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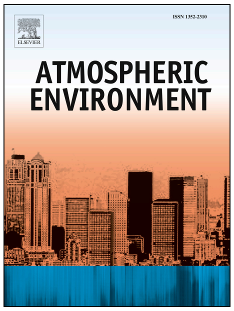

Enhanced ozone loss by active inorganic bromine chemistry in the tropical troposphere

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Enhanced ozone loss by active inorganic bromine chemistry in the tropical troposphere

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Abstract: Bromine chemistry, particularly in the tropics, has been suggested to play an important role in tropospheric ozone loss (Theys *et al*., 2011)) although a lack of measurements of active bromine species impedes a quantitative understanding of its impacts. Recent modelling and measurements of bromine monoxide (BrO) by Wang *et al*. (2015) have shown current models under predict BrO concentrations over the Pacific Ocean and allude to a missing source of BrO. Here, we present the first simultaneous aircraft measurements of atmospheric bromine monoxide, BrO (a radical that along with atomic Br catalytically destroys ozone) and the inorganic Br precursor compounds HOBr, BrCl and Br_2 over the Western Pacific Ocean from 0.5 to 7 km. The presence of 0.17-1.64 pptv BrO and 3.6-8 pptv total inorganic Br from these four species throughout the troposphere causes 10-20% of total ozone loss, and confirms the importance of bromine chemistry in the tropical troposphere; contributing to a 6 ppb decrease in ozone levels due to halogen chemistry. Observations are compared with a global chemical transport model and find that the observed high levels of BrO, BrCl and HOBr can be reconciled by active multiphase oxidation of halide (Br^- and Cl^-) by HOBr and ozone in cloud droplets and aerosols. Measurements indicate that 99% of the instantaneous free Br in the troposphere up to 8 km originates from inorganic halogen photolysis rather than from photolysis of organobromine species.

Keywords

BrO, CIMS, ozone, troposphere

1. Introduction

Ozone (O_3) is one of the most important short-lived gases contributing to greenhouse radiative forcing (RF) and plays a critical role in atmospheric chemistry and air quality (Crutzen *et al.*, 1988). Therefore, it is vital to determine the mechanisms that control its regional and global levels. In the troposphere O_3 has two sources: in situ photochemical production from anthropogenic precursors such as volatile organic compounds (VOCs) and nitrogen oxides, and transport from the stratosphere **(**Liu *et al.*, 2002). Subsequently, the temporal and spatial resolution of O_3 is rather complex and our current understanding cannot account for the observed O_3 variation in the tropical troposphere (*Prather et al*., 2001)**.**

The primary loss route of tropospheric ozone is photolysis in the presence of water vapour. However, recent studies have indicated that reactive halogens in the troposphere could make an important contribution to photochemical O_3 depletion. Especially in tropical regions where higher concentrations of halogenated species (assuming a biological source) are found due to warmer waters, higher biological activity, and fast convective transport into the free troposphere (FT) (Liang *et al*., 2010, Holmes *et al.,* 2010, *Parella et al*., 2012, Wang *et al.,* 2015). Inorganic bromine radicals (BrO and Br) are known to be efficient catalysts for O_3 destruction. Sources of tropospheric bromine are poorly constrained (Parella *et al*., 2012) and include photochemical breakdown of halocarbons (e.g. $CHBr_3$ and CH_2Br_2), debromination of sea salt aerosol, and input of inorganic bromine (Bry) from the stratosphere (Read *et al*., 2008). Model calculations have indicated that bromine chemistry may be responsible for a reduction in the zonal mean O_3 mixing ratio by up to 18% and locally even up to 40% (Holmes *et al*., 2006) and account for the majority of global oxidation of elemental mercury (Read *et al*., 2008).

Only a few pptv (parts per trillion by volume) of BrO are required to have a significant impact on tropospheric chemistry (Holmes *et al*., 2006). There is recent observational evidence for the ubiquitous presence of BrO at these levels in the global troposphere, although reported BrO background levels vary widely (Volkammer et al., 2015, Yang *et al*., 2005, Wang *et al*., 2015, Mahajan *et al.,* 2010) whilst global models under predict these levels of BrO. Wang *et al.* (2015) have recently measured and modelled BrO over the tropical Eastern Pacific Ocean and shown concentrations are up to 2-4 times greater than that predicted in the tropical free troposphere. Their modelling results also show a bias at the lower tropical transition layer, indicating possible missing sources supplying activated inorganic bromine, which current models are unable to account for. Inorganic precursors to BrO such as BrCl, Br_2 and HOBr have previously been measured in the Arctic at significant concentrations to account for high BrO concentrations (Liao et al., 2011). To date, there have been no previous simultaneous measurements of these inorganic halogens in the tropics. Model simulations of their concentrations and importance to ozone loss are currently constrained by experimental observations of BrO concentrations.

2. Flight Campaign

The NERC CAST (Co-ordinated Airborne Studies in the Tropics) campaign took place in the West Pacific in January/February 2014. The field campaign had two components: (i) the NERC FAAM BAe-146 research aircraft based in Guam (13.5^{o}N, 144.8^{o}E); and (ii) ground-based and ozone sonde measurements in Manus, Papua New Guinea (2.1^{o}S, 147.4^{o}E). CAST was part of an international collaboration involving the NASA ATTREX (Airborne Tropical Tropopause Experiment) project based around the Global Hawk, the NCAR-led CONTRAST (Convective Transport of Active Species in the Tropics) campaign based around the Gulfstream V (HIAPER) aircraft, and the Japanese SOWER project (Soundings of Ozone and Water in the Equatorial Region). Together, detailed measurements of atmospheric structure and composition were made from the ocean surface to 20 km. An overview of this campaign can is given by Harris *et al*. (2016), describing the experimental setup, flying conditions and general meteorological and core chemistry results.

In this coordinated campaign, the FAAM BAe-146 made measurements in the lower tropical troposphere below ~8 km altitude with an emphasis on the boundary layer. The flights were made to the south of Guam and occasionally penetrated the southern hemisphere (See figure S1 in supplementary). In total, 25 flights were made between January 25th and 18th 2014 with 90 hours of measurements. Other composition measurements included H_2O, CO, CO_2, CH_4, N_2O, VSLS (very Short Lived Substances) including many bromocarbons, NO, IO (although never above the limit of detection), black carbon and aerosol. NOx concentrations averaged at 6 ppt, indicating no influence of pollution outflow.

3. Materials and Methods

A chemical ionisation mass spectrometer (CIMS) was used for real-time detection of BrO, Br_2, HOBr and BrCl. The CIMS instrument employed here was built by the Georgia Institute of Technology and was set up as in previous studies (Le Breton *et al.*, 2013, 2014). The inlet consisted of 9.5 mm outer diameter PFA tubing of length 580 mm, which was heated to 40^0C to reduce surface losses. The fast inlet pump (Picolino VTE-3, Gardner Denver Thomas) delivered ambient air to the IMR (Ion Molecule reaction) chamber at a flow rate of 5.8 SLM which was subsampled using an orifice of diameter 0.2 mm positioned at the front of the inlet to restrict the flow into the IMR to 0.8 SLM. The pressure in the ionisation region was maintained at 19 Torr (133.3 Pa) throughout the flight by controlling the flow of nitrogen into the ionisation region using a mass flow meter.

The I^- ionization scheme was used for the detection of BrO, Br_2, BrCl and HOBr as previously utilised by Liao *et al.*, (2011, 2012). To generate I^- a flow of 20 SCCM flow of the ionization gas mix (15 Torr CH_3I, 20 Torr H_2O and 47.3 PSI N_2) combined with a 2 SLM flow of N_2 and passed through a ^{210}Po Nuclecel ionizer (NRD inc.). The reagent ion was then carried into the ion-molecule region where Br_2 and BrO were detected as an I^- adduct producing $I.BrO^-$ and $I.Br_2^-$. BrCl was detected as the ionized ion $BrCl^-$ due to ion transfer. HOBr was detected as an adduct of both I^- and H_2O as $I^-.HOBr.H_2O$. Contrary to Liao *et al.*, (2012) under our conditions it is not observed at mass 223 and 225 ($I.HOBr^-$) even with up to 12 ppb of HOBr calibrant and therefore cannot interfere with the BrO signal. A variation of voltage tuning through the collisional dissociation chamber (CDC) and quadrupole can drastically change the clustering abilities of the produced ions and possibly explain this difference. An example in the literature of such variation can be viewed for N_2O_5, where it has been reported as the adduct $I.N_2O_5^-$ (Kecher *et al.,* 2009) and NO_3^- declustered by the CDC (Le Breton *et al.,* 2014).

Calibration and gas preparation

The CIMS was calibrated to attain a sensitivity for BrO, HOBr, Br_2, BrCl and formic acid in the laboratory before and after the campaign. Here, we describe the BrO setup, whereas the calibrations for other compounds can be found in the supplementary material. BrO was produced in a flow tube *via* a moveable injector and produced from the reaction

$$Br_2 + O \rightarrow BrO + Br \quad (R1)$$

Oxygen atoms were generated using a Beenakker microwave discharge cavity operating at 60W. A 1 SLM flow of He (99.999 %) purified using a molecular sieve trap cooled to 78 K was combined with a 1 SCCM flow of 0.1 % O_2 (>99.9995 %) and passed through quartz tubing within the microwave discharge cavity. A 1-10 SCCM flow of a 0.5 % gas mixture of bromine was added into the side arm of the sliding injector, combined with a 3 SLM flow of He, downstream of the microwave discharge cavity reacting with O atoms to produce BrO preceding entrance to the CIMS, which was identified at mass m224; $I.BrO^-$.

The BrO signal calibration was achieved by adding NO to the flow tube via the moveable injector at a constant contact time of 20 ms and by monitoring the resultant NO_2 formed by reaction with BrO, using a Thermo Fisher, model 42i NO-NO_2-NO_x Analyser.

$$BrO + NO \rightarrow NO_2 + Br \quad (R2)$$

NO (Technical grade 98.5%, Sigma-Aldrich) was purified by freeze-pump-thaw cycles, and selective freezing of NO_2 impurities. NO_2 (Technical grade, Air Products 99.5+%, Sigma-Aldrich) was purified by freeze-pump-thaw cycles. He (CP Grade, BOC) was passed through N_2 (l) containing a molecular sieve (5Å 4-8 mesh bead, Sigma-Aldrich) before entering the Beenakker cell. All gas mixtures entering the microwave cavities were made up in electronic grade He (99.9999 %, BOC).

Complete removal of BrO was ensured by adding sufficient NO, confirmed by a constant NO_2 signal with further increases in (NO). The sensitivity was estimated for BrO to be 50 ion counts ppt^{-1} s^{-1}. Validation of the BrO production was confirmed using a flow tube chemical ionization mass spectrometer implementing the SF_6^- ionization scheme, as reported previously by Shallcross *et al.* (2012).

A time series and mass scan of the BrO signal can be seen in figure 1 where the raw 1 Hz data and 30 second averaged data are displayed to show how the limit of detection (0.1 ppt) was achieved. The increased standard deviation during the calibration is as a result of the increased noise from use of the microwave discharge in the production of BrO in the flow tube and not an instrumental factor. This would increase a limit of detection (LOD) to 0.36 ppt if these data were used for the calculation, although this would not change any of the analysis as this value is below the 5th percentile. The uncertainty of the BrO data is therefore ±15%. The low LOD can be attributed to the tuning of the instrument which has a signal of 0 Hz during background periods. The instrument was tuned to maximise sensitivity and minimize the LOD by optimisation of the most well characterised species the CIMS detects, formic acid. Simultaneous tuning of the formic acid peak area and minimisation of non-formic acid peaks during a formic acid calibration ensured an increase in counts was not due to increased MCP voltage noise or instrumental interference. This ensures minimal signal at the BrO mass is observed during background periods and attributes. To validate this limit of detection for field measurements, dry nitrogen was introduced into the inlet before and after a flight to simulate zero ppt BrO ambient air.

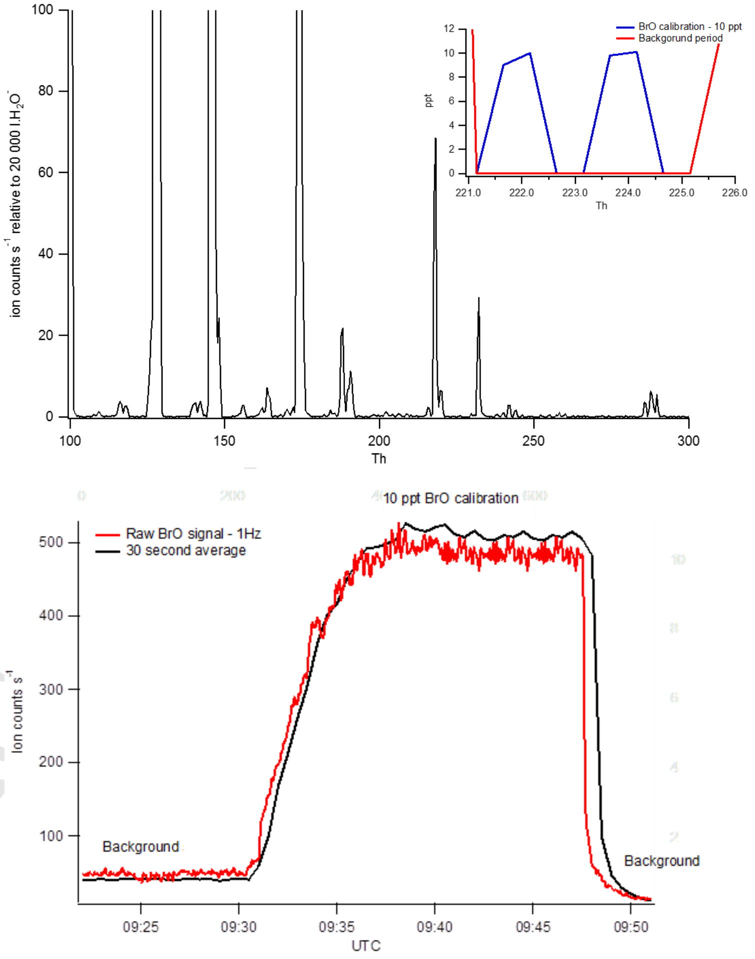


Fig. 1a. BrO time series and mas scan during a calibration and background period. The standard deviations are reported for both 1 Hz and 30 second averaged data.

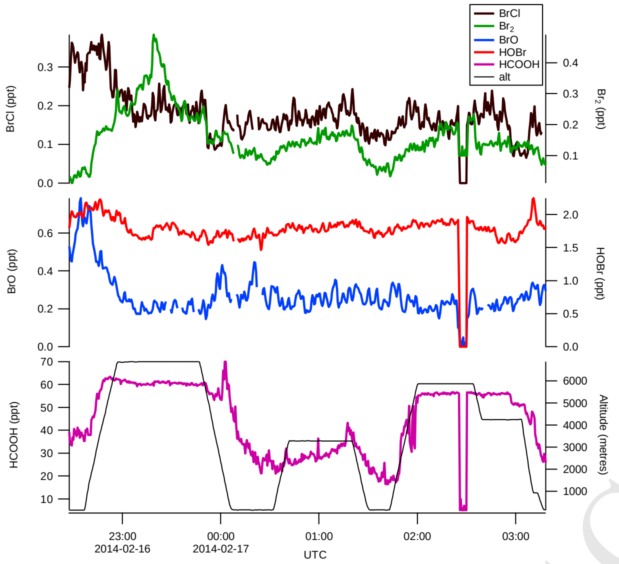


Figure 1b. Timer series of in flight data utilising the nylon scrubber as a background technique for formic acid and the inorganic halogens.

All calibrations were performed relative to in-flight formic acid calibrations and pre-flight ground calibrations, previously described by Le Breton *et al.* (2012). Calibrations of BrO, Br_2, HOBr and BrCl were performed alongside formic acid calibrations in the laboratory, under varying water vapour conditions, to assess relative changes in the instrument's sensitivity. The sensitivity of the instrument were found to have no dependence on relative humidity. This is attributed to a tuning of excess reagent ions and the $I.(H_2O)^-$ cluster which ensures IMR water availability and sensitivity is not dependent on atmospheric relative humidity.

Inlet losses

The loss of HOBr onto instrument and inlet walls was quantified using a perfluoroalkoxy (PFA) flow tube inlet system which varied in length from 0.2 m to 2 m. Up to 15 % of HOBr was seen to convert to Br_2 on the inlet walls, although this value did not vary with inlet length. Therefore, it was assumed that 15 % of the Br_2 signal resulted from HOBr. This was factored into every data point collected during the campaign.

4. Measurement Results

Here, we report the first simultaneous airborne real-time observations of BrO, Br_2, BrCl and HOBr, in tropical marine air with minimal influence from anthropogenic activity. The 1 Hz inorganic halogen data were averaged to 30 seconds in order to facilitate comparison with other in-flight measurements and model outputs. A time series of these data can be seen in figure 2, displaying the concentration of BrO, HOBr, BrCl and Br_2 during flight B830 with the time displayed as local time, together with O_3 and altitude. In figure 2 Br_2, BrCl and HOBr are all above the limit of detection threshold throughout the flight. O_3 and altitude measurements are also displayed in the figure 2. The measurement uncertainties are 10%, 10%, 10% and 15% respectively. BrO concentrations throughout the campaign ranged from below the limit of detection (0.1 ppt for 30 second averaged data) up to 1.71 ppt, with a mean of 0.69 ppt. These concentrations are within the range of that reported at other equatorial mid-ocean sites such as Cape Verde (Mahajan *et al.*, (2010) and the Canary Islands (Leser *et al.*, (2003). Our results further confirm that BrO is present in the tropical troposphere at globally significant levels.

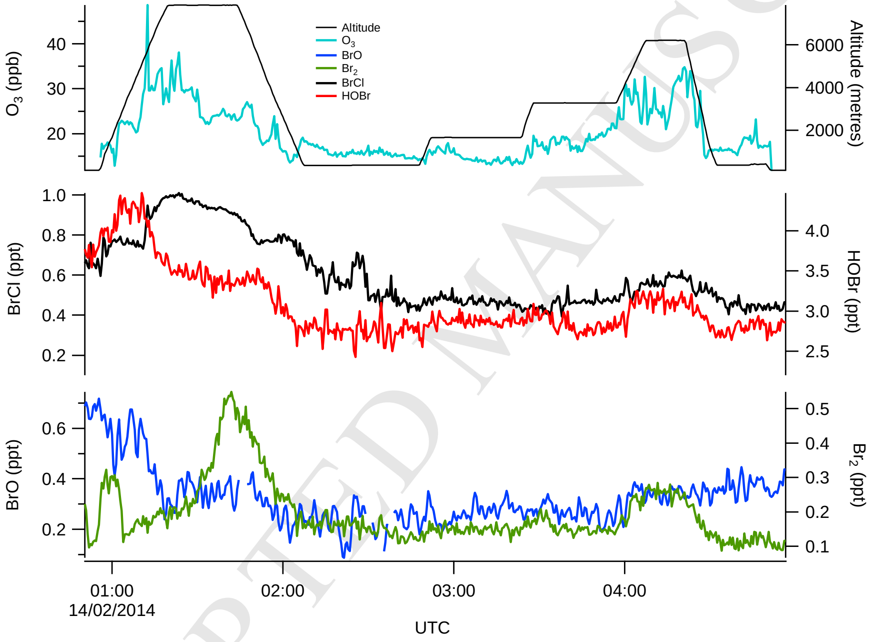
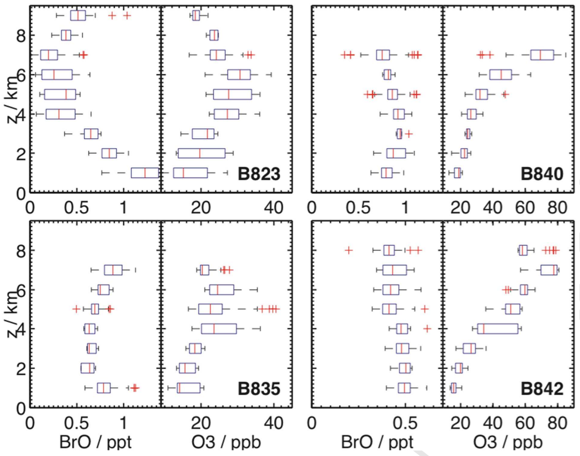


Fig. 2. A time series during flight B841 (14/02/14) of BrO (blue), Br_2 (green), HOBr (red) and BrCl (black) 30 second averaged concentrations from the CIMS and O_3 (light blue). The aircraft altitude (black) is also displayed.

The altitude profile of BrO and O_3 can be seen in figure 3A for 4 flights during the campaign. A broad anti-correlation was observed between BrO and O_3 during these flights, even though individual profiles varied from flight to flight. Tracer-tracer analysis of all the flight data over 4 altitude bins (figure 3B) is consistent with surface deposition being the dominant route for O_3 loss although at higher altitude bins, a larger anti correlation is observed. Further analysis of 2 altitude bins (0-2 km and 2-8 km), where the BrO is split into two samples; above and below the 50th percentile, shows a near identical level of O_3 below and above the 50th percentile in the 0-2 km bin. The 2-8 km bin shows an 8 ppb reduction in O_3 compared with the low BrO sample (the green bar).

This is consistent with the model results, i.e. Br driven ozone loss is small in the MBL (most likely due to the already very short life time of O_3 at the surface), but is significant above the MBL in the Free Troposphere. It must be noted that this correlation was not observed during every profile. The possibility that observed features were of stratospheric origin was dismissed after analysis of N_2O measured by a Quantum Cascade Laser absorption spectrometer (QCL) (Pitt *et al*., 2015) exhibited no concentrations characteristic of that from a stratospheric source.



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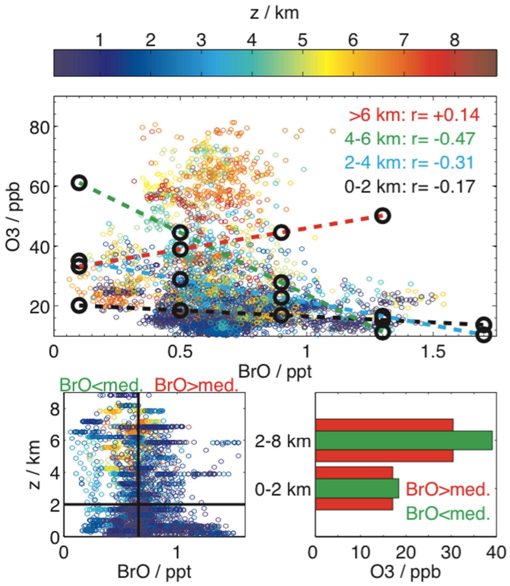

B

Fig.3 Figure A shows altitude profile box plots of BrO and O_3 for 4 flights. The median, mean, 25th, 75th, 5th and 95th quartile ranges are indicated. Graph B shows a correlation plot of ozone and BrO split into 4 altitude bins (red > 6 km, green 4 -6 km, blue 2 – 4 km, black 0 – 2 km) and also a bar chart of binned BrO data by altitude split into BrO concentrations above the 50th percentile (red) and below the 50th percentile (green).

5. Global model simulations

A GEOS-Chem (www.geos-chem.org) global chemical transport model is utilised to interpret observed inorganic bromine mixing ratios. The model is driven by GEOS-5 assimilated meteorological data from the NASA Global Modeling and Assimilation Office with 1/2°x2/3° horizontal resolution and 47 vertical layers extending from the surface up to about 80 km. The horizontal resolution is degraded to 4°x5°. The model includes a detailed ozone-NOx-VOC-aerosol-Br-Cl tropospheric chemistry mechanism as described in great detail by Schmidt et al., (2016) building on the previous bromine mechanism of Parrella *et al.* (2012) by including chlorine chemistry and more extensive halogen multiphase chemistry. Model sources of inorganic bromine include sea salt debromination, oxidation of bromocarbon ($CHBr_3$, CH_2Br_2, CH_3Br) and input from the stratosphere. In simulating the source of bromine from sea salt aerosol (SSA) we assume that 50% of bromide in newly emitted SSA is activated and released as Br_2. Model $CHBr_3$ and CH_2Br_2 emissions are based on emission fields of Hossaini *et al*. (2013) and modelled bromocarbon mixing ratios are consistent with aircraft observations from an ensemble of field campaigns (Parella *et al.,* 2012). Stratospheric concentrations (monthly and diurnally varying) of Bry (Br, BrO, HOBr, HBr, $BrNO_3$ and BrCl) are taken from a Goddard Earth Observing System Chemistry-Climate Model (GEOSCCM) simulation that has been demonstrated to yield stratospheric BrO profiles consistent with balloon observations (Holmes *et al*., 2006). The halogen and heterogeneous chemistry mechanism yields BrO column densities and mixing ratios broadly consistent with ground based and recent aircraft observations (Mahajan *et al*., 2010 Volkamer *et al*., 2015, Wang *et al*., 2015).

Simulated BrO and HOBr (figure 4) show fair agreement (over 55% and 75% of the data points agreeing within error respectively) with observations in the MBL and FT. Agreement is only achieved when heterogeneous chemistry is included, as shown in figure 4. Bromine driven O_3 loss takes place by cycling between Br, BrO and HOBr. Bromine driven oxidation of NO_x (a key ozone precursor) also reduces the level of ozone in the troposphere. The BrO measurements in the Pacific by Wang *et al.,* (2015) suggested that their consistent high BrO concentrations were due to a missing inorganic source. Here, the measured inorganic halogen concentrations, similar to that by Wang *et al.,* (2015) further support their hypothesis that inorganic halogen concentrations may often be several ppt in the Pacific. The increase in BrO from heterogeneous chemistry results in a further 6 ppb O_3 loss in the model.

The model predicts higher levels of BrCl than Br_2 in direct contrast with observations. The inconsistent pattern in simulated levels of BrCl and Br_2 may be due to multiphase halide exchange reactions ($BrCl + Br^- \rightarrow Br_2 + Cl^-$) that are not accounted for in the simulations, which has previously been reported to initiate O_3 depletion reactions (Wachsmuth *et al.*, 2002). The model results are unable to account for the observed high levels of Br_2 throughout the campaign, seen in figure 4 where the measured sum of BrCl and Br_2 is on average 0.5 ppt higher than the model. It must be stated that this value represents absolute reported concentrations and does not account for experimental uncertainty. Extensive laboratory studies have assessed a possible inlet loss of HOBr to form Br_2 (Liao *et al*. 2012 and Neuman *et al*., 2010). Our results indicate that a maximum of 15% of HOBr is lost on the walls, which could not account for the discrepancy between model and measurement. O_3 may play in halogen activation on the inlet, although no sign of this interference was found; i.e. no correlation between observed Br_2 and O_3 is observed (see figure S4 in the supporting material). Furthermore, there remains the possibility that our inlet walls could become coated in sea salt and thus increase the Br_2 production along the inlet which would be difficult to take into account. However, Huey and co-workers (see e.g. Neuman *et al*., 2010) experimentally determined the efficiency of inlet conversion of HOBr on the inlet on various PFA in comparison with a pure salt substrate and showed that there is a factor of 5 increase in Br_2 production. For the data presented in the manuscript there would have to be a factor of 20 increase in wall loss efficiency to explain our observed Br_2, thus we are confident that wall loss can not explain the observed Br_2. Liao et al., (2012) found that NaBr deliquescence in the presence of OH and the photolysis of O_3 could produce significant levels of molecular bromine. This source of bromine is not represented in the model and could therefore account for its underestimation compared to the measurements.

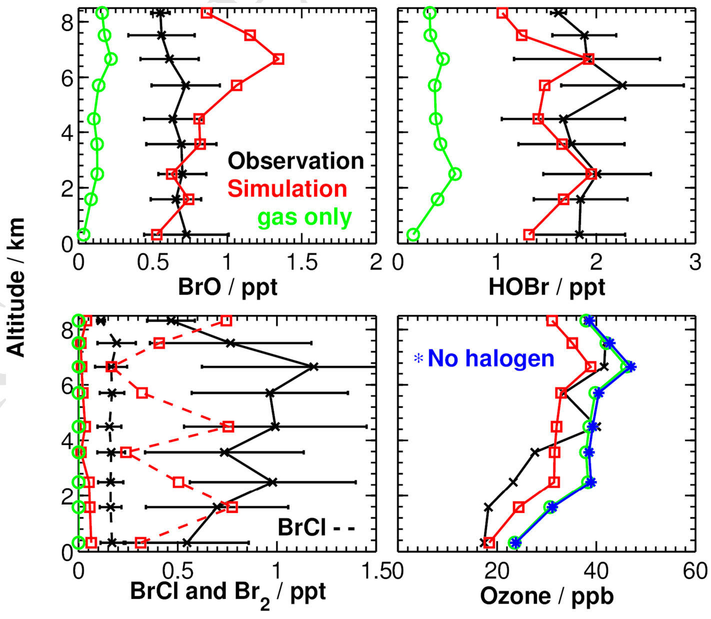

Fig. 4. Altitude profile box plot of the measured (CIMS) and modelled (GEOS-Chem) concentration of BrO (upper left), HOBr (upper right), BrCl (lower left, dashed), Br_2 (lower left, full), and ozone (lower right)

throughout the campaign for 16 flights. Black lines represent the measurements. The red line is output from our GEOS-Chem simulation. The green curve is model output from a simulation without multiphase halogen chemistry (no oxidation of Br^- and Cl^- and no halogen release from SSA). The cyan curve shows simulated ozone when halogen chemistry is not included. The horizontal bars on the observed data lines correspond to the maximum and minimal values in the data set

6. Contribution of inorganic bromine to ozone loss

CAST aircraft measurements of organobromine compounds taken by Whole Air Samples (WAS) (Lidster *et al.,* 2014) and measured by GC-MS (Hopkins *et al*., 2011) coupled with modelled photooxidation rates show that their contribution to the Br loading is minimal. Our results indicate that at least 99% of Br radicals originates from inorganic halogen species, in contrast to other model studies (Liu *et al*., 2002). Non-halogen related O_3 loss, from photolysis and reactions with OH and HO_2 radicals (Yang *et al*., 2005) was estimated using a steady state approximation implementing all other inorganic halogen measurements as described in the SOM. The average HO_2 concentration calculated in the steady state approximation in the upper free troposphere was 6 ppt, consistent with Jagle et al., (1997) and Tin *et* al, (2001). The results from this analysis imply that Br from inorganic halogen photolysis can account for up to 20% of the O_3 loss in the FT and MBL as shown in figure 5. The figure also suggests that HO_2 can account for up to 80% loss of O_3 in the upper troposphere.

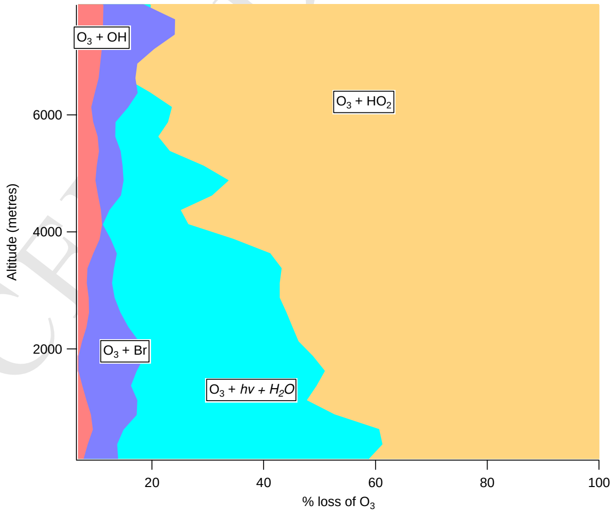

Fig. 5. The graph represents the contribution to O_3 loss in the FT and MBL from reaction with HO_2 (yellow), O^1D (blue), Br from inorganic halogens measured by the CIMS (purple) and OH (red). These values have been calculated from the steady state approximation explained in the SOM.

There remains the possibility that we have overestimated the impact of Br_2 photolysis as a result of inlet conversion of HOBr. However, even if we assume that all the Br_2 that we observe is resultant from HOBr, that would not alter the conclusions of this work. Inorganic Bromine would still be the major source (99%) of Br atoms in the MBL, the source being either from Br_2 or HOBr.

7. Conclusions

The recent work by Wang *et al*., (2015) showing the capacity for inorganic halogen chemistry to destroy ozone in the Pacific region and suggestioning that such high concentrations of BrO may result from high concentrations of inorganic halogens in the region have been further supported by the work presented here. The first simultaneous airborne measurements of BrO, Br_2, HOBr and BrCl suggest inorganic halogen photochemistry is the overwhelmingly dominant source of Br in the FT and MBL in comparison with that of organobromine compounds. Analysis of data from this work reveals that Br radicals generated from inorganic halogen photolysis can account for up to 20% of O_3 in the FT and to a lesser extent in the MBL as shown in figure 5. Previous model studies suggested that there could be up to 20% less ozone in the tropics as a result of bromine chemistry (von Glasow *et al.,* 2004, Long *et al*., 2014) and this study has provided the direct evidence of the inorganic sources of bromine. This study also builds on the advancements in this field by Wang *et al.* (2015) and further supports the hypothesis that a missing source of BrO production may propagate through the debromination of sea salt.

Acknowledgments

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Enhanced ozone loss by active inorganic bromine chemistry in the tropical troposphere

Highlights

Ozone (O_3) is one of the pivotal species in the lower atmosphere, initiating production of key radicals OH, NO_3 and Criegee Intermediates, as well as being a powerful oxidizing agent in its own right. Hence, O_3 plays a vital role in controlling atmospheric chemistry and air quality and in addition is a key greenhouse gas. The role of O_3 in the tropical troposphere is none more important where its photochemistry drives high OH production in the lower marine boundary layer through the availability of high solar fluxes and water vapour. This region is where significant removal of pollutants occurs and is, dynamically, the gateway to the stratosphere. Therefore, the O_3 budget in the region is critical and yet there are significant gaps in our knowledge. For example, it is currently assumed that low concentrations of O_3 observed in the tropical marine boundary are due to higher photolysis rates in the presence of high water vapour concentrations. However, recent measurements of extremely low O_3 concentrations (<10 ppb) indicate that another unexplained mechanism is responsible for O_3 loss in the tropics, which models cannot explain.

In this work we present results from simultaneous measurements of a number of gaseous inorganic bromine species in the tropics onboard the FAAM 146 Research Aircraft. The results show that BrO, HOBr, BrCl and Br_2 represent 99% of the free Br, contrary to current theory in which organobromine species dominate the Br production pathway. This suite of inorganic bromine species can rapidly recycle Br during sunlit hours and provide an efficient catalytic cycle that removes significant levels of ozone. Good agreement with GEOS Chem, a global 3-D chemical transport model which implemented a new multi phase chemistry scheme, reveals the underestimation of halogen chemistry within standard models and accounts for their under prediction of O_3 loss in the tropical troposphere. Model results show that the concentrations of inorganic bromine species presented here can contribute up to 6 ppb O_3 loss in the tropical troposphere, representing 20% of the total O_3 destruction which in this region is a significant additional loss. Implementation of this inorganic halogen chemistry into future models is imperative to accurately quantify O_3 variability in the tropics and therefore the oxidizing power of the atmosphere.