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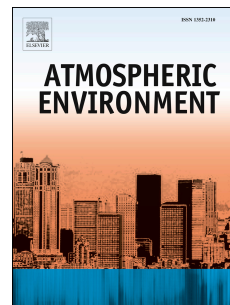
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Enhanced ozone loss by active inorganic bromine chemistry in the tropical troposphere

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

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20

21 **Abstract:** Bromine chemistry, particularly in the tropics, has been suggested to play an important
22 role in tropospheric ozone loss (Theys *et al.*, 2011)) although a lack of measurements of active
23 bromine species impedes a quantitative understanding of its impacts. Recent modelling and
24 measurements of bromine monoxide (BrO) by Wang *et al.* (2015) have shown current models
25 under predict BrO concentrations over the Pacific Ocean and allude to a missing source of BrO.
26 Here, we present the first simultaneous aircraft measurements of atmospheric bromine monoxide,
27 BrO (a radical that along with atomic Br catalytically destroys ozone) and the inorganic Br
28 precursor compounds HOBr, BrCl and Br₂ over the Western Pacific Ocean from 0.5 to 7 km. The
29 presence of 0.17-1.64 pptv BrO and 3.6-8 pptv total inorganic Br from these four species
30 throughout the troposphere causes 10-20% of total ozone loss, and confirms the importance of
31 bromine chemistry in the tropical troposphere; contributing to a 6 ppb decrease in ozone levels due
32 to halogen chemistry. Observations are compared with a global chemical transport model and find

33 that the observed high levels of BrO, BrCl and HOBr can be reconciled by active multiphase
34 oxidation of halide (Br^- and Cl^-) by HOBr and ozone in cloud droplets and aerosols. Measurements
35 indicate that 99% of the instantaneous free Br in the troposphere up to 8 km originates from
36 inorganic halogen photolysis rather than from photolysis of organobromine species.

37 **Keywords**

38 BrO, CIMS, ozone, troposphere

39 **1. Introduction**

40 Ozone (O_3) is one of the most important short-lived gases contributing to greenhouse radiative
41 forcing (RF) and plays a critical role in atmospheric chemistry and air quality (Crutzen *et al.*,
42 1988). Therefore, it is vital to determine the mechanisms that control its regional and global levels.
43 In the troposphere O_3 has two sources: in situ photochemical production from anthropogenic
44 precursors such as volatile organic compounds (VOCs) and nitrogen oxides, and transport from the
45 stratosphere (Liu *et al.*, 2002). Subsequently, the temporal and spatial resolution of O_3 is rather
46 complex and our current understanding cannot account for the observed O_3 variation in the tropical
47 troposphere (Prather *et al.*, 2001).

48

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

62

63 Only a few pptv (parts per trillion by volume) of BrO are required to have a significant impact on
64 tropospheric chemistry (Holmes *et al.*, 2006). There is recent observational evidence for the

65 ubiquitous presence of BrO at these levels in the global troposphere, although reported BrO
66 background levels vary widely (Volkammer et al., 2015, Yang *et al.*, 2005, Wang *et al.*, 2015,
67 Mahajan *et al.*, 2010) whilst global models under predict these levels of BrO. Wang *et al.* (2015)
68 have recently measured and modelled BrO over the tropical Eastern Pacific Ocean and shown
69 concentrations are up to 2-4 times greater than that predicted in the tropical free troposphere. Their
70 modelling results also show a bias at the lower tropical transition layer, indicating possible missing
71 sources supplying activated inorganic bromine, which current models are unable to account for.
72 Inorganic precursors to BrO such as BrCl, Br₂ and HOBr have previously been measured in the
73 Arctic at significant concentrations to account for high BrO concentrations (Liao et al., 2011). To
74 date, there have been no previous simultaneous measurements of these inorganic halogens in the
75 tropics. Model simulations of their concentrations and importance to ozone loss are currently
76 constrained by experimental observations of BrO concentrations.

77

78 **2. Flight Campaign**

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

91

92 In this coordinated campaign, the FAAM BAe-146 made measurements in the lower tropical
93 troposphere below ~8 km altitude with an emphasis on the boundary layer. The flights were made
94 to the south of Guam and occasionally penetrated the southern hemisphere (See figure S1 in
95 supplementary). In total, 25 flights were made between January 25th and 18th 2014 with 90 hours of
96 measurements. Other composition measurements included H₂O, CO, CO₂, CH₄, N₂O, VSLs (very
97 Short Lived Substances) including many bromocarbons, NO, IO (although never above the limit of

98 detection), black carbon and aerosol. NO_x concentrations averaged at 6 ppt, indicating no influence
99 of pollution outflow.

100

101 **3. Materials and Methods**

102 A chemical ionisation mass spectrometer (CIMS) was used for real-time detection of BrO, Br₂,
103 HOBr and BrCl. The CIMS instrument employed here was built by the Georgia Institute of
104 Technology and was set up as in previous studies (Le Breton *et al.*, 2013, 2014). The inlet consisted
105 of 9.5 mm outer diameter PFA tubing of length 580 mm, which was heated to 40⁰C to reduce
106 surface losses. The fast inlet pump (Picolino VTE-3, Gardner Denver Thomas) delivered ambient
107 air to the IMR (Ion Molecule reaction) chamber at a flow rate of 5.8 SLM which was subsampled
108 using an orifice of diameter 0.2 mm positioned at the front of the inlet to restrict the flow into the
109 IMR to 0.8 SLM. The pressure in the ionisation region was maintained at 19 Torr (133.3 Pa)
110 throughout the flight by controlling the flow of nitrogen into the ionisation region using a mass flow
111 meter.

112

113 The I⁻ ionization scheme was used for the detection of BrO, Br₂, BrCl and HOBr as previously
114 utilised by Liao *et al.*, (2011, 2012). To generate I⁻ a flow of 20 SCCM flow of the ionization gas
115 mix (15 Torr CH₃I, 20 Torr H₂O and 47.3 PSI N₂) combined with a 2 SLM flow of N₂ and passed
116 through a ²¹⁰Po Nuclecel ionizer (NRD inc.). The reagent ion was then carried into the
117 ion-molecule region where Br₂ and BrO were detected as an I⁻ adduct producing I.BrO⁻ and I.Br₂⁻.
118 BrCl was detected as the ionized ion BrCl⁻ due to ion transfer. HOBr was detected as an adduct of
119 both I⁻ and H₂O as I.HOBr.H₂O. Contrary to Liao *et al.*, (2012) under our conditions it is not
120 observed at mass 223 and 225 (I.HOBr⁻) even with up to 12 ppb of HOBr calibrant and therefore
121 cannot interfere with the BrO signal. A variation of voltage tuning through the collisional
122 dissociation chamber (CDC) and quadrupole can drastically change the clustering abilities of the
123 produced ions and possibly explain this difference. An example in the literature of such variation
124 can be viewed for N₂O₅, where it has been reported as the adduct I.N₂O₅⁻ (Kecher *et al.*, 2009) and
125 NO₃⁻ declustered by the CDC (Le Breton *et al.*, 2014).

126

127 ***Calibration and gas preparation***

128 The CIMS was calibrated to attain a sensitivity for BrO, HOBr, Br₂, BrCl and formic acid in the
129 laboratory before and after the campaign. Here, we describe the BrO setup, whereas the calibrations
130 for other compounds can be found in the supplementary material. BrO was produced in a flow tube
131 *via* a moveable injector and produced from the reaction



133 Oxygen atoms were generated using a Beenakker microwave discharge cavity operating at 60W. A
134 1 SLM flow of He (99.999 %) purified using a molecular sieve trap cooled to 78 K was combined
135 with a 1 SCCM flow of 0.1 % O₂ (>99.9995 %) and passed through quartz tubing within the
136 microwave discharge cavity. A 1-10 SCCM flow of a 0.5 % gas mixture of bromine was added into
137 the side arm of the sliding injector, combined with a 3 SLM flow of He, downstream of the
138 microwave discharge cavity reacting with O atoms to produce BrO preceding entrance to the
139 CIMS, which was identified at mass m224; I.BrO⁻.

140 The BrO signal calibration was achieved by adding NO to the flow tube via the moveable injector
141 at a constant contact time of 20 ms and by monitoring the resultant NO₂ formed by reaction with
142 BrO, using a Thermo Fisher, model 42i NO-NO₂-NO_x Analyser.



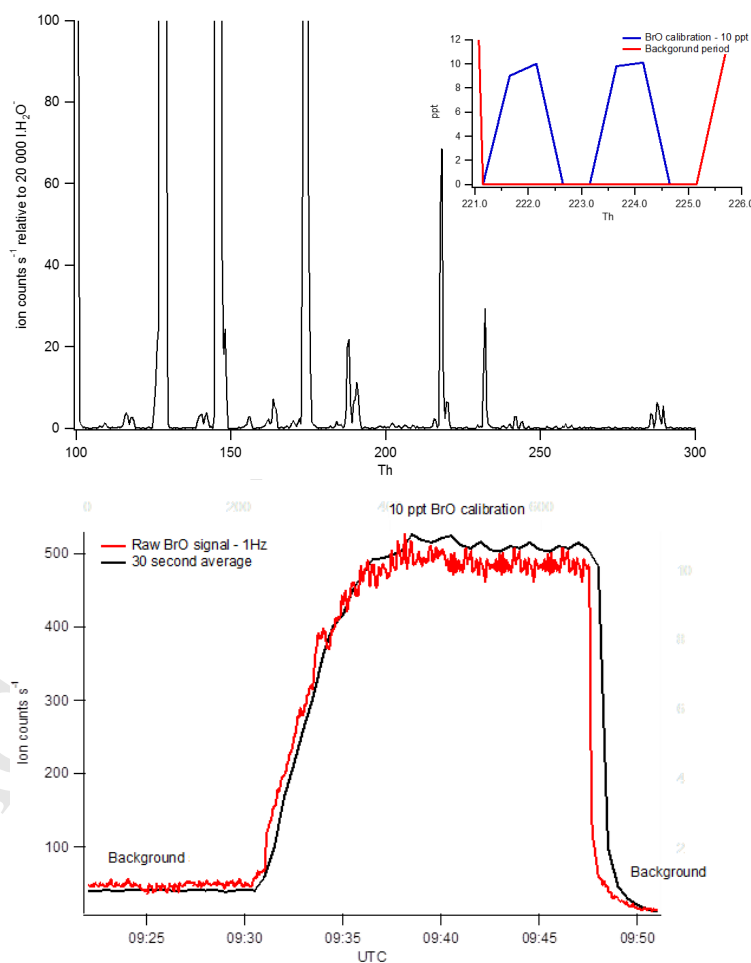
144 NO (Technical grade 98.5%, Sigma-Aldrich) was purified by freeze-pump-thaw cycles, and
145 selective freezing of NO₂ impurities. NO₂ (Technical grade, Air Products 99.5+%, Sigma-Aldrich)
146 was purified by freeze-pump-thaw cycles. He (CP Grade, BOC) was passed through N₂ (l)
147 containing a molecular sieve (5Å 4-8 mesh bead, Sigma-Aldrich) before entering the Beenakker
148 cell. All gas mixtures entering the microwave cavities were made up in electronic grade He
149 (99.9999 %, BOC).

150 Complete removal of BrO was ensured by adding sufficient NO, confirmed by a constant NO₂
151 signal with further increases in (NO). The sensitivity was estimated for BrO to be 50 ion counts ppt⁻¹
152 s⁻¹. Validation of the BrO production was confirmed using a flow tube chemical ionization mass
153 spectrometer implementing the SF₆⁻ ionization scheme, as reported previously by Shallcross *et al.*
154 (2012).

155

156 A time series and mass scan of the BrO signal can be seen in figure 1 where the raw 1 Hz data and
157 30 second averaged data are displayed to show how the limit of detection (0.1 ppt) was achieved.
158 The increased standard deviation during the calibration is as a result of the increased noise from use

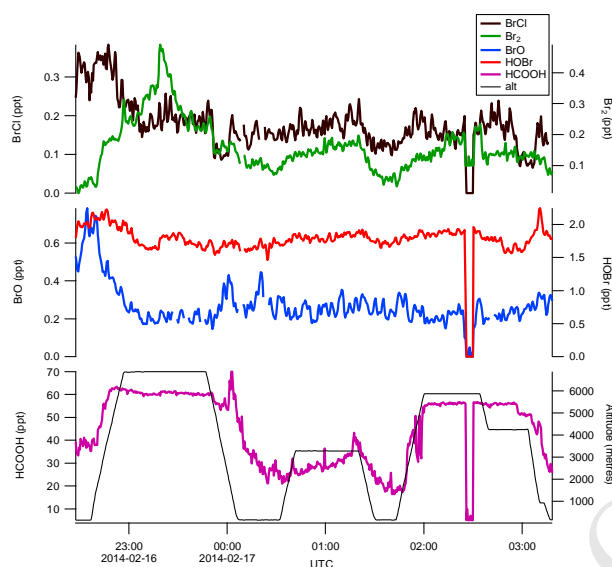
159 of the microwave discharge in the production of BrO in the flow tube and not an instrumental
 160 factor. This would increase a limit of detection (LOD) to 0.36 ppt if these data were used for the
 161 calculation, although this would not change any of the analysis as this value is below the 5th
 162 percentile. The uncertainty of the BrO data is therefore $\pm 15\%$. The low LOD can be attributed to
 163 the tuning of the instrument which has a signal of 0 Hz during background periods. The instrument
 164 was tuned to maximise sensitivity and minimize the LOD by optimisation of the most well
 165 characterised species the CIMS detects, formic acid. Simultaneous tuning of the formic acid peak
 166 area and minimisation of non-formic acid peaks during a formic acid calibration ensured an
 167 increase in counts was not due to increased MCP voltage noise or instrumental interference. This
 168 ensures minimal signal at the BrO mass is observed during background periods and attributes. To
 169 validate this limit of detection for field measurements, dry nitrogen was introduced into the inlet
 170 before and after a flight to simulate zero ppt BrO ambient air.



171

172

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



175

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

178

179 All calibrations were performed relative to in-flight formic acid calibrations and pre-flight ground
 180 calibrations, previously described by Le Breton *et al.* (2012). Calibrations of BrO, Br₂, HOBr and
 181 BrCl were performed alongside formic acid calibrations in the laboratory, under varying water
 182 vapour conditions, to assess relative changes in the instrument's sensitivity. The sensitivity of the
 183 instrument were found to have no dependence on relative humidity. This is attributed to a tuning of
 184 excess reagent ions and the I.(H₂O)⁻ cluster which ensures IMR water availability and sensitivity is
 185 not dependent on atmospheric relative humidity.

186 **Inlet losses**

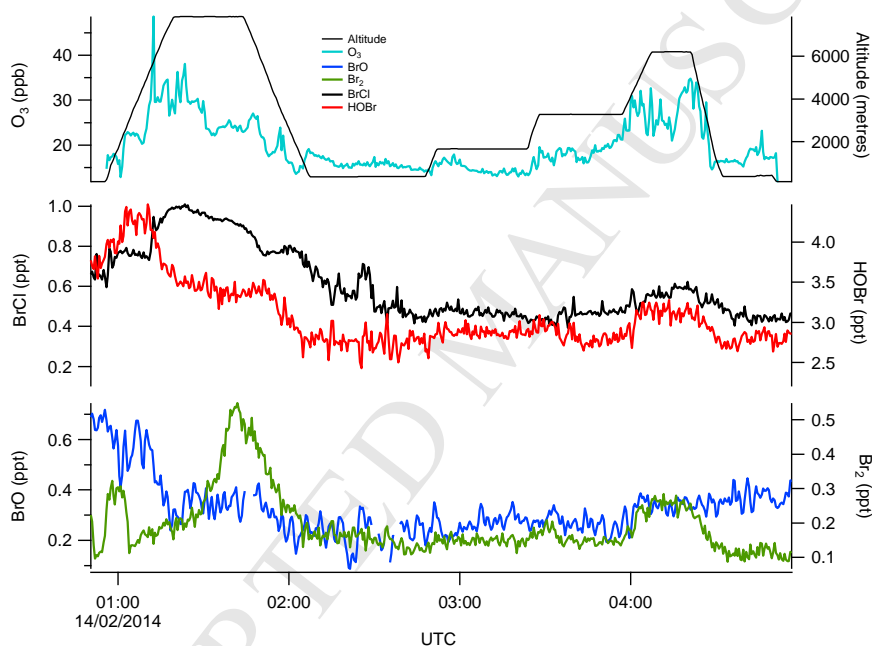
187 The loss of HOBr onto instrument and inlet walls was quantified using a perfluoroalkoxy (PFA)
 188 flow tube inlet system which varied in length from 0.2 m to 2 m. Up to 15 % of HOBr was seen to
 189 convert to Br₂ on the inlet walls, although this value did not vary with inlet length. Therefore, it
 190 was assumed that 15 % of the Br₂ signal resulted from HOBr. This was factored into every data
 191 point collected during the campaign.

192

193 **4. Measurement Results**

194 Here, we report the first simultaneous airborne real-time observations of BrO, Br₂, BrCl and HOBr,
 195 in tropical marine air with minimal influence from anthropogenic activity. The 1 Hz inorganic
 196 halogen data were averaged to 30 seconds in order to facilitate comparison with other in-flight

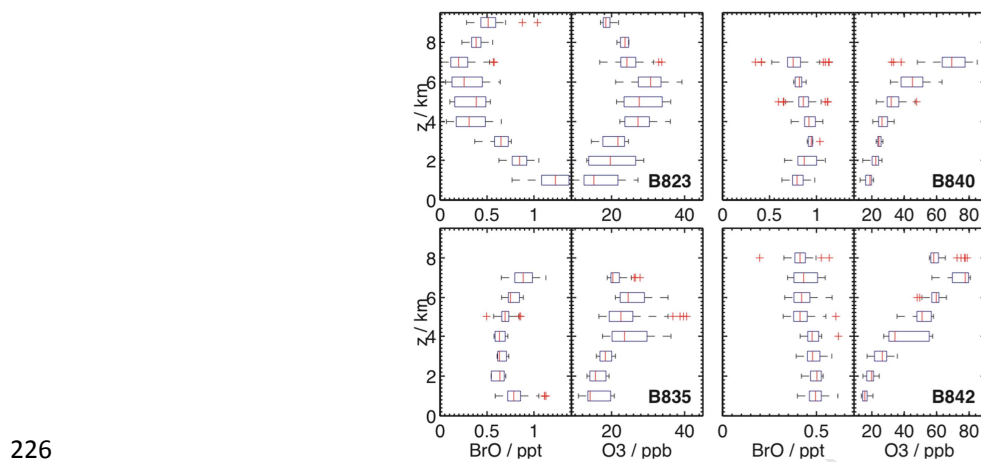
197 measurements and model outputs. A time series of these data can be seen in figure 2, displaying the
 198 concentration of BrO, HOBr, BrCl and Br₂ during flight B830 with the time displayed as local time,
 199 together with O₃ and altitude. In figure 2 Br₂, BrCl and HOBr are all above the limit of detection
 200 threshold throughout the flight. O₃ and altitude measurements are also displayed in the figure 2.
 201 The measurement uncertainties are 10%, 10%, 10% and 15% respectively. BrO concentrations
 202 throughout the campaign ranged from below the limit of detection (0.1 ppt for 30 second averaged
 203 data) up to 1.71 ppt, with a mean of 0.69 ppt. These concentrations are within the range of that
 204 reported at other equatorial mid-ocean sites such as Cape Verde (Mahajan *et al.*, (2010) and the
 205 Canary Islands (Leser *et al.*, (2003). Our results further confirm that BrO is present in the tropical
 206 troposphere at globally significant levels.



207
 208 **Fig. 2. A time series during flight B841 (14/02/14) of BrO (blue), Br₂ (green), HOBr (red) and BrCl (black) 30**
 209 **second averaged concentrations from the CIMS and O₃ (light blue). The aircraft altitude (black) is also**
 210 **displayed.**

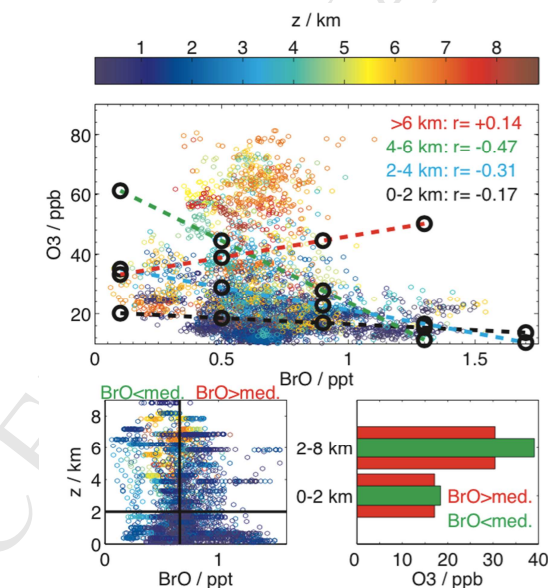
211
 212 The altitude profile of BrO and O₃ can be seen in figure 3A for 4 flights during the campaign. A
 213 broad anti-correlation was observed between BrO and O₃ during these flights, even though
 214 individual profiles varied from flight to flight. Tracer-tracer analysis of all the flight data over 4
 215 altitude bins (figure 3B) is consistent with surface deposition being the dominant route for O₃ loss
 216 although at higher altitude bins, a larger anti correlation is observed. Further analysis of 2 altitude
 217 bins (0-2 km and 2-8 km), where the BrO is split into two samples; above and below the 50th
 218 percentile, shows a near identical level of O₃ below and above the 50th percentile in the 0-2 km bin.
 219 The 2-8 km bin shows an 8 ppb reduction in O₃ compared with the low BrO sample (the green bar).

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



226

227 A



228

229 B

230

231 **Fig.3** Figure A shows altitude profile box plots of BrO and O_3 for 4 flights. The median, mean, 25th, 75th, 5th and
 232 95th quartile ranges are indicated. Graph B shows a correlation plot of ozone and BrO split into 4 altitude bins
 233 (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
 234 split into BrO concentrations above the 50th percentile (red) and below the 50th percentile (green).

235

236 **5. Global model simulations**

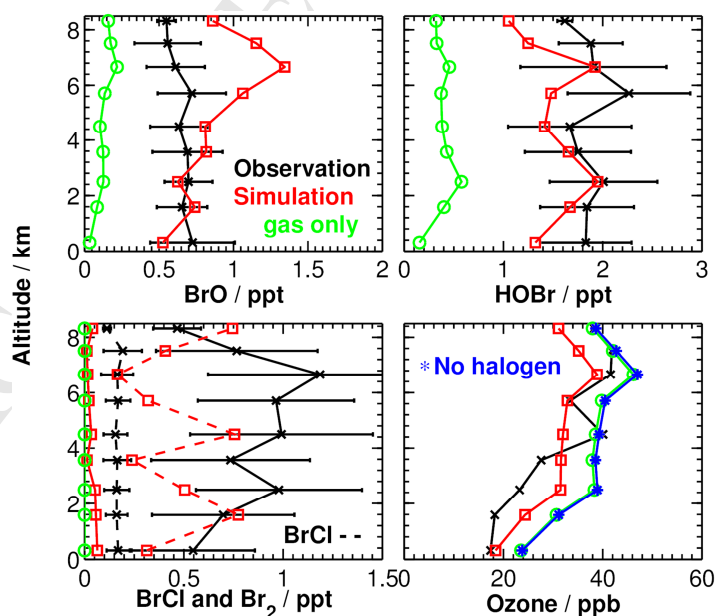
237 A GEOS-Chem (www.geos-chem.org) global chemical transport model is utilised to interpret
238 observed inorganic bromine mixing ratios. The model is driven by GEOS-5 assimilated
239 meteorological data from the NASA Global Modeling and Assimilation Office with $1/2^\circ \times 2/3^\circ$
240 horizontal resolution and 47 vertical layers extending from the surface up to about 80 km. The
241 horizontal resolution is degraded to $4^\circ \times 5^\circ$. The model includes a detailed ozone-NO_x-VOC-
242 aerosol-Br-Cl tropospheric chemistry mechanism as described in great detail by Schmidt *et al.*,
243 (2016) building on the previous bromine mechanism of Parrella *et al.* (2012) by including chlorine
244 chemistry and more extensive halogen multiphase chemistry. Model sources of inorganic bromine
245 include sea salt debromination, oxidation of bromocarbon (CHBr₃, CH₂Br₂, CH₃Br) and input from
246 the stratosphere. In simulating the source of bromine from sea salt aerosol (SSA) we assume that
247 50% of bromide in newly emitted SSA is activated and released as Br₂. Model CHBr₃ and CH₂Br₂
248 emissions are based on emission fields of Hossaini *et al.* (2013) and modelled bromocarbon mixing
249 ratios are consistent with aircraft observations from an ensemble of field campaigns (Parrella *et al.*,
250 2012). Stratospheric concentrations (monthly and diurnally varying) of Br_y (Br, BrO, HOBr, HBr,
251 BrNO₃ and BrCl) are taken from a Goddard Earth Observing System Chemistry-Climate Model
252 (GEOSCCM) simulation that has been demonstrated to yield stratospheric BrO profiles consistent
253 with balloon observations (Holmes *et al.*, 2006). The halogen and heterogeneous chemistry
254 mechanism yields BrO column densities and mixing ratios broadly consistent with ground based
255 and recent aircraft observations (Mahajan *et al.*, 2010 Volkamer *et al.*, 2015, Wang *et al.*, 2015).

256

257 Simulated BrO and HOBr (figure 4) show fair agreement (over 55% and 75% of the data points
258 agreeing within error respectively) with observations in the MBL and FT. Agreement is only
259 achieved when heterogeneous chemistry is included, as shown in figure 4. Bromine driven O₃ loss
260 takes place by cycling between Br, BrO and HOBr. Bromine driven oxidation of NO_x (a key ozone
261 precursor) also reduces the level of ozone in the troposphere. The BrO measurements in the Pacific
262 by Wang *et al.*, (2015) suggested that their consistent high BrO concentrations were due to a
263 missing inorganic source. Here, the measured inorganic halogen concentrations, similar to that by
264 Wang *et al.*, (2015) further support their hypothesis that inorganic halogen concentrations may
265 often be several ppt in the Pacific. The increase in BrO from heterogeneous chemistry results in a
266 further 6 ppb O₃ loss in the model.

267 The model predicts higher levels of BrCl than Br₂ in direct contrast with observations. The
268 inconsistent pattern in simulated levels of BrCl and Br₂ may be due to multiphase halide exchange
269 reactions ($\text{BrCl} + \text{Br}^- \rightarrow \text{Br}_2 + \text{Cl}^-$) that are not accounted for in the simulations, which has

270 previously been reported to initiate O₃ depletion reactions (Wachsmuth *et al.*, 2002). The model
 271 results are unable to account for the observed high levels of Br₂ throughout the campaign, seen in
 272 figure 4 where the measured sum of BrCl and Br₂ is on average 0.5 ppt higher than the model. It
 273 must be stated that this value represents absolute reported concentrations and does not account for
 274 experimental uncertainty. Extensive laboratory studies have assessed a possible inlet loss of HOBr
 275 to form Br₂ (Liao *et al.* 2012 and Neuman *et al.*, 2010). Our results indicate that a maximum of
 276 15% of HOBr is lost on the walls, which could not account for the discrepancy between model and
 277 measurement. O₃ may play in halogen activation on the inlet, although no sign of this interference
 278 was found; i.e. no correlation between observed Br₂ and O₃ is observed (see figure S4 in the
 279 supporting material). Furthermore, there remains the possibility that our inlet walls could become
 280 coated in sea salt and thus increase the Br₂ production along the inlet which would be difficult to
 281 take into account. However, Huey and co-workers (see e.g. Neuman *et al.*, 2010) experimentally
 282 determined the efficiency of inlet conversion of HOBr on the inlet on various PFA in comparison
 283 with a pure salt substrate and showed that there is a factor of 5 increase in Br₂ production. For the
 284 data presented in the manuscript there would have to be a factor of 20 increase in wall loss
 285 efficiency to explain our observed Br₂, thus we are confident that wall loss can not explain the
 286 observed Br₂. Liao *et al.*, (2012) found that NaBr deliquescence in the presence of OH and the
 287 photolysis of O₃ could produce significant levels of molecular bromine. This source of bromine is
 288 not represented in the model and could therefore account for its underestimation compared to the
 289 measurements.



290

291 **Fig. 4.** Altitude profile box plot of the measured (CIMS) and modelled (GEOS-Chem) concentration of BrO
 292 (upper left), HOBr (upper right), BrCl (lower left, dashed), Br₂ (lower left, full), and ozone (lower right)

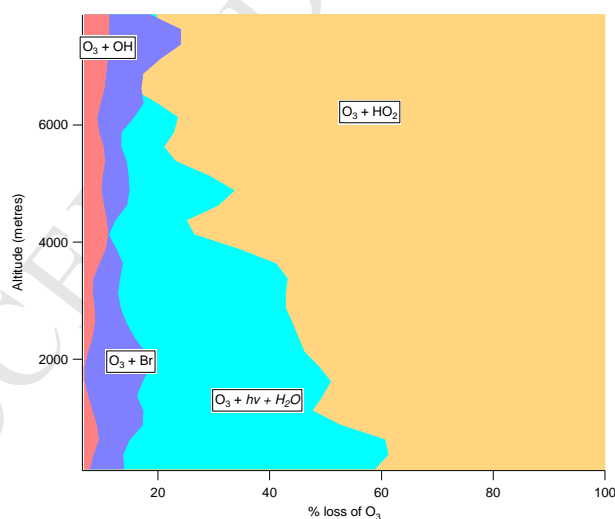
293 throughout the campaign for 16 flights. Black lines represent the measurements. The red line is output from our
 294 GEOS-Chem simulation. The green curve is model output from a simulation without multiphase halogen
 295 chemistry (no oxidation of Br^- and Cl^- and no halogen release from SSA). The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

298

299

300 6. Contribution of inorganic bromine to ozone loss

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



313

314

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

318

319 There remains the possibility that we have overestimated the impact of Br₂ photolysis as a result of
320 inlet conversion of HOBr. However, even if we assume that all the Br₂ that we observe is resultant
321 from HOBr, that would not alter the conclusions of this work. Inorganic Bromine would still be the
322 major source (99%) of Br atoms in the MBL, the source being either from Br₂ or HOBr.

323

324 7. Conclusions

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326 The recent work by Wang *et al.*, (2015) showing the capacity for inorganic halogen chemistry to
327 destroy ozone in the Pacific region and suggesting that such high concentrations of BrO may
328 result from high concentrations of inorganic halogens in the region have been further supported by
329 the work presented here. The first simultaneous airborne measurements of BrO, Br₂, HOBr and
330 BrCl suggest inorganic halogen photochemistry is the overwhelmingly dominant source of Br in
331 the FT and MBL in comparison with that of organobromine compounds. Analysis of data from this
332 work reveals that Br radicals generated from inorganic halogen photolysis can account for up to
333 20% of O₃ in the FT and to a lesser extent in the MBL as shown in figure 5. Previous model studies
334 suggested that there could be up to 20% less ozone in the tropics as a result of bromine
335 chemistry (von Glasow *et al.*, 2004, Long *et al.*, 2014) and this study has provided the direct
336 evidence of the inorganic sources of bromine. This study also builds on the advancements in this
337 field by Wang *et al.* (2015) and further supports the hypothesis that a missing source of BrO
338 production may propagate through the debromination of sea salt.

339

340

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349 (<http://catalogue.ceda.ac.uk/uuid/565b6bb5a0535b438ad2fae4c852e1b3>) and the use of data
350 produced in the context of the CAST project is governed by the protocols outlined at
351 <https://badc.nerc.ac.uk/conditions/cast.html>.

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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.