric Science, Rosenstiel School of Marine & Atmospheric Sciences (RSMAS), University of Miami, Miami, FL, USA
\textsuperscript{15}Department of Chemistry, University of California, Irvine, CA, USA
\textsuperscript{16}School of Earth & Atmospheric Sciences, Georgia Tech, Atlanta, Georgia, USA
\textsuperscript{17}Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, USA
\textsuperscript{18}Joint Center for Earth Systems Technology, University of Maryland, Baltimore County, Baltimore, MD, USA
\textsuperscript{a}now at: Chemical Sciences Division, National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
\textsuperscript{b}now at: National Center for Atmospheric Research (NCAR), Boulder, CO, USA
\textsuperscript{d}now at: Department of Chemistry, University of Drexel, Philadelphia, PA, USA
\textsuperscript{c}now at: Department of Chemical Engineering, Carnegie Mellon University (CMU), Pittsburgh, PA, USA

Correspondence: Rainer Volkamer (rainer.volkamer@colorado.edu)

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Abstract. We report measurements of bromine monoxide (BrO) and use an observationally constrained chemical box model to infer total gas-phase inorganic bromine (Br$_y$) over the tropical western Pacific Ocean (TWPO) during the CONTRAST field campaign (January–February 2014). The observed BrO and inferred Br$_y$ profiles peak in the marine boundary layer (MBL), suggesting the need for a bromine source from sea-salt aerosol (SSA), in addition to organic bromine (CBr$_y$). Both profiles are found to be C-shaped with local maxima in the upper free troposphere (FT). The median tropospheric BrO vertical column density (VCD) was measured as 1.6×10$^{13}$ molec cm$^{-2}$, compared to model predictions of 0.9×10$^{13}$ molec cm$^{-2}$ in GEOS-Chem (CBr$_y$ but no SSA source), 0.4×10$^{13}$ molec cm$^{-2}$ in CAM-Chem (CBr$_y$ and SSA), and 2.1×10$^{13}$ molec cm$^{-2}$ in GEOS-Chem (CBr$_y$ and SSA). Neither global model fully captures the C-shape of the Br$_y$ profile. A local Br$_y$ maximum of 3.6 ppt (2.9–4.4 ppt; 95% confidence interval, CI) is inferred between 9.5 and 13.5 km in air masses influenced by recent convective outflow. Unlike BrO, which increases from the convective tropical tropopause layer (TTL) to the aged TTL, gas-phase Br$_y$ decreases from the convective TTL to the aged TTL. Analysis of gas-phase Br$_y$ against multiple tracers (CFC-11, H$_2$O/O$_3$ ratio, and potential temperature) reveals a Br$_y$ minimum of 2.7 ppt (2.3–3.1 ppt; 95% CI) in the aged TTL, which agrees closely with a stratospheric injection of 2.6±0.6 ppt of inorganic Br$_y$ (estimated from CFC-11 correlations), and is remarkably insensitive to assumptions about heterogeneous chemistry. Br$_y$ increases to 6.3 ppt (5.6–7.0 ppt; 95% CI) in the stratospheric “middleworld” and 6.9 ppt (6.5–7.3 ppt; 95% CI) in the stratospheric “overworld”. The local Br$_y$ minimum in the aged TTL is qualitatively (but not quantitatively) captured by CAM-Chem, and suggests a more complex partitioning of gas-phase and aerosol Br$_y$ species than previously recognized. Our data provide corroborating evidence that inorganic bromine sources (e.g., SSA-derived gas-phase Br$_y$) are needed to explain the gas-phase Br$_y$ budget in the upper free troposphere and TTL. They are also consistent with observations of significant bromide in Upper Troposphere–Lower Stratosphere aerosols. The total Br$_y$ budget in the TTL is currently not closed, because of the lack of concurrent quantitative measurements of gas-phase Br$_y$ species (i.e., BrO, HOB, HBr, etc.) and aerosol bromide. Such simultaneous measurements are needed to (1) quantify SSA-derived Br$_y$ in the upper FT, (2) test Br$_y$ partitioning, and possibly explain the gas-phase Br$_y$ minimum in the aged TTL, (3) constrain heterogeneous reaction rates of bromine, and (4) account for all of the sources of Br$_y$ to the lower stratosphere.

1 Introduction

Gas-phase Bromine in the atmosphere can be divided into organic and inorganic species. Inorganic bromine in the gas phase (Br$_y$) can be further divided into active bromine (BrO$_2$ = Br + BrO), reservoir species (HBr, HOB, BrNO$_2$, and BrONO$_2$), and photolabile compounds (Br$_2$ and BrCl). Atomic bromine (Br) and bromine monoxide (BrO) rapidly interconvert, primarily by reaction with O$_3$ and photolysis.

Reactions of BrO$_2$ have a number of important impacts on the troposphere. First, BrO$_2$ participates in catalytic reaction cycles that destroy ozone (von Glasow et al., 2004; Read et al., 2008; Saiz-Lopez and von Glasow, 2012; Schmidt et al., 2016; Simpson et al., 2015; Wofsy et al., 1975). Second, BrO$_2$ modifies NO$_x$ (= NO + NO$_2$) by increasing the ratio of NO$_2$ / NO (Bloss et al., 2010), and is an overall sink of NO$_x$ (Schmidt et al., 2016) among other chemical effects (Custard et al., 2015; Evans et al., 2003; Lary, 2005). Third, BrO$_2$ adds to oxidative capacity and exerts a number of competing effects on HO$_x$ (= OH + HO$_2$). In particular, the lower ozone leads to a lower production of OH radicals from ozone photolysis, lower NO$_x$ leads to a decrease in the OH / HO$_2$ ratio, and HOB photolysis increases the OH / HO$_2$ ratio. Fourth, BrO$_2$ is thought to be the primary oxidant of mercury in the atmosphere (Coburn et al., 2016; Goodsite et al., 2004; Holmes et al., 2006) and an important loss mechanism for dimethyl sulfide (Boucher et al., 2003). Fifth, the net-effect of BrO$_2$ impacts on O$_3$, NO$_x$, and HO$_x$ leads to an increase in the lifetime of CO, hydrocarbons, and climate-active gases such as methane (Lelieveld et al., 1998; Parrella et al., 2012; Saiz-Lopez and von Glasow, 2012).

Bromine also has important impacts on the stratosphere, where the ozone destruction potential is ~60 times greater than that of chlorine (on a per atom basis; Sinnhuber et al., 2009). Historically, the source of stratospheric bromine has been thought to be analogous to chlorine, resulting from the source gas (SG) injection (SGI) of longer-lived organic bromine species (LLS) – of both anthropogenic and natural origin – into the stratosphere. However, measurements of stratospheric Br$_y$ generally exceed the abundance of Br$_y$ that can be explained from SGI of LLS alone (Carpenter et al., 2014; Salawitch et al., 2005). Very short-lived species (VSLS; e.g., bromoform, CHBr$_3$, dibromomethane, CH$_2$Br$_2$) directly add to SGI, and their photolysis and oxidation in the troposphere adds Br$_y$ as product gas (PG) injection (PGI) into the LS (lower stratosphere; Ko et al., 2003). Recent measurements of elevated BrO in the free troposphere (FT) suggest sea-salt sources may contribute to Br$_y$ in the FT (Volkamer et al., 2015; Wang et al., 2015; Schmidt et al., 2016), but the relative contribution of sea-salt-derived Br$_y$ and VSLS-derived PGI contributions to stratospheric Br$_y$ injection has not, to our knowledge, previously been experimentally evaluated. One objective of the CONvective TRansport of Active Species in the Tropics (CONTRAST) and the Airborne Tropical TRopopause EXperiment (ATTREX) field campaigns.
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(December and February 2014) in Guam was to provide observational constraints to Br₇ from aircraft measurements of BrO in the upper troposphere–lower stratosphere (UTLS) over the tropical western Pacific Ocean (tWPO; Chen et al., 2016; Jensen et al., 2016; Pan et al., 2017; Werner et al., 2017).

Differential optical absorption spectroscopy (DOAS) measurements of BrO have been made in the tropics from satellites (Chance, 1998; Richter et al., 2002; Theys et al., 2011; Wagner et al., 2001), ground-based Multi-AXis–DOAS (MAX-DOAS; Theys et al., 2007), balloon profiles (Dorf et al., 2006, 2008; Pundt et al., 2002), and airborne platforms (Volkamer et al., 2015; Wang et al., 2015; Werner et al., 2017). In addition to DOAS, microwave radiometry has also been employed to measure BrO (Millán et al., 2012; Stachnik et al., 2013). Chemical ionization mass spectrometry (CIMS) measurements of atmospheric Brᵥ, using I⁻ or SF₆⁻, have largely been limited to BrO, although BrCl, HOBr, and Br₂ have also been detected (Le Breton et al., 2017; Chen et al., 2016; Neuman et al., 2010).

Here we describe measurements of BrO by the University of Colorado airborne MAX-DOAS instrument aboard the NCAR/NSF Gulfstream V (GV) aircraft during the CONTRAST field campaign (January and February 2014) in Guam. The GV carried a suite of in situ and remote-sensing instruments designed to characterize atmospheric composition targeting bromine species, including bromocarbons and inorganic bromine species as well as dynamical properties. An overview of the campaign is available in Pan et al. (2017). The campaign consisted of 17 research flights (RFs). Numerous flights were in or near clouds and thus presented challenges for DOAS retrievals. We focus the analysis on portions of five flights shown in Fig. 1: RF03, RF04, RF06, RF07, and RF15, which were conducted in largely cloud-free air. RF03, RF04, and RF07 were chosen for vertical profiles over the tWPO, covering altitudes from the boundary layer up to the lower tropical tropopause layer (TTL) on 19, 21, and 27 January 2014. The flight paths of RF06 and RF15 were to the north of Guam and targeted the Northern Hemisphere extratropical jet stream on 25 January and 25 February 2014, respectively. For RF15, the GV crossed the jet stream and sampled the Northern Hemisphere LS.

The measurements and models are presented in Sect. 2. Section 3 describes the DOAS measurements aboard the GV, as well as measurements used to constrain a chemical box model to infer total gas-phase inorganic bromine (Brᵥ); this includes sensitivity studies and a discussion of different chemical regimes for heterogeneous chemistry that recycles Brᵥ. Section 4 discusses the results by comparing with two global models (GEOS-Chem and CAM-Chem), and places them in context with the existing literature. The atmospheric implications of tropospheric halogens for atmospheric composition and our understanding of bromine sources are summarized and discussed. Section 5 presents the conclusions and provides an outlook.

Figure 1. Flight tracks with the locations of profile case studies (0–15 km) used in this work. For northbound flights, RF06 and RF15, the times reflect periods used for detailed modeling. For RF03, RF04, and RF07, the locations of the vertical profiles are indicated by the black dashed ellipses, and the times listed are those of the profiles, and low-level flight legs in the boundary layer.

2 Experimental

The University of Colorado Airborne Multi-AXis Differential Optical Absorption Spectroscopy (CU AMAX-DOAS) instrument aboard the GV measured trace gases including the halogen oxides BrO and IO, as well as NO₂. Additional species such as formaldehyde (HCHO), O₃, H₂O, and glyoxal (CHOCHO) can also be retrieved. Other instruments and measurements aboard the GV included but were not limited to the following: the Advanced Whole Air Sampler (AWAS), which measured species including halocarbons and a variety of chemical tracers; the HIAPER Atmospheric Radiation Package (HARP), which measured actinic flux and photochemical rates; a trace organic gas analyzer (TOGA), which measured organic species including halocarbons and aldehydes; chemiluminescent measurements of NO, NO₂, and O₃; the Picarro CRDS instruments, which measured CO₂ and CH₄; a vacuum ultra violet (VUV) fluorescence instrument (Aerolaser), which measured CO; the In Situ Airborne Formaldehyde (ISAF) instrument, which measured HCHO; and an ultra-high sensitivity aerosol spectrometer (UHSAS), which measured size-resolved Aitken and accumulation mode aerosol. The measurements used in this work are summarized in Table 1.
Table 1. Instruments aboard the NSF GV research aircraft used to constrain the box model.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Parameters used in this work</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMAX-DOAS</td>
<td>BrO, NO₂</td>
<td>30 s</td>
</tr>
<tr>
<td>AWAS</td>
<td>Ethane, Propane, Isobutane, n-Butane, CFC-11, Benzene</td>
<td>minutes*</td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>NO, NO₂, O₃</td>
<td>1 s</td>
</tr>
<tr>
<td>HARP</td>
<td>Actinic flux (upward and downward) is used to calculate photolysis rates</td>
<td>1 s</td>
</tr>
<tr>
<td>ISAF</td>
<td>HCHO</td>
<td>1 s</td>
</tr>
<tr>
<td>PIRARRO</td>
<td>Methane</td>
<td>1 s</td>
</tr>
<tr>
<td>TOGA</td>
<td>Propane, Isobutane, n-Butane, HCHO, CFC-11, Benzene</td>
<td>2.8 min</td>
</tr>
<tr>
<td>UHSAS</td>
<td>Aitken and accumulation mode aerosol surface area</td>
<td>1 s</td>
</tr>
<tr>
<td>Aerosol VUV fluorescence</td>
<td>CO, pressure, temperature, water, location</td>
<td>2 s</td>
</tr>
<tr>
<td>GV</td>
<td>Pressure, temperature, water, location</td>
<td>1 s</td>
</tr>
</tbody>
</table>

* AWAS samples were collected at intervals determined in flight by an operator.

2.1 The CU AMAX-DOAS instrument

The CU AMAX-DOAS instrument has been deployed during field campaigns in urban air (Baidar et al., 2013; Oetjen et al., 2013), and over remote oceans (Dix et al., 2013; Volkamer et al., 2015), and is described in detail in these papers. Briefly, the CU AMAX-DOAS consists of a wing-mounted pylon containing a motion-stabilized telescope and two spectrographs housed in the interior of the aircraft. Scattered sunlight enters the telescope along a well-defined field of view (vertical dispersion of 0.17°) and is actively motion-stabilized with a pointing accuracy better than 0.2° of view. The specific settings used are detailed in Sect. 2.1.1.

When using parameterization data in the box model, we account for the fact that the AMAX-DOAS instrument detects photons scattered at a variety of distances along the line of sight. The median photon is scattered 5–70 km forward of the plane, depending on altitude and aerosol conditions. This difference between air masses sampled by AMAX-DOAS and the in situ observations was accounted for as follows: when the aircraft maintains its heading, AMAX-DOAS data are taken to correspond to the air mass where the median photon was scattered, which is then sampled by in situ instruments with some delay (typically 4.5–6.0 min). The atmosphere used for radiative transfer modeling accounts for this delay using model information from the AMAX-DOAS.

2.1.1 DOAS retrieval

Trace gases were fitted using the DOAS method (Platt and Stutz, 2008) using the QDOAS software package (Danckaert et al., 2012). The wavelength calibration for each spectrum is precisely determined by measuring the mercury atomic emission at 404.7 nm. This slit function was further refined by fitting two wavelength-dependent degrees of freedom, using the Kurucz spectrum as reference (Chance and Kurucz, 2010; Kurucz et al., 1984). The slit function was fixed for final calibration of the instrument wavelength mapping. High-resolution laboratory cross sections (species and references given in Table 2) are convolved with the instrument.
function for analysis. Broadband extinction including Mie and Rayleigh scattering is accounted for by a polynomial. Trace gases with broad-band absorption components such as O$_3$ and NO$_2$ are orthogonalized to this polynomial. A linear intensity offset is included in some settings to account for instrumental stray light and imperfect knowledge of the Ring effect (Grainger and Ring, 1962). Absorption by relevant species is fitted simultaneously using the non-linear Marquardt–Levenberg algorithm with full non-linear treatment reserved for shift, stretch, and intensity offset (Danckaert et al., 2012). This is done in finite wavelength windows targeting specific trace gases. The analysis settings for BrO, NO$_2$, and O$_3$ (360 nm) are summarized in Table 2.

BrO was analyzed using a four-band analysis in the window 335–359 nm. The broader window was chosen to maximize information on other absorbers. The overlapping O$_3$ was accounted for by first determining accurate O$_3$ dSCDs using an optimized fit window, and prescribing these O$_3$ dSCDs in the BrO fit. Information on O$_3$ in the BrO fitting window is maximized at wavelengths of greatest differential absorption by this dimer, namely at the peak at 343 nm and the shoulder at the window edge at 359 nm. The O$_3$ cross section has been scaled to reflect the shorter path length of photons through the atmosphere at the lower wavelengths, using a $\lambda^{-4}$ dependence, which is based on the assumption that Rayleigh scattering dominates. The mixing ratio of NO$_2$ was retrieved for the RF15 case study and was used to constrain the box model (Supplement and Fig. S1).

2.1.2 Radiative transfer modeling

Simulations were run using the Monte Carlo radiative transfer model McArtim (Deutschmann et al., 2011) in a 1-D spherical atmosphere. Aerosol extinction is accounted for by taking advantage of the fact that the atmospheric profile of [O$_3$] is highly predictable, namely it scales as the square of the [O$_2$], which has an essentially constant mixing ratio at altitudes of interest and scales linearly as a function of density (Spinei et al., 2015; Thalman and Volkamer, 2013). Comparison of modeled and measured O$_3$ SCDs (slant column densities) is done in one of two ways: parameterization (Dix et al., 2016) of aerosol effects using a ratio, or retrieval of explicit aerosol profiles (Baidar et al., 2013; Volkamer et al., 2015). The high accuracy of the Rayleigh scattering cross sections represented in the radiative transfer model and O$_3$ dSCDs measurements used by the parameterization method has been independently evaluated by laboratory measurements (Thalman et al., 2014), and field observations in the absence of (Spinei et al., 2015) and in the presence of aerosols (Volkamer et al., 2015).

The parameterization method is discussed in detail in Dix et al. (2016). Briefly, the method makes use of the fact that spectra recorded with EA $0^\circ$ are strongly sensitive to the atmospheric layer at instrument altitude. Recorded EA $0^\circ$ spectra are analyzed using reference spectra that largely cancel out column contributions from above and below the instrument. The conversion of dSCDs into VMRs (volume mixing ratios) is realized by calculating box air mass factors for a Rayleigh atmosphere and applying a scaling factor constrained by O$_3$ dSCDs to account for aerosol extinction. The color ratio of the measured intensities at 477 and 640 nm is used to identify and filter measurements affected by clouds. Cloud filtering is manually quality controlled using aircraft video data and adapted where needed. An iterative VMR retrieval scheme corrects for trace gas profile shape effects. Profile information is gained from DOAS measurements during ascents and descents, and interpolated above the aircraft based on CAM-Chem profiles. For stratospheric absorbers like BrO and NO$_2$, a stratospheric correction is included. The magnitude of the stratospheric correction is characterized by periodically upward looking EA $10^\circ$ spectra and interpolated between successive EA $10^\circ$ measurements, assuming profile shapes from CAM-Chem. During portions of RF15, the telescope pointing exhibited a small positive bias of less than 1°. This effect was well characterized at all times, and has been accounted for in the analysis. To account for horizontal concentration gradients, especially near the jet, photons are modeled in a horizontally homogeneous atmosphere constructed using measurements and models for the zonal location of the median photon scattering. Errors are the total of the following three components added in quadrature: (1) a parameterization error of 30% but no better than 0.5 ppt, (2) the standard error of the mean of the component 30 s dSCDs, (3) the

### Table 2. DOAS fitting windows used in fitting BrO, O$_3$, and NO$_2$ in QDOAS software.

<table>
<thead>
<tr>
<th>Cross section</th>
<th>Wavelength window</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrO $a$</td>
<td>335–359 nm $b$</td>
</tr>
<tr>
<td>HCHO $b$</td>
<td>×</td>
</tr>
<tr>
<td>NO$_2$ $c$</td>
<td>×</td>
</tr>
<tr>
<td>O$_3$ $d$</td>
<td>×</td>
</tr>
<tr>
<td>O$_3$ $e$</td>
<td>×</td>
</tr>
<tr>
<td>O$_3$ $\lambda$ $c$</td>
<td>×</td>
</tr>
<tr>
<td>Ring $f$</td>
<td>×</td>
</tr>
<tr>
<td>Ring $\times \lambda$ $g$</td>
<td>×</td>
</tr>
</tbody>
</table>

$^a$ Wilmouth et al. (1999) at 228 K.
$^b$ Meller and Moortgat (2000) at 298 K.
$^c$ Vanaelke et al. (1998) at 220 K.
$^d$ Thalman and Volkamer (2013) at 296 K. The O$_3$ in the BrO window was not fitted, but rather constrained to the value obtained in the O$_3$ optimized fit and scaled to the wavelength of the O$_3$ peak at 350 nm.
$^e$ Serdyuchenko et al. (2014) at 223 and 243 K, the wavelength scaled O$_3$ uses the 223 K cross section. This and the 243 K cross section are orthogonalized to the 223 K cross section.
$^f$ Ring was calculated using the QDOAS (Danckaert et al., 2012) tool using the reference spectrum for wavelength calibration.
$^g$ This matches the treatment in Langford et al. (2007).
$^h$ The BrO window used a polynomial of order 5 and a linear offset correction. O$_3$ and NO$_2$ were orthogonalized to the first 3 terms of the polynomial.
$^i$ The O$_3$ window used a polynomial of order 5 and a linear offset correction. O$_3$ and NO$_2$ were orthogonalized to the first 3 terms of the polynomial.
$^j$ The NO$_2$ window used a polynomial of order 5 and a linear offset correction.
quadratic mean of the proportional dSCD errors of the component 30 s dSCDs.

For the optimal estimation method, aerosol profiles are retrieved by seeking to reproduce the measured \( O_4 \) SCDs. \( O_4 \) SCDs are primarily sensitive to aerosol extinction over other aerosol radiative properties, which are set to values expected to be typical of the local atmosphere. Settings are summarized in Table S1 in the Supplement. Where \( O_4 \) dSCDs are lower than modeled, aerosol extinction is increased to achieve better agreement (Volkamer et al., 2015). An onion peeling approach is used to retrieve an initial aerosol profile, which is adjusted by hand until modeled and measured \( O_4 \) SCDs converge (Baidar et al., 2013). Extinction profiles retrieved at 200 m vertical resolution at 360 nm are presented in Fig. S2a1–a3. Total aerosol optical depth was 0.304 in RF03, 0.272 in RF04, and 0.231 in RF07. Agreement between measured and modeled \( O_4 \) was 0.304 in RF03, 0.272 in RF04, and 0.231 in RF07.

2.2 Other measurements

A number of other instruments were aboard the NCAR GV during the CONTRAST field campaign (Pan et al., 2017). Data used to constrain the box model are summarized in Table 1. More detailed descriptions of the instruments can be found in the Supplement.

2.3 Model descriptions

Data from the AMAX-DOAS and other instruments were combined and used to initialize a box model (Wang et al., 2015) in order to examine partitioning of inorganic bromine (\( \text{Br}_y \)), specifically the ratio \( \text{BrO} / \text{Br}_y \), and infer gas-phase \( \text{Br}_y \) from the \( \text{BrO} \) measurements. In addition, \( \text{BrO} \), \( \text{Br}_y \), and \( \text{Br}_y \) speciation were also obtained from two chemical transport models: the Goddard Earth Observing System with Chemistry model (GEOS-Chem; Schmidt et al., 2016; Sherwen et al., 2016) and the Community Atmospheric Model with Chemistry model (CAM-Chem; Fernandez et al., 2014) for purposes of comparison.

2.3.1 Box model

The box model has been previously described in Wang et al. (2015). The model calculates gas-phase \( \text{Br}_y \) partitioning, and is constrained to measurements of chemical species and meteorological parameters as summarized in Table 1 and Sect. 2.2. The model was initialized every 5 min along the flight track. In general, data collected at a time resolution of \( \sim 30 \) s or at higher frequency were averaged into 5 min bins, and used as inputs to the box model; lower frequency data were linearly interpolated. For profile case studies, horizontal homogeneity was assumed and in situ and remote-sensing data were matched by altitude. For horizontal case studies, the AMAX-DOAS data were matched with in situ data sampled from the location of the median photon, as elaborated below. The primary box-model output is the ratio \( \text{BrO} / \text{Br}_y \) computed with 30 % error (Dix et al., 2013; Wang et al., 2015). This is added in quadrature with the \( \text{BrO} \) errors outlined above in Sect. 2.1.2 when computing the error in \( \text{Br}_y \). Sensitivity studies were conducted to bound the impacts of uncertainties in chemical kinetics and available surface area; these are described further below.

Box model sensitivity studies

The four box-model cases (0–3) are summarized in Table 3. Cases 0–2 use different constraints for the amount of aerosol surface area available for heterogeneous chemical reactions, and case 3 adjusts the gas-phase kinetics of bromine reactions.

The base case (case 0) used JPL (Jet Propulsion Laboratory) kinetics and UHSAS measured surface area. Size-specific particle concentrations for particles between 84 nm and 1 \( \mu \)m were measured by the UHSAS and were used to compute a surface area, assuming spherical particles. This is taken to be the minimum aerosol surface area available, because a previous optical closure study using AMAX-DOAS and High Spectral Resolution Lidar (HSRL; Volkamer et al., 2015) found that the airborne UHSAS may underestimate particle size by about a factor of 2 for reasons that are currently not well understood. Examination of CONTRAST
data confirms that this is again the case (Supplement and Fig. S3).

The first chemical sensitivity study (case 1) is identical to case 0, but used the measured UHSAS surface area multiplied by 4, based on results of these optical closure studies. The rationale for case 1 is that heterogeneous and multiphase chemistry (uniformly represented using heterogeneous kinetics in the box model) can be deterministic to the gas-phase lifetime of Br$_x$ reservoirs (i.e., HBr, and to a lesser extent also HOBr and BrONO$_2$). The fact that measured surface area is a lower limit has implications for heterogeneous reaction rates, bromine recycling, and the BrO / Br$_x$ ratio, and case 1 provides the best estimate of the available aerosol surface area.

The second sensitivity study (case 2) explores the possible effect of ice particles on bromine partitioning. Even very low ice concentrations add significant surface area that has the potential to rapidly impact local chemistry. CDP (cloud droplet probe) and 2D-C (two-dimensional cloud probe) measure super-micron-sized particles, cloud droplets, and ice. Sparse ice particles present a sampling challenge, and measurements were used as qualitative indicators for the presence of ice. 2D-C sometimes detected the presence of ice under conditions when ice should have sublimed, which may be due to rapid gravitational settling of ice particles. There might be insufficient time for the gas-phase Br$_x$ partitioning to equilibrate to the surface area of such ice particles, and as a result case 2 likely indicates a lower limit of gas-phase Br$_x$. Case 2 used an ice climatology constructed from GEOS-5 data (Molod et al., 2015) whenever 2D-C indicated the presence of ice. An additional sensitivity study (not shown) explored the potentially large surface area contribution from super-micron particles (not measured by UHSAS) that are visible in the CDP data at lower altitudes and found no significant difference from case 1.

Finally, the third sensitivity study (case 3) used the Br$_x$ kinetics suggestion of Kreycy et al. (2013) to represent the conversion of BrO and BrONO$_2$. This is mediated by the reaction BrO + NO$_2$ and the photolysis of BrONO$_2$. Kreycy et al. (2013) investigated BrO, O$_3$, and NO$_2$ concentrations in the polar stratosphere at sunset and found the measured variations with respect to solar zenith angle deviated from theory based on JPL kinetics (Sander et al., 2011). Their recommended modifications of $k_{\text{BrO + NO}_2}^{\text{Kreycy}} = 0.75 \times k_{\text{BrO + NO}_2}^{\text{JPL}}$ and $J_{\text{BrONO}_2}^{\text{Kreycy}} = 1.27 \times J_{\text{BrONO}_2}^{\text{JPL}}$ are used only for our case 3. These changes are relevant only in stratospheric air, where BrONO$_2$ is a significant daytime reservoir species.

**Box model heterogeneous chemical regimes**

The following heterogeneous chemical regimes (HCRs) are distinguished to evaluate partitioning among Br$_x$ and BrO$_x$ species:

HCR1 – low surface area density (SA): SA $< 2 \times 10^{-3}$ cm$^2$ m$^{-3}$. Partitioning among BrO$_x$ and the reservoirs is well approximated as three independent (gas-phase) equilibria of BrO$_x$ with the Br$_x$ reservoir species HOBr, HBr, and BrONO$_2$. HBr is typically the major Br$_x$ species, and the BrO$_2$ / Br$_x$ ratio is low (0.20–0.40). This regime is most relevant in the upper FT and convective TTL (all box-model cases). These regions are further characterized by low O$_3$ and high J$_{\text{BrO}}$ (photolysis rate of BrO) and as a result Br atoms make up near-half of the majority of BrO$_x$. The BrO / Br$_x$ ratio is typically less than 0.15, and Br$_x$ estimates are moderately sensitive to the available SA.

HCR2 – moderate SA: $2 \times 10^{-3} < SA < 1 \times 10^{-2}$ cm$^2$ m$^{-3}$. Heterogeneous reactions have the potential to shift the HBr / BrO$_x$ equilibrium dramatically. HBr does not readily photolysate, and reacts slowly with OH radicals to form BrO$_x$ in the gas phase. As a result, heterogeneous reactions are the dominant loss process for HBr. Further, HOBr and O$_3$ can facilitate the heterogeneous conversion of condensed-phase bromide back into the gas phase. In this regime HBr / Br$_x$ is strongly sensitive to the available SA as well as the rates of heterogeneous reactions. The BrO$_x$ / Br$_x$ ratio can increase rapidly from 0.20 to 0.70 (depending strongly on SA; see Sect. 3.3 and Fig. S4). The upper limit of BrO$_x$ / Br$_x$ is sensitive to both [H$_2$O] vapor and [O$_3$], which control the concentration of HO$_x$. The abundance of HO$_x$ is important due to the reactions BrO + H$_2$O $\rightarrow$ HOBr + O$_2$, and to a lesser extent Br + OH $\rightarrow$ HOBr and Br + HO$_2$ $\rightarrow$ HBr + O$_2$. HCR2, which is relevant in the mid- and upper FT and convective TTL (base case) and the upper FT and the convective TTL (case 1). The SA that accompanies the presence of ice (case 2) is such that HCR2 is eliminated. The BrO$_x$ / Br$_x$ ratio is strongly correlated with SA, changing by up to a factor of 4 between cases 0 and 1. O$_3$ and H$_2$O concentrations and changes to J$_{\text{BrO}}$ over this regime in the FT and TTL modulate BrO / Br$_x$ between 0.14 and 0.40 (see Fig. 5).

HCR3 – high SA: SA $> 1 \times 10^{-2}$ cm$^2$ m$^{-3}$. Heterogeneous reactions have the potential to eliminate HBr as a meaningful gas-phase Br$_x$ reservoir. HOBr is the main Br$_x$ reservoir species. In the HCR3 regime, BrO$_x$ / Br$_x$ is insensitive to SA, as gas-phase reactions become limiting, and typically varies between 0.20 and 0.50. Further increasing SA, such as by including super-micron particles measured by the CDP, does not modify the chemistry. This regime is relevant from the surface to the lower FT and in the aged TTL/stratosphere (case 0), surface to mid-FT and aged TTL/stratosphere (case 1), and in the entire model atmosphere (case 2). In the troposphere, BrO / Br$_x$ increases with altitude (from 0.15–0.25 near the surface to 0.45–0.50 in the mid-FT), due to decreasing humidity and O$_3$ concentration (molec cm$^{-3}$), as well as the increasing value of J$_{\text{HOBr}}$ with altitude. In the aged TTL, low humidity, low oxygenated volatile organic compounds (OVOCs), and high O$_3$ give rise to BrO / Br$_x$ > 0.35. In the stratosphere, BrONO$_2$ becomes a
significant Br\textsubscript{y} reservoir species, and caps the BrO / Br\textsubscript{y} ratio near 0.50.

### 2.3.2 CAM-Chem

The 3-D chemistry climate model Community Atmospheric Model with Chemistry (CAM-Chem) is described in Lamarque et al. (2012). CAM-Chem includes all of the physical parameterizations of CAM4 (Neale et al., 2013) and a finite volume dynamical core (Lin, 2004) for the tracer advection. In the present configuration, meteorological analysis (from GEOS-5) specific to the observational periods are used to constrain the meteorological fields (horizontal wind components and temperature) in CAM-Chem. The horizontal resolution is 0.9° × 1.25° and the vertical resolution of 52 levels includes full coverage of the troposphere and stratosphere, with a full representation of tropospheric and stratospheric chemistry. The VSLS version used here includes geographically distributed and time-dependent oceanic emissions of six bromocarbons (CHBr\textsubscript{3}, CH\textsubscript{2}Br\textsubscript{2}, CH\textsubscript{2}BrCl, CHBrCl\textsubscript{2}, CHBr\textsubscript{2}Cl, CH\textsubscript{2}IBr) as well as an additional source of inorganic bromine and chlorine in the lower troposphere due to sea-salt aerosol (SSA) dehalogenation (Fernandez et al., 2014; Ordóñez et al., 2012; Saiz-Lopez et al., 2012). In particular, it considers heterogeneous processes for halogen species on a variety of surfaces including uptake and recycling of HBr, HOBr, and BrONO\textsubscript{2} on ice crystals and sulfate aerosols. The importance of these reactions, as well as the contribution from each independent VSLS and sea-salt source to the halogen burden of SG and PG species in the TTL, are discussed in Fernandez et al. (2014). CAM-Chem output was used to examine how well modeled coupled chemistry and dynamics captured the BrO observations of the AMAX-DOAS and Br\textsubscript{y} inferred by the box model. Stratospheric concentrations (monthly and diurnally varying) of Br\textsubscript{y} are taken from a GEOS-CCM (chemistry climate model) simulation (Liang et al., 2010). Halogen chemistry in the model from Parr ella et al. (2012) as referenced in Wang et al. (2015) has been updated (Schmidt et al., 2016; Sherwen et al., 2016, 2017a) and now includes more extensive heterogeneous chemistry including reactions on ice crystals and cross-halogen coupling. These changes have led to a reduction in modeled HBr / Br\textsubscript{y} as well as Br\textsubscript{y} washout, leading to an increase in BrO\textsubscript{x} / Br\textsubscript{y} (Schmidt et al., 2016).

### 3 Results and atmospheric modeling context

#### 3.1 Bromine vertical profiles

The locations of the vertical profiles are shown in Fig. 1 with details as follows: (1) descent from RF03 on 17 January 2014 starting at 01:11 UTC at 9.0° N, 150.1° E at 12.2 km heading southeast, and ending at 01:40 UTC at 7.4° N, 151.8° E at 300 m over the Chuuk atoll; (2) ascent from RF04 on 19 January 2014 heading due north at 133.0° E starting at 03:20 UTC at 9.2° N at 400 m and ending at 03:38 UTC at 12.2° N at 13.2 km; and (3) ascent from RF07 on 29 January, heading due west at 1.1° N starting at 03:23 UTC at 150.5° E at 500 m, and ending at 03:53 UTC at 147.6° E at 13.8 km. These profiles represent conditions that are well suited to profile retrievals (solar zenith angle < 70°, mostly cloud free) and contain at least two measurements in each 500 m altitude bin.

Measured BrO profiles are shown in Fig. 2a, e, and i, and they exhibit significant variability. BrO concentrations in the lowest 500 m were 1.0±0.5 ppt (RF03; Fig. 2a), 1.7±1.2 ppt (RF04; Fig. 2e), and < 0.5 ppt (RF07, below detection limit; Fig. 2i). The uncertainty reflects the overall retrieval error here. The BrO variability was further characterized during level flight at low altitude following the RF03 descent over Chuuk and prior to the RF04 ascent. Mean mixing ratios retrieved from these data varied between 0.9 and 1.6 ppt BrO (RF03) and 1.6–4.4 ppt BrO (RF04). The higher value is not the result of a single outlier but rather represents the maximum of several minutes of data acquisition, for which retrieved BrO is greater than 3.5 ppt. These results suggest that BrO heterogeneity in the lowest 500 m is likely significant.

#### Table 3. Box model sensitivity studies probing the effects of aerosol surface area, ice, and kinetics for BrONO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Box model case</th>
<th>Surface areas</th>
<th>Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 0</td>
<td>UHSAS measured surface area</td>
<td>JPL (Sander et al., 2011)</td>
</tr>
<tr>
<td>Case 1</td>
<td>UHSAS measured surface area × 4\textsuperscript{a}</td>
<td>JPL idem</td>
</tr>
<tr>
<td>Case 2</td>
<td>UHSAS measured surface area × 4 and GEOS-Chem ice climatology</td>
<td>JPL idem</td>
</tr>
<tr>
<td>Case 3</td>
<td>UHSAS measured surface area × 4 and GEOS-Chem ice climatology</td>
<td>Kreycy et al. (2013)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Based on results of optical closure study in Sect. 3.1 and Fig. 3 of Volkamer et al. (2015).
Figure 2. BrO, Br\textsubscript{y}, and Br\textsubscript{y} partitioning for RF03 (a–d), RF04 (e–h), RF07 (i–l). BrO mixing ratios were obtained by optimal estimation. Partitioning of Br\textsubscript{y} species: (b, f, j) case 0; (c, g, k) case 2; (black line) BrO / Br\textsubscript{y} ratio. (d, h, l) Br\textsubscript{y} from case 0 (grey); case 1 (red); case 2 (cyan).

on both local and regional scales. At these altitudes, AMAXDOAS spectra average over path lengths of 5 km horizontally, which eases the comparison with model predictions on regional scales.

There is significant BrO variability also in the transition layer (TL: 0.5–2 km), where BrO mixing ratios are elevated relative to the lower FT. The mean mixing ratios below 2 km are 0.9 ± 0.4 ppt (RF03), 1.3 ± 0.6 ppt (RF04), and 0.7 ± 0.7 ppt (RF07). Unless otherwise noted, error bars reflect the variance in atmospheric variability, and retrieval errors with statistical leverage added in quadrature. The profiles also show variable structure through the lower and middle FT (2.0–9.5 km), with mean BrO mixing ratios of 0.5 ± 0.3 ppt (RF03), 1.0 ± 0.3 ppt (RF04), and 0.5 ± 0.2 ppt (RF07). In the upper FT and lowermost TTL (tropospheric air > 9.5 km), the mean BrO mixing ratios are 0.4 ± 0.2 ppt (RF03) and 0.6 ± 0.2 ppt (RF07).

The distribution of Br\textsubscript{y} species was modeled for each altitude grid point separately for the three profiles. Figure 2 show results for cases 0 and 2. The additional error from modeling is not immediately apparent in Fig. 2d, h, and l because the 30 % error contribution (Sect 2.3.1) is relatively small compared to the error in the BrO measurements (mean proportional error of 54 %). Here we present results for case 0, leaving the other cases for the sensitivity study presented in Sect. 3.3. The profiles contain significant structure in aerosol SA, humidity, and O\textsubscript{3}, which can be characterized in the context of the HCR1-3 regimes outlined in Sect. 2.3.1. HCR1 applies at altitudes above 7–10 km, while HCR3 dominates in the lower troposphere. The chemistry transitions from HCR3 to HCR2, and from HCR2 to HCR1, occur at 8.0 and
10.0 km (RF03), 6.0 and 7.0 km (RF04), and 5.5 and 9.0 km (RF07), respectively. The mean ratio \( \text{BrO} / \text{Br}_y \) from the surface through the mid-FT (< 9.5 km) is 0.24 ± 0.05 (RF03), 0.18 ± 0.03 (RF04), and 0.21 ± 0.05 (RF07). The inferred \( \text{Br}_y \) in the MBL and TL (< 2.0 km) is 4 ± 2 ppt (RF03), 9 ± 3 ppt (RF04), and 4 ± 3 ppt (RF07). All three flights have \( \text{Br}_y \) minima in the lower to mid-FT (2.0–9.5 km), for which the mean \( \text{Br}_y \) is 2 ± 1 ppt (RF03), 4 ± 1 ppt (RF04), and 2 ± 1 ppt (RF07).

In the lower troposphere, bromine chemistry resides in the HCR3 regime. There is significant variability in the \( \text{BrO} / \text{Br}_y \) ratio, which can be explained by the factors most important to HCR3 partitioning: humidity and \( \text{O}_3 \). Average water vapor mixing ratios below 6.5 km are 1.08 % (RF03), 1.28 % (RF04), and 0.97 % (RF07) and the mean \( \text{O}_3 \) is 30 ppb (RF03), 25 ppb (RF04), and 33 ppb (RF07). The higher humidity favors HOBt over \( \text{BrO} \) in RF04 compared to RF03 and RF07. Lower \( \text{O}_3 \) in RF04, particularly in two filaments with \( \text{O}_3 \) below 20 ppb between 1–2 and 3–4 km, further compounds the difference with the other two flights and drives \( \text{BrO} / \text{Br}_y \) to even lower values.

In the mid-FT, bromine chemistry resides in the HCR2 regime. The decreasing SA with altitude allows HBr to be an increasingly important reservoir (i.e., heterogenous processing of HBr becomes slow) and drives down the computed value of \( \text{BrO} / \text{Br}_y \). In parallel, the trends in HCR3 chemistry from below continue in the mid-FT; i.e., \( \text{BrO} \) is increasingly favored over HOBt as [\( \text{H}_2\text{O} \)] decreases and J_{HOBt} increases, and the \( \text{BrO} / \text{Br}_y \) ratio shifts toward \( \text{Br}_y \) as low temperatures and low \( \text{O}_3 \) slow \( \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \), and J_{HOBt} increases with altitude. Overall, \( \text{BrO} / \text{Br}_y \) remains roughly constant at 0.30 ± 0.07 (RF03), 0.23 ± 0.02 (RF04), and 0.17 ± 0.03 (RF07). The mean surface area in RF03 is ~3 times that in RF04, and RF07, driving the higher average value of the \( \text{BrO} / \text{Br}_y \) ratio. The variability in \( \text{BrO} / \text{Br}_y \) in RF03 and RF07 is also driven by greater variability in SA, which is relatively constant at these altitudes in RF04.

HCR1 applies in the upper FT and TTL, where HBr is the primary reservoir species of \( \text{Br}_y \). The \( \text{BrO}_x / \text{Br}_y \) ratio is low, almost constant in the box model at these altitudes, with values of 0.10 ± 0.01 (RF03) and 0.09 ± 0.02 (RF07). The \( \text{BrO}_x \)–reservoir equilibria are relatively stable; changes in the \( \text{BrO} / \text{Br}_y \) ratio result from displacements of the \( \text{Br} / \text{BrO} \) partitioning. Observed mixing ratios of \( \text{O}_3 \) are low – decreasing from 26 ppb at 9 km to 18 ppb at 12.5 km in RF03, and varying between 23 and 24 ppb over the same altitudes in RF07, before dropping to 18 ppb at 14 km. Temperature decreases from 248 K at 9 km to 223 K at 12.5 km in RF03 and from 250 to 222 K over the same altitudes in RF07 then further to 213 K at 14 km. Measured J_{HOBt} continues to increase with altitude. In the upper FT, the \( \text{BrO} / \text{Br}_y \) ratio is ~1, while in the TTL \( \text{BrO} \) is reduced to as little as 28 % of \( \text{BrO}_x \), yet \( \text{BrO} \) remains well above the DOAS detection limit. Note that \( \text{BrO} \) is flat or only mildly increasing in the upper FT and TTL. However, the decrease in \( \text{BrO} / \text{Br}_y \) drives an increase in \( \text{Br}_y \) from 2.1 ppt at 9 km to 5.6 ppt at 12.5 km, with a maximum of 7.2 ppt \( \text{Br}_y \) at 11 km (RF03), and 3.6 ppt at 9 km to 12.8 ppt at 14 km (RF07).

### 3.2 TTL and LS

The \( \text{BrO} \) mixing ratios during flight track legs flown at a level altitude were retrieved using the parameterization technique outlined in Dix et al. (2016), as described in Sect. 2.1.2. Figures 3 and S5 show a number of tracers used to define the TTL and LS during RF06 and RF15. These are simplified into four regimes with simple, single-variable definitions that allow separation for ease of examination. The LS is defined as air above 12.5 km and \( \text{O}_3 > 200 \text{ ppb} \), and the TTL is above 12.5 km and \( \text{O}_3 < 200 \text{ ppb} \).

As can be seen in Fig. 3, the LS defined in this way is poleward of the jet stream and is characterized by consistently low \( \text{H}_2\text{O} \) and \( \text{CO} \), and high \( \text{O}_3 \) varying between 200 and 900 ppb. The transition from the TTL to the LS is marked by greatest \( \text{O}_3 \), above the levels found elsewhere in the stratosphere. CFCC-11, not shown in Fig. 3, is below 230 ppt in the stratosphere. The LS is further divided into the middleworld LS and overworld LS. The division from Hoskins (1991) of 380 K potential temperature (\( \theta \)) is slightly modified to 377 K to obtain two contiguous regions (Fig. 3a). The transition from the middleworld to the overworld is also marked by high \( \text{O}_3 \), much like the LS entrance and exit.

The TTL is divided into the convective TTL defined as air masses with \( \text{H}_2\text{O} / \text{O}_3 > 0.1 \text{ ppm ppb}^{-1} \) and the aged TTL where \( \text{H}_2\text{O} / \text{O}_3 < 0.1 \text{ ppm ppb}^{-1} \). Observations from the profiling case studies are all in the convective TTL by these criteria. This is to be expected, given that the profiles are in the western Pacific warm pool, where convection to 15 km and above is persistent. The GV can only probe the TTL closer to the tropopause through latitudinal transects where the relevant region is at lower altitude. Figure S6 compares this classification to tracer–tracer classifications of the TTL from other works. The left panel uses the definition from Pan et al. (2014) as proxy for the TTL: [\( \text{H}_2\text{O} \)] > [\( \text{H}_2\text{O} \)]_stratospheric and [\( \text{O}_3 \)] > [\( \text{O}_3 \)]_stratospheric. Using this definition, the convective TTL as defined here includes high-altitude tropospheric air and the aged TTL includes stratospheric air. The right panel correlates [\( \text{CO} \)] and [\( \text{O}_3 \)] examining CONTRAST RF15, as done in Chen et al. (2016). The aged TTL as defined in this work is nearly equivalent to the TTL-LMS (tropical tropopause layer–lowermost stratosphere) transition defined in Chen et al. (2016); i.e., [\( \text{CO} \)] is correlated with [\( \text{O}_3 \)] with a slope of ~0.4. Exceptions to this are that portions of the convective TTL, and a mid-FT filament (RF07), fall on the same line (would be TTL-LMS in Chen et al., 2016), and portions of the aged TTL (RF06, RF15) organize as parallel lines with slopes of ~0.03, which would classify as stratospheric in Chen et al. (2016).

As the tracer–tracer correlations make apparent, the aged TTL is characterized by \( \text{O}_3 \), \( \text{H}_2\text{O} \), and \( \text{CO} \) changing in con-
Figure 3. Meteorological and chemical tracers during RF15. (a) (Red) horizontal wind speed; (black) potential temperature (θ). The subtropical jet stream is visible where the horizontal wind maxima have tropospheric and stratospheric halves (indicated by arrows). The black arrow indicates the overworld (here: θ above 377 K). (b) (Red) O₃; (blue) H₂O. The troposphere–stratosphere transition is marked at 200 ppb O₃. Positive departures in H₂O mark convective air masses. (c) (Green) CO; (blue) H₂O / O₃ ratio. The 0.1 ppm ppb⁻¹ line is used to separate the aged TTL from the convective TTL. The times marked indicate the transitions (from left to right) 01:01 convective TTL to aged TTL, 01:35 aged TTL to middleworld LS, 02:32 middleworld LS to overworld LS, 03:25 overworld LS to aged TTL, and 04:21 aged TTL to convective TTL.

Bromine in the jet-crossing case studies

Comparing Figs. 4 and S7 to Fig. 2, the mean BrO 0.53 ± 0.08 ppt (RF06) and 1.01 ± 0.08 ppt (RF15) in air recently impacted by convection (H₂O / O₃ > 0.3 ppm ppb⁻¹) was similar to that observed at the highest altitudes in RF03 and RF07. Again, as in Fig. 2, the error from modeling is not always apparent in Figs. 4e and S7d (see Sect. 2.3.1). Chemically, Br₂ partitioning was characterized as HCR1 (see Sect. 2.3.1), HBr dominated Br₂, and Br made up the majority of BrO. This drove BrO / Br₂ down to 0.12 ± 0.01 (RF06) and 0.13 ± 0.03 (RF15) (compared to 0.10 ± 0.01 at 12.5 km in RF03 and 0.09 ± 0.02 at 14.0 km in RF07). The inferred Br₂ in turn was 4.3 ± 0.5 and 7.9 ± 1.3 ppt for RF06 and RF15 in the TTL influenced by recent convection.

Portions of the convective TTL nearer to the aged TTL, including the convective TTL transition (see Sect. 3.2) in RF06, had more BrO, 0.9 ± 0.1 ppt (RF06) and 1.1 ± 0.5 ppt (RF15). This region included a rapid increase in aerosol surface area and ozone as the aircraft moved into lower stratospheric air. The increased SA lead to a transition from HCR1 to HCR2; however, the higher O₃ in the TTL gives rise to a higher BrO / Br₂ compared to that of the mid- and upper FT. Overall, BrO / Br₂ rose (RF06: 0.18 ± 0.05; RF15: 0.30 ± 0.12) and more than compensated for the increase in BrO, and as a result inferred Br₂ stayed largely flat at 4.2 ± 0.6 ppt (RF06) and 4.4 ± 0.5 ppt (RF15).

Moving to the aged TTL in Figs. 4 and S7, BrO concentrations were elevated relative to the convective TTL (1.0 ± 0.2 ppt RF06 and 1.6 ± 0.1 ppt RF15). The greatest BrO mixing ratios in RF15 were observed nearest the stratosphere, since RF06 never reached the stratosphere this may in part explain the higher mean in RF15. Elevated O₃ caused BrO to dominate BrO₂. However, the high O₃ coupled with increased NO₂ caused BrONO₂ to make up to 20% of day-
time Br$_y$ for case 0, while BrONO$_2$ is converted to HOBBr for the cases including efficient recycling. This had a limiting effect on BrO / Br$_y$ as illustrated in Fig. S4. Chemical uncertainty in these air masses is driven by this increase in BrONO$_2$, see also Sect. 3.3. BrO / Br$_y$ is high in the aged TTL (0.466 ± 0.008 in RF15), giving an inferred Br$_y$ of 2.0 ± 0.3 ppt Br$_y$ (RF06) and 3.49 ± 0.17 ppt (RF15). A contributing factor to this difference may again be that the highest Br$_y$ values in RF15 are observed nearest the stratosphere, a region that RF06 did not sample.

BrO was observed to rise rapidly upon entering the stratosphere during RF15, i.e., from 1.97 ± 0.12 to 2.90 ± 0.16 ppt in the middleworld. Though the middleworld changes in BrO paralleled changes in O$_3$, but Br$_y$ partitioning could not explain these changes. Instead, the BrO / Br$_y$ ratio was rather constant at 0.44 ± 0.03. In the middleworld, O$_3$ and NO$_2$ mixing ratios were both higher than in the aged TTL, which caused BrONO$_2$ to be competitive with HOBBr as a daytime reservoir species. Consequently the modeled BrO / Br$_y$ ratio is suppressed with increasing O$_3$, which is consistent with Fernandez et al. (2014). Figure S4, illustrates that the magnitude of this suppression is strongest when SA is high, as is the case in the middleworld LS.

Following the climb into the overworld at the northern most point, the mean BrO slightly increased to 3.15 ± 0.13 ppt, and the largest mixing ratio of 3.35 ppt BrO (5 min average, 3.78 ppt is the 30 s maximum) was observed. Chemically, conditions were similar to the middleworld, BrONO$_2$ essentially replaced HOBBr as a reservoir for Br$_y$, and the BrO / Br$_y$ ratio remains flat. The small variations in BrO were mirrored by corresponding variations in BrO / Br$_y$ leading to a consistent Br$_y$ of 7.2 ± 0.6 ppt, without any overall trend in the overworld.

### 3.3 Box model sensitivity studies

The BrO-inferred Br$_y$ estimates from the box model sensitivity studies (Table 3, Sect. 2.3.1) are summarized in Table 4. For detailed results from each model case see Table S3. Broadly, for case 0 in the lower FT (< 6.5 km), aged TTL, and stratosphere, the SA is high enough to remove HBr in the box model. As a consequence, Br$_y$ estimates are insensitive to further increases in SA, and the BrO / Br$_y$ ratio is solely determined by gas-phase chemistry. In contrast, between 6.5 and 13.5 km the inferred Br$_y$ is sensitive to assumptions about the available SA and heterogeneous chemistry. The higher SA of case 1 leads to higher BrO / Br$_y$ ratios...
Table 4. Summary of BrO and Br$_y$ mixing ratios over the tWPO.

<table>
<thead>
<tr>
<th>Altitude</th>
<th>BrO ppt$^a$</th>
<th>Br$_y$ ppt$^b$</th>
<th>pooled</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>case 0</td>
<td>case 1</td>
<td>case 2</td>
</tr>
<tr>
<td>MBL, 0–0.5 km</td>
<td>1.7 (1.0, 3.8)</td>
<td>13.8</td>
<td>13.8</td>
</tr>
<tr>
<td>TL, 0.5–2.0 km</td>
<td>0.7 (0.4, 0.9)</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Lower FT, 2.0–6.5 km</td>
<td>0.6 (0.5, 1.0)</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Mid-FT, 6.5–9.5 km</td>
<td>0.6 (0.3, 0.7)</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Upper FT, 9.5–12.5 km</td>
<td>0.9 (0.5, 1.1)</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Convective TTL$^c$</td>
<td>3.1 (2.8, 3.2)</td>
<td>6.9</td>
<td>6.9</td>
</tr>
</tbody>
</table>

$^a$ BrO is reported as follows: median (1st quartile, 3rd quartile). $^b$ Br$_y$ values are the medians for each of the chemical cases, the “pooled” values report the median (1st quartile, 3rd quartile) for cases 0, 1 and 2. Air masses above 12.5 km are classified as follows: $^c$ Convective TTL H$_2$O / O$_3$ < 0.1 ppm ppb$^{-1}$. $^d$ Aged TTL H$_2$O / O$_3$ < 0.1 ppm ppb$^{-1}$. $^e$ LS O$_3$ > 200 ppt.

Assumptions about reaction probabilities on surfaces, $\gamma$, also play a role; SA and $\gamma$ are indistinguishable and the product of SA $\times$ $\gamma$ determines many heterogeneous reaction rates. The box model does not represent washout, and this too is indistinguishable from SA and $\gamma$ as the total Br$_y$ burden in the FT and above is the net result of the competition between Br$_y$ sources, washout, and the heterogeneous reaction rates for BrONO$_2$, HBr, and HOBr.

When moving from case 0 to case 1, the altitude at which HCR3 shifts into HCR2 increases to higher altitudes, i.e., from 8.0 to 9.5 km (RF03), 6.0 to 8.0 km (RF04), and 5.5 to 9.5 km (RF07). The transition from HCR2 to HCR1 is not encountered in case 1 during RF03 and RF04, but it is observed for RF07 (the altitude of this transition shifts from typically 10.5 km, case 0, to 12.0 km, case 1). The convective TTL during both jet-crossing flights (which in case 0 is HCR1 and HCR2) shifts to HCR2 and HCR3 in case 1, with implications for the sensitivity to infer gas-phase Br$_y$.

The remaining HCR2 air masses are those with the greatest H$_2$O / O$_3$ ratio, i.e., those that have the most convective character and are most similar to the upper FT.

In case 2, ice greatly increases SA and has the further effect of converting BrONO$_2$ to HOBr. The presence of ice shifts heterogeneous chemistry to higher SA than shown in Figs. 5 and S4, and all air moves into the HCR3 regime in the box model. Case 2 has no effect on Br$_y$ estimates at altitudes below 6 km (no ice observed), and no significant effect in the aged TTL. A minor effect to increase the BrO / Br$_y$ ratio is visible in the upper FT and convective TTL in Fig. S8 (cyan whiskers). Note that within case 2, BrO$_x$ represents more than 80 % of total Br$_y$, a fraction that increases as ambient ozone is reduced (Fig. S4). Under these conditions, the ratio Br / BrO > 1 and atomic bromine becomes the dominant Br$_y$ species within the convective TTL (see Figs. 2c, k.
Figure 6. Tropospheric vertical profiles of BrO and Br$_y$ over the tWPO and comparison with global models. Boxes and whiskers are for BrO observations (black) and inferred Br$_y$ (red; box-model cases 0, 1, and 2). Boxes indicate the 25th and 75th percentile, whiskers the 5th and 95th percentile. Data points from the LS and aged TTL have been removed here to avoid bias, and emphasize tropospheric data. Lines indicate median global model profiles; the dashed magenta lines indicate the 5th and 95th percentile for CAM-Chem.

Kreycy et al. (2013), proposed that BrONO$_2$ is relatively unstable, and recommend increasing BrONO$_2$ photolysis and decreasing BrONO$_2$ formation. Because ice similarly disrupts BrONO$_2$ both effects are included in case 3 to determine the maximum combined effect on BrONO$_2$. No discernible impact on Br$_y$ is found for tropospheric air masses, and only a minor impact is visible in the stratosphere for the case studies of this work. The impact on Br$_y$ partitioning in the stratosphere is visible in Fig. 4; however, the impact on BrO / Br$_y$ can be difficult to discern. In the TTL BrO / Br$_y$ increases by 2.9–6.5 % over case 0, and 1.5–3.1 % over case 2. The impact is greater in the aged TTL and hence greater in RF15 than RF06. The effect in the stratosphere is an increase in BrO / Br$_y$ by 5.5–7.1 %, leading to a slight reduction in the inferred Br$_y$. Since BrO / Br$_y$ is $\sim$ 50 %, the change in leverage is minimal, and the effect on inferred Br$_y$ is not significant.

4 Discussion and atmospheric implications

4.1 Tropospheric BrO and Br$_y$

The overall median tropospheric BrO and Br$_y$ profiles are shown in Fig. 6. These profiles exhibit a C-shaped profile characteristic of convective transport (Kley et al., 1996; Pan et al., 2017). To our knowledge, these are the first observations of C-shaped profiles for tropospheric inorganic bromine species (MBL into the convective TTL). The data are further summarized in Table 4. The median BrO profile decreases with altitude, from an MBL median of 1.72 ppt to a minimum around 0.5 ppt in the mid- to upper FT, and increases again in the convective TTL (see Fig. 6 and Table 4).

The trends in Br$_y$ for the simulation case 1 (red in Fig. S8) are similar to those for BrO. Br$_y$ decreases from a MBL median of 13.8 ppt toward a minimum of 1.6 ppt in the mid-FT where Br$_y$ is roughly constant with altitude. Br$_y$ begins to increase in the uppermost portion of the upper FT and reaches a local maximum in the convective TTL of 3.3 ppt. However, unlike BrO (which increases from the convective TTL to the aged TTL) gas-phase Br$_y$ decreases from the convective TTL to the aged TTL, as is further discussed in Sect. 4.2 below (see also Fig. 7).

The box model sensitivity study medians are summarized in Table 4, and a comprehensive summary for all cases is given in Table S3. As seen in Fig. S8, a common feature to all model results is the C-shaped profile in Br$_y$, which is most pronounced in case 0, and least pronounced in case 2. The estimated Br$_y$ concentration is most sensitive to chemical assumptions in the mid- and upper FT, as well as in the convective TTL, and responds sensitively to the available SA and assumptions about heterogeneous reaction rates that recycle bromine. Case 0 (grey in Fig. S8) has significantly more Br$_y$ in all three regions, but especially in the upper FT, where the inferred Br$_y$ is 3–5 times higher in case 0 compared to cases 1 and 2. Indications of an artificially high bias in Br$_y$ for case 0...
Figure 7. Br$_{y}$ vertical structure in the UTLS; (colored circles) Br$_{y}$ from box-model case 1; the color represents different air mass types. (grey squares) case 0; (grey triangles) case 3. Tracer correlations with (a) CFC-11, (b) potential temperature, and (c) H$_2$O/O$_3$ ratio have been constructed such that the top is more stratospheric, while the bottom is tropospheric. The dashed lines in (b) and (c) indicate separation between data from profiling and jet-crossing case studies – the data are inseparable in panel (a).

arise from a step change in the Br$_{y}$ vertical distribution between 12 and 13 km altitude (case 0). No similar step change is observed for model cases 1 and 2, which show a gradual and smooth Br$_{y}$ increase from the mid-FT into the convective TTL. A previous optical closure study had revealed a low-bias in the UHSAS measured aerosol SA for reasons that are currently not well understood (Volkamer et al., 2015), which can lead to a high bias in inferred Br$_{y}$ in the upper FT unless corrected (Wang et al., 2015). The step change in the Br$_{y}$ profile for case 0 shown in Fig. S8, and the continuous behavior exhibited in case 1, provides corroborating evidence that SA is more accurately represented in case 1. The median Br$_{y}$ from case 1 has thus been listed in Table 4. Case 2 (cyan in Fig. S8) has overall less Br$_{y}$ in the mid- and upper FT, and TTL than case 1, and likely represents a lower limit for Br$_{y}$.

If heterogeneous bromine recycling on the much larger ice SA is as effective as on aerosols, the potential impact of ice shifts the Br$_{y}$ minimum from the mid-FT into the upper FT. The differences in Br$_{y}$ from cases 1 and 2 are smaller than 0.5 ppt in the convective and aged TTL, as is indicated by the 1st quartiles in Table 4, and further discussed in Sect. 4.2.

4.2 Br$_{y}$ structure in the UTLS

Figure 7 shows inferred Br$_{y}$ against different tracers of the stratosphere and troposphere. Colored points show case 1, grey squares case 0, and grey triangles case 3. Figure 7a has vertically decreasing CFC-11 as an indicator of stratospheric photochemical processing. Fig. 7b, shows increasing $\theta$ indicating the stable vertical positions of different air masses locally, and Fig. 7c shows decreasing H$_2$O/O$_3$ on a logarithmic scale as an indicator of increasing stratospheric and decreasing tropospheric character. Thick dashed lines separate data from the jet-crossing and profiling case studies; trends continue smoothly across the separation. Consistently in Fig. 7, there is significant variability in the Br$_{y}$ across the tropospheric–stratospheric interface. A distinct minimum in gas-phase Br$_{y}$ is visible in the aged lower TTL, and Br$_{y}$ increases both towards lower and higher altitudes, i.e., with decreasing CFC-11 (Fig. 7a), increasing $\theta$ (Fig. 7b), and decreasing H$_2$O/O$_3$ ratio (Fig. 7c). Figure 7a shows the correlation of Br$_{y}$ against CFC-11, a tracer of photochemical age. CFC-11, similar to long-lived bromocarbons, does not photolyse significantly in the troposphere, where the mixing ratio is constant at about 237 ppt (Carpenter et al., 2014). TTL data has CFC-11 levels that are tropospheric or very near tropospheric, and the convective and aged TTL cannot be separated by CFC-11. This suggests that the aged TTL contains mostly tropospheric air, and contributions from the stratosphere are small. The photochemical liberation of Br$_{y}$ from bromocarbons, including VSLS, in the aged TTL is indistinguishable from the variance in the convective inputs. CFC-11 decreases in the middleworld, consistent with the inferred Br$_{y}$ increase. This matches the expected behavior as long-lived bromocarbons and possibly VSLS are photolysed along with CFC-11, liberating Br$_{y}$. However, this correlation does not extend into the overworld, where despite greater depletion of CFC-11 the Br$_{y}$ expected to result from bromocarbon photolysis is not observed. Notably, gas-phase Br$_{y}$ does not include aerosol bromide, which is unconstrained by CONTRAST observations. Gas-phase Br$_{y}$ is not a conservative quantity, rather it is a lower limit of total bromine in the UTLS.

Taking [CFC-11] = 237 ppt as the definition of the tropopause, the gas-phase inorganic Br$_{y}$ injected into the
stratosphere – the PGI – is found to be $2.6 \pm 0.6$ ppt Br$_y$ for case 1. The slope of the Br$_y$–CFC-11 correlation fitted for all data is 0.15 $\pm$ 0.03. The middleworld points with 210 ppt < [CFC-11] < 230 ppt show the clearest correlation, with a slope of 0.22 $\pm$ 0.01. Assuming no other source or sink for Br$_y$, this indicates that on average CBr$_y$ liberates Br$_y$ at 0.15 (and up to 0.22) the rate of CFC-11 decay in the stratosphere. Modeling of sea-salt-derived Br$_y$ in the troposphere without any contribution from organics suggests such sources are responsible for 2 $\pm$ 1 ppt Br$_y$ in the TTL (Long et al., 2014). Additionally, previous CAM-Chem sensitivity studies determined that the contribution of sea-salt-derived bromine to the lower TTL was small (< 0.5 ppt) for the global-mean TTL (equivalent to the aged TTL here), but represented more than 3.6 pptv within strong convective regions such as the (middleworld) (compare blue and grey triangles in Fig. 7), which is fundamentally a model-model comparison. However, significant information can be gleaned by leveraging the constraints on the box model and the representation of transport processes in the global models. Table 5 compares the corresponding partial and total tropospheric BrO VCDs. Examining the latter, the observations have a median value of 1.65 $\times$ 10$^{13}$ molec cm$^{-2}$, while CAM-Chem predicts about 25 $\%$ of this value (0.41 $\times$ 10$^{13}$ molec cm$^{-2}$). GEOS-Chem without SSA source that predicts 55 $\%$ or 0.91 $\times$ 10$^{13}$ molec cm$^{-2}$, the closest to the observed value is GEOS-Chem with the SSA source predicts 125 $\%$ or 2.07 $\times$ 10$^{13}$ molec cm$^{-2}$.

In the MBL, the high concentrations of BrO observed and inferred Br$_y$ are intermediate between the GEOS-Chem simulations including and excluding the SSA Br$_y$ source. The 95th percentile trace of CAM-Chem further illustrates that CAM-Chem captures instances where BrO is above 4 ppt near the surface, though examination of the specific case studies reveals it does not match the location of observations. GEOS-Chem roughly reproduces the near-surface vertical distribution of both BrO and Br$_y$ with a TL partial VCD roughly twice that in the MBL (Table 5). For both BrO and Br$_y$ when a SSA bromine source is excluded, the decrease with altitude is greater than observed, while the reverse is true when the SSA source is included; some intermediate profile seems to best reproduce the observations.

In the FT, the model simulations shown in Fig. 6 exhibit a high degree of variability. However, the variability in the observations spans a similar range. In the lower FT, the median observed BrO is between 0.6 and 0.9 ppt, and is larger than predicted by global models, which show less than 0.5 ppt between 2 and 5 km (Fig. 6a). Continuing up through the FT, the CAM-Chem median approximates the BrO and Br$_y$ profile shapes reasonably well in the mid-FT, but follows the low end of the BrO observations, while tracking median box-modeled Br$_y$. As the 5th percentile and median CAM-Chem profiles in Fig. 6 help illustrate, CAM-Chem often has almost no BrO in the FT. GEOS-Chem shows significant enhancements of BrO and Br$_y$ in the mid-FT, which are not observed. In the upper FT, consistent with the results from Wang et al. (2015), a SSA source best reproduces the median BrO observations. Furthermore, two global models with SSA source differ in their Br$_y$ predictions in the upper FT by a factor of 3–4, bracketing the box-model-inferred Br$_y$. While excluding the SSA source from GEOS-Chem reproduces inferred Br$_y$ in the mid-FT, it does not show the increase in inferred Br$_y$ in the upper FT and convective TTL. Revisions to the ozone-induced source of HOBr from aerosol bromide at the air–water interface (Artiglia et al., 2017) – which is partic-

4.3 Comparison with global models

Observed BrO and inferred Br$_y$ in different portions of the atmosphere, as summarized in Table 4, are compared to output from GEOS-Chem and CAM-Chem global models in Fig. 6. Br$_y$ from the experimentally constrained box-model estimates is compared with chemistry climate models, this is fundamentally a model-model comparison. However, significant information can be gleaned by leveraging the constraints on the box model and the representation of transport processes in the global models. Table 5 compares the corresponding partial and total tropospheric BrO VCDs. Examining the latter, the observations have a median value of 1.65 $\times$ 10$^{13}$ molec cm$^{-2}$, while CAM-Chem predicts about 25 $\%$ of this value (0.41 $\times$ 10$^{13}$ molec cm$^{-2}$). GEOS-Chem without SSA source that predicts 55 $\%$ or 0.91 $\times$ 10$^{13}$ molec cm$^{-2}$, the closest to the observed value is GEOS-Chem with the SSA source predicts 125 $\%$ or 2.07 $\times$ 10$^{13}$ molec cm$^{-2}$.

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ularly important in the tropical upper troposphere (Schmidt et al., 2016; see Sect. 4.5) – might explain the difference in behavior by global models.

In the TTL, GEOS-Chem (with and without the SSA source) shows some increase in BrO and Br$_2$, at the highest altitudes, but only after a minimum in the same region. CAM-Chem does not show this increase in the median, though the 95th percentile makes it transparent that elevated BrO is predicted in certain instances. CAM-Chem includes an explicit representation of the stratosphere, and as a result captures more of the variability in the UTLS (not included in Fig. 5). Examination of CAM-Chem model output versus $\theta$ (Fig. S9) reveals a gas-phase Br$_y$ minimum, albeit at lower $\theta$ (~350 K) and with less Br$_2$ (1.2 ppt) than observed. As in Fig. 4, the CAM-Chem output with highest Br$_y$ is more consistent with observations. Notably, CAM-Chem modeling of iodine chemistry (which has some similarities) has predicted a local minimum in gas-phase inorganic iodine in the TTL (Saiz-Lopez et al., 2015), consistent with observations (Volkamer et al., 2015; Dix et al., 2016).

Notably, while both BrO and Br$_2$ are broadly consistent, partitioning of Br$_2$ is different between the box-model and global models. The greatest difference is for HBr, where the tropospheric column abundance differs by over a factor of 15 over the total column, as shown in Table S2. Broadly, GEOS-Chem has more BrONO$_2$ and HBr, and less HOBr compared to the box model. When the SSA bromine source is excluded the BrO / Br$_2$ ratio roughly matches as the different components cancel out (visible as the BrO and Br$_2$ comparing similarly in Fig. 6a and b). Furthermore, O$_3$ is slightly higher in GEOS-Chem than observed, resulting in a greater BrO / Br$_2$ ratio. In CAM-Chem, however, Br$_2$ partitioning is broadly similar to the box model, with the key exception of HBr. The larger amount of HBr in CAM-Chem is responsible for the agreement in Br$_2$ in the FT, despite underestimating BrO observations. GEOS-Chem with a SSA source also has substantially more HBr near the surface, significantly lowering the BrO / Br$_2$ ratio. Notably, the additional HBr in GEOS-Chem falls off more rapidly with altitude than in CAM-Chem, suggesting that transport, recycling, and/or washout are different between the global models. These differences manifest differently in the TTL, where HBr falls off more rapidly in CAM-CHEM than in GEOS-Chem. As Table S2 highlights, only in the upper FT (HCR1) is HBr in the global models consistent with that in the box model. This further reinforces the strong impact of uncertainties in HBr heterogeneous chemistry when coupled to transport and washout.

### 4.4 Comparison with other studies

Tropospheric measurements of BrO and other Br$_2$ species were obtained by two CIMS instruments over the IWOPO during the same period as the AMAX-DOAS measurements described above. The Georgia Tech CIMS (GT CIMS) was on the same GV platform as the AMAX-DOAS and measured BrO and Br$_2$ + HOBr, with results summarized in Chen et al. (2016). There was no overlap between the tropospheric case studies presented here and those in Chen et al. (2016); the CIMS had calibration challenges for early flights, while cloudy conditions precluded AMAX-DOAS retrievals for later flights. The Manchester University CIMS (MU CIMS) was aboard the British Aerospace 146 (BAe-146) aircraft as part of the Coordinated Airborne Studies in the Tropics (CAST) project (Harris et al., 2017). During CAST, the BAe-146 had a ceiling altitude of 9 km on flights between and out of Guam, Chuuk, and Palau (Koror) which are indicated in Fig. 1. The MU CIMS sampled the troposphere during CAST in broadly the same region as the tropospheric case studies presented for the AMAX-DOAS during CONTRAST. Measurements from the MU CIMS cover BrO, Br$_2$, BrCl, and HOBr, all reported separately (Le Breton et al., 2017).

A comparison of tropospheric data from the AMAX-DOAS and the two CIMS instruments is presented in Fig. S10. The GT CIMS has a detection limit of ~1 ppt for BrO, which is substantially higher than that of MU CIMS and AMAX-DOAS. The BrO measured by MU CIMS and AMAX-DOAS is below the GT CIMS detection limit of greater than 75–90% of the time for altitudes between 2 and 12.5 km. There are no GT CIMS measurements below 1 km, where AMAX-DOAS shows significant variability for BrO. While AMAX-DOAS mostly samples clear-sky con-

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**Table 5. Comparison of partial and total tropospheric BrO VCDs measured by AMAX-DOAS with different models. Values in parentheses indicate the 1st and 3rd quartile.**

<table>
<thead>
<tr>
<th>Altitude</th>
<th>BrO VCD \times 10^{12} (AMAX-DOAS measurements)</th>
<th>BrO VCD (GEOS-Chem no SSA source)</th>
<th>BrO VCD (GEOS-Chem with SSA source)</th>
<th>BrO VCD (CAM-Chem)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBL</td>
<td>2.1 (1.2, 4.7)</td>
<td>1.0 (0.2, 1.5)</td>
<td>3.6 (0.5, 9.0)</td>
<td>0.2 (0.1, 0.6)</td>
</tr>
<tr>
<td>TL</td>
<td>4.0 (2.8, 7.3)</td>
<td>2.0 (0.8, 3.3)</td>
<td>6.1 (3.1, 10.6)</td>
<td>0.4 (0.2, 1.3)</td>
</tr>
<tr>
<td>Lower FT</td>
<td>5.7 (2.9, 6.8)</td>
<td>2.1 (1.2, 4.1)</td>
<td>4.5 (2.4, 8.0)</td>
<td>1.4 (0.7, 2.2)</td>
</tr>
<tr>
<td>Mid-FT</td>
<td>2.2 (1.4, 3.2)</td>
<td>2.7 (1.7, 3.8)</td>
<td>4.6 (3.3, 5.9)</td>
<td>1.1 (0.7, 1.6)</td>
</tr>
<tr>
<td>Upper FT</td>
<td>1.3 (0.7, 1.7)</td>
<td>0.8 (0.4, 1.6)</td>
<td>1.2 (0.6, 2.2)</td>
<td>0.5 (0.3, 0.9)</td>
</tr>
<tr>
<td>TTL</td>
<td>1.1 (0.8, 1.5)</td>
<td>0.6 (0.2, 1.4)</td>
<td>0.7 (0.2, 1.7)</td>
<td>0.5 (0.3, 1.0)</td>
</tr>
<tr>
<td>Troposphere</td>
<td>16.5 (9.6, 25.2)</td>
<td>9.1 (4.5, 15.8)</td>
<td>20.7 (10.1, 37.4)</td>
<td>4.1 (2.4, 7.6)</td>
</tr>
</tbody>
</table>
conditions, the GT CIMS was operating mostly during cloudy flights near convection. Such conditions favor the uptake of bromine into the condensed phase, and as a result the differences in the BrO measurements between these two instruments may in part reflect true differences in the sampled atmospheric conditions. Below 3.5 km AMAX-DOAS observes more BrO than the MU CIMS (Fig. S10a), though there is overlap in the distribution of observations. The MU CIMS does observe instances where BrO is high near the surface (Le Breton et al., 2017) corroborating the variability observed by the AMAX-DOAS. The AMAX-DOAS and MU CIMS data generally agree for BrO in the altitude range from 3.5 to 9.0 km (Fig. S10a). The measured Br$_y$ from MU CIMS (i.e., BrO + 2× Br$_2$ + HOBr + BrCl) is in rather good agreement with Br$_y$ inferred from AMAX-DOAS over the 3.5 to 9.0 km altitude range, providing support for the overall veracity of our study (Fig. S10b). There are no MU CIMS measurements above 9 km. In the TTL, the differences between the GT CIMS and AMAX-DOAS are not readily resolved. These discrepancies are unlikely explained by atmospheric variability as is discussed below.

Both the AMAX-DOAS and GT CIMS operated concurrently aboard the GV during the RF15 case study, where elevated BrO was expected due to sampling of the overworld. CAM-Chem suggests that there should be 1–2 ppt BrO just prior to entering the LS (01:15 UTC of Fig. 8), which is in excellent agreement with between 1.3 and 2.1 ppt BrO observed by AMAX-DOAS in the aged TTL. By comparison, the GT CIMS observes no significant BrO in the aged TTL. Notably, the lack of change in BrO is consistent with a Br$_y$ minimum; BrO would be expected to increase significantly by 25–150% for constant Br$_y$, given the change in physical and chemical conditions (see Fig. 5). Just prior to the entry into the stratosphere, GT CIMS reported 0.48 ± 0.58 ppt BrO, which is below the GT CIMS level of detection (0.6–1.6 ppt during RF15 for BrO; Chen et al., 2016), and significantly lower than both AMAX-DOAS and CAM-Chem. In the LS, GT CIMS BrO rapidly increases to ∼3.8 ppt BrO (averaged for 02:09–02:14 UTC). The AMAX-DOAS measurements also rise, but more modestly to 2.9 ppt during the same period. The discrepancies cannot be readily explained by horizontal inhomogeneity, the air probed by the AMAX-DOAS has near-complete turnover within 12 min along the straight-line flight path. Notably, the GT CIMS does not report data when [O$_3$] exceeds 480 ppb, owing to unrealistically high BrO that was measured, but is not trusted under such conditions. This data filter precludes a comparison of measurements in the remainder of the stratosphere.

First, tropospheric BrO profiles had recently been measured from aircraft over the ePPO during the TORERO field campaign (Volkamer et al., 2015). Tropospheric BrO VCDs from five case studies in pristine marine air showed sig-
significant variability (0.5–3.0 × 10^{13} \text{molec cm}^{-2}; \text{Volkamer et al., 2015; Wang et al., 2015}). Dix et al. (2016) examined the TORERO BrO data set more fully, and found a campaign median tropospheric BrO VCD of 1.8 × 10^{13} \text{molec cm}^{-2} (this median excludes measurements below detection limit, and thus may be an upper limit). This is similar to the tropospheric BrO VCD of 1.6 × 10^{13} \text{molec cm}^{-2} measured over the tWPO in this study. However, there are important differences in the tropospheric BrO profile shape between the tEPO and tWPO. While we find 37\% of the BrO below 2 km over the tWPO, no significant BrO had been observed in the MBL and TL over the tEPO during TORERO, where essentially all (> 95\%) BrO was located above 2 km in the FT (Dix et al., 2016; Volkamer et al., 2015; Wang et al., 2015). Decreasing BrO with altitude had previously been observed during the TORERO RF04 case study (Wang et al., 2015).

The overall TORERO data set supports observations of decreasing BrO in the lower TTL. The campaign mean BrO was 1.86 ± 0.16 ppt (95\% CI, \text{N} = 162) at 13.5 km, and decreased to 1.38 ± 0.16 ppt BrO (95\% CI, \text{N} = 78) at 14.5 km. This is consistent with 0.9 to 1.2 ppt BrO in the TTL measured here. As noted in Dix et al. (2016), this decreasing BrO with altitude is highly significant during TORERO, and not inconsistent with results by Werner et al. (2017) as discussed below.

DOAS observations of BrO have also been reported from the Global Hawk platform at high altitudes (14–18 km) over the tWPO and tEPO (Stutz et al., 2017; Werner et al., 2017). The retrieved composite profile has BrO increase gradually from 0.7 ppt at 14.5 km to 1.1 ppt at 16.5 km, then more rapidly to 3.6 ppt at 18.5 km. The consistency between Br\textsubscript{r} estimated from AMAX-DOAS of this work and the value of Br\textsubscript{r} from Werner et al. (2017) is illustrated in Fig. 9. Werner et al. (2017) utilize a criterion of CH\textsubscript{4} = 1790 ppm to separate “young” air with more CH\textsubscript{4} and “old” air with less. Applying this same criterion to the CONTRAST DOAS data reproduces the TTL–LS separation. Utilizing the 10 K \texttheta bins we find good agreement of Br\textsubscript{r} in the TTL. In the LS, there is a mismatch wherein the Global Hawk and GV sampled old air at different \texttheta. However, CH\textsubscript{4} concentrations span a similar range of 1690–1790 ppm indicating similar aging, and a general agreement for Br\textsubscript{r} is also found in the LS. Notably, Werner et al. do not show a significant Br\textsubscript{r} minimum in the TTL, probably due to the limited Global Hawk observations at \texttheta < 355 K, where such a trend is most apparent in our data. Moreover, the LS Br\textsubscript{r} inferred in the Northern Hemisphere LS are consistent with the Br\textsubscript{r} inferred under double tropopause conditions in the Southern Hemisphere mid-latitude LS (Wang et al., 2015). Finally, CAM-Chem shows good agreement with the Br\textsubscript{r} from the box model in this work below 340 K and above 360 K. However, between 340 and 360 K the model predicts systematically lower Br\textsubscript{r} than inferred. Navarro et al. (2015) have shown that the CAM-Chem VSLS are consistent with CONTRAST observations. The PGI injection of VSLS, which are important for predicting Br\textsubscript{r} profiles through the LS (Liang et al., 2010), are captured well by the model. The differences in the Br\textsubscript{r} profile shape through the TTL are therefore unlikely to be related to VSLS alone, but most likely require additional processes.

Elevated concentrations of BrO (up to 3 ppt) in pristine air masses over the tEPO (Dix et al., 2016; Volkamer et al., 2015; Wang et al., 2015), and above Florida (Coburn et al., 2016) most likely reflect a variable influence of bromine sources from the lower atmosphere (e.g., SSA) downwind of marine convection (Long et al., 2014; Schmidt et al., 2016). Interestingly, the source region of the TORERO flights observed deep convective outflow that originated over the tWPO warm pool in the area south of the CONTRAST study area, where we observe significant BrO in the MBL consistent with SSA bromine sources. This is in contrast to low upper limits of less than 0.5 ppt MBL-BrO over the tEPO (Mahajan et al., 2012; Volkamer et al., 2015). Atmospheric models that represent sea-salt sources consistently predict several ppt BrO over tropical oceans (Long et al., 2014; Ordóñez et al., 2012; Schmidt et al., 2016; Yang et al., 2005). This conundrum is a primary reason why recent state-of-the-art models such as GEOS-Chem have decided not to represent the sea-salt source of bromine in their default configuration (Sherwen et al., 2016). The BrO profiles measured...
during this study suggests that SSA is a significant source of bromine over the tWPO. The reason for the low BrO over the tEPO MBL (Volkamer et al., 2015; Wang et al., 2015) deserves further study.

4.5 Atmospheric implications

4.5.1 Relevance of halogens for atmospheric composition

Bromine is important for the oxidation of atmospheric mercury (Coburn et al., 2016; Goodsite et al., 2004; Holmes et al., 2006; Parrella et al., 2012), the destruction of ozone (von Glasow et al., 2004; Read et al., 2008; Saiz-Lopez and von Glasow, 2012; Schmidt et al., 2016; Simpson et al., 2015; Wofsy et al., 1975), and oxidative capacity. Recent first simultaneous measurements of BrO and IO over the entire height of the tropical troposphere (Volkamer et al., 2015) suggest that bromine and iodine together account regionally for 34% of column-integrated ozone loss over the tEPO (Wang et al., 2015). Globally, the impact of bromine and other halogens reduces the ozone burden between 10 and 18%, which is comparable to the ozone sink from the HO2 + O3 reaction (Saiz-Lopez et al., 2012, 2014; Sherwen et al., 2016, 2017b). Bromine oxidation of NOx is an important NOx sink, and contributes to ozone reduction by reducing the photochemical formation of ozone (Schmidt et al., 2016). Halogen chemistry is responsible for an 11% reduction in global average OH radical concentrations (Schmidt et al., 2016), and increases the atmospheric lifetimes of methane from 7.47 to 8.28 years (Sherwen et al., 2016). However, the most recent papers (Schmidt et al., 2016; Sherwen et al., 2016) do not consider the SSA source when estimating the impacts of bromine and other halogens in the troposphere. This suggests that the above impacts may be lower estimates, as our results strongly support the need for a SSA source in the lower marine atmosphere.

Knowledge of heterogeneous/condensed-phase reactions is rapidly evolving. Recent work has found that an improved implementation of the condensed-phase reaction of HOBr with S(IV) significantly inhibits recycling of HOBr and lowers the global gas-phase Bry burden by 50% (Chen et al., 2017). Our models are not optimized to include these condensed-phase reactions, but including these sinks for Bry would lower Bry estimates from global models in Fig. 6 (and Table 5). However, recent laboratory observations of surface-active BrO3− (primary ozonide; Artiglia et al., 2017) also support the important role of O3 reactive uptake for the heterogeneous recycling of gas-phase Bry, which is most relevant in the upper troposphere (Schmidt et al., 2016). The surface activity of the primary ozonide suggests that recycling of Bry to the gas phase may be in competition with bulk accommodation of HOBr and subsequent S(IV) chemistry, which would reduce the efficiency of Bry washout. Furthermore, the role of organic surfactants is unclear. If organics reduce the rate of heterogeneous recycling, our Bry estimates could be lower limits; if surfactants are neutral or accelerate heterogeneous reactions, our box-model-inferred Bry would be rather insensitive since HBr is only a very minor reservoir species already. The impact of uncertain heterogeneous chemistry is transparent from Fig. 5 (and Fig. S4), and most relevant in the altitude range between 6.5 and 14.5 km, where Bry inferred from BrO observations is sensitive to assumptions about heterogeneous chemistry, and estimated conservatively here. Uncertain heterogeneous chemistry is less relevant for our Bry estimates in the aged TTL and LS (where the BrO / Bry ratio is flat in Figs. 5 and S4). Future development of chemical transport and climate models needs to refine the representation of heterogeneous/multiphase reactions of halogens, which is currently highly simplified yet important to assess the impacts of heterogeneous halogen sources for atmospheric composition and climate.

4.5.2 Inorganic bromine sources

The choice by recent global models (Schmidt et al., 2016; Sherwen et al., 2016) to estimate halogen impacts only based on CBrx sources, i.e., without considering the SSA source, is justified by the ability to approximate the vertical profiles of BrO over the tEPO (Volkamer et al., 2015; Wang et al., 2015) reasonably well without a SSA source, and by the lack of any measurable BrO in the remote MBL over the tEPO (see Sect. 4.4). A key difference between profiles over the tWPO and tEPO is that significant BrO is measured in the aged TTL and LS (where the BrO / Bry ratio is flat in Figs. 5 and S4). Future development of chemical transport and climate models needs to refine the representation of heterogeneous/multiphase reactions of halogens, which is currently highly simplified yet important to assess the impacts of heterogeneous halogen sources for atmospheric composition and climate.
The mechanism driving the gas-phase Br$_y$ minimum in the aged TTL is currently not well known, and could have dynamical or chemical reasons. The contribution of bromine to ozone destruction is largest in the vicinity of the tropopause (Fernandez et al., 2014; Salawitch et al., 2005; Schmidt et al., 2016; Sherwen et al., 2016), and the observed reduction in gas-phase Br$_y$ in the aged TTL is likely to have a significant impact on ozone and OH that is relevant for the lifetime of brominated VSLS. The lifetime of VSLS in the TTL affects the ratio at which CBr$_x$ is injected into the stratosphere as organic source gases or inorganic product gases (Gao et al., 2014; Nicely et al., 2016; Rex et al., 2014). Since the complex structure of Br$_y$ in the TTL is only partially captured by a model like CAM-Chem, this suggests the need for further development and testing of models that dynamically couple the troposphere and the stratosphere.

5 Conclusions

We identify a gas-phase Br$_y$ minimum in the aged TTL that is robust to assumptions regarding heterogeneous chemistry. Single-tailed Wilcoxon–Mann–Whitney rank tests (Mann and Whitney, 1947; refer to supplement for details) suggest that Br$_y$ in the aged TTL is: (1) a local minimum (> 95% confidence), (2) lower than in the LS (> 99% confidence), and (3) lower than in the convective TTL and upper FT (> 96% confidence). To our knowledge, such a Br$_y$ minimum has not previously been observed or hypothesized.

The Br$_y$ minimum in the aged TTL is consistent with previous observations that BrO decreases from the upper FT into the lower TTL over the eastern Pacific Ocean (Dix et al., 2016), and with several recent Br$_y$ estimates in the LS over the subtropical and tropical Pacific (Wang et al., 2015; Stutz et al., 2017; Werner et al., 2017). The 2.7 ppt (2.4–3.0 ppt; 95% CI) gas-phase Br$_y$ inferred in the aged TTL minimum and the tropospheric intercept of the fit of Br$_x$ against CFC-11 (2.6 ± 0.6 ppt) constrain PGI into the stratosphere, and are in reasonable agreement with the latest World Meteorological Organization assessment of 1.1–4.3 ppt PGI (Carpenter et al., 2014).

Notably, a significant fraction of this Br$_y$ may be SSA-derived. It is furthermore currently unknown how much Br$_y$ is transported into the stratosphere as aerosol bromide, as all currently available quantitative assessments of Br$_y$ in the UTLS rely on measurements of gas-phase Br$_y$ species alone. The lack of quantitative aerosol bromine measurements leaves the total Br$_y$ budget in the UTLS open to speculation. Indeed, aerosol measurements show a local maximum in aerosol halogen signals in the UTLS (Froyd et al., 2010; Murphy et al., 2006; Murphy and Thomson, 2000). Together with the Br$_y$ minimum identified here, this suggests that the partitioning of bromine between the gas- and aerosol phases is significant and cannot be ignored. Whether this bromide is available for ozone destruction in the LS is currently unknown. The proportional contribution of bromine to ozone destruction is largest in the vicinity of the tropopause (Fernandez et al., 2014; Salawitch et al., 2005; Schmidt et al., 2016; Sherwen et al., 2016). A reduction in available bromine could thus have a significant impact on ozone in the TTL.

Our data provide evidence that a SSA-derived bromine source is necessary to reproduce the observed profiles of BrO and Br$_y$ near the surface (up to 3.5 km), and provides corroborating evidence that marine convection lofts a source of inorganic bromine into the upper FT (Wang et al., 2015). Sensitivity studies indicate that the inferred Br$_y$ is highly sensitive to assumptions about the rate of heterogeneous bromine recycling (depends on the surface area of ice/aerosols, among others) between 6.5 and 14.5 km, limiting reliable inferences of total gas-phase Br$_y$ in the upper FT.

Notably, two global models that include a SSA bromine source predict gas-phase Br$_y$ that differs by a factor of 6–12 in the MBL, and by a factor of 3–4 in the upper FT. The global models bracket the amount of Br$_y$ inferred from the box model. CAM-Chem, which dynamically couples the troposphere and stratosphere, qualitatively reproduces the tropospheric BrO profile shape, but underestimates the BrO VCD; it captures a Br$_y$ minimum in the TTL, though not quantitatively. GEOS-Chem with SSA has discrepancies in the profile shapes but best matches the measured BrO VCD. The most recent modeling estimates of the global impact of bromine (Schmidt et al., 2016; Sherwen et al., 2016) do not include a SSA source and are likely lower limits.

Models diverge as to the fraction of gas-phase Br$_y$ that exists as HBr, especially in the lower atmosphere. Further modeling studies will be necessary to determine the magnitude of revised impacts that account for SSA-derived Br$_y$. Major areas for future development of chemistry climate transport models include uncertainties about the SSA source, a more detailed representation of aerosol and cloud chemistry (i.e., heterogeneous reactions, multiphase chemistry), and convective transport. Concurrent quantitative measurements of gas-phase Br$_y$ species (BrO, HOBr, HBr, etc.) and aerosol bromide are currently missing to evaluate models. Reducing the uncertainties in impacts of halogens for atmospheric composition and climate will require comprehensive experimental field and laboratory work to close the total Br$_y$ budget.

Data availability. The AMAX-DOAS BrO data are available from the CONTRAST data archive: http://data.eol.ucar.edu/master_list/?project=CONTRAST. The CONTRAST data set is open for use by the public, subject to the data policy: https://www.eol.ucar.edu/content/contrast-data-policy. The archive contains aircraft and atmosphere state parameters, in situ measurements, flight videos, and links to the concurrent ATTREX and CAST campaign data archives and other ancillary measurements.
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Competing interests. The authors declare that they have no conflict of interest.

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