# Modelling the Inorganic Bromine Partitioning in the Tropical Tropopause over the Pacific Ocean.

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**Abstract.** The stratospheric inorganic bromine burden ($Br_y$) arising from the degradation of brominated very short-lived organic substances ($VSL_{org}$), and its partitioning between reactive and reservoir species, is needed for a comprehensive assessment of the ozone depletion potential of brominated trace gases. Here we present modelled inorganic bromine abundances over the Pacific tropical tropopause based on aircraft observations of $VSL_{org}$ of two campaigns of the Airborne Tropical TRopopause EXperiment (ATTREX 2013 carried out over eastern Pacific and ATTREX 2014 carried out over the western Pacific) and chemistry-climate simulations (along ATTREX flight tracks) using the specific meteorology prevailing. Using the Community Atmosphere Model with Chemistry (CAM-Chem), we model that BrO and Br are the daytime dominant species. Integrated across all ATTREX flights BrO represents ~ 43 % and 48 % of daytime $Br_y$ abundance at 17 km over the Western and Eastern Pacific, respectively. The results also show zones where Br/BrO >1 depending on the solar zenith angle (SZA), ozone concentration and temperature. On the other hand, BrCl and $BrONO_2$ were found to be the dominant night-time species with ~ 61% and 56 % of abundance at 17 km over the Western and Eastern Pacific, respectively. The western-to-eastern differences in the partitioning of inorganic bromine are explained by different abundances of ozone ($O_3$), nitrogen dioxide ($NO_2$), and total inorganic chlorine ($Cl_y$).

## 1 Introduction

The role of bromine in stratospheric ozone depletion has been discussed in several studies (Daniel et al., 1999; Hossaini et al., 2015; Prather and Watson, 1990; Salawitch et al., 2005; Wofsy et al., 1975). Many of these discuss the contribution of brominated very short-lived organic substances ($VSL_{org}$) in addition to long-lived halons and methyl bromide, as an important source of stratospheric bromine. The reaction mechanisms of $VSL_{org}$ that lead to the formation of inorganic bromine ($Br_y$) involve complex sets of reactions that have been described in previous modelling studies (Krysztofiak et al.,

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2012;Ordóñez et al., 2012;Hossaini et al., 2010). The chemistry is initiated mainly via reaction with OH and photolysis and leads to the formation of several unstable organic halogenated radicals. The fate of these radicals, and their mechanisms of reaction, are controlled by $NO_x$ conditions and OH levels. In polluted environments (high $NO_x$ regime) the radicals react to produce $NO_2$ or halogenated nitrates that can decompose, experience oxidation or photolysis, washout or react on surfaces.

5  In "clean" environments (low $NO_x$ regime) the radicals undergo a series of cross reactions (including reaction with $HO_2$) leading to the formation of several different products that can continue reacting with OH (or Cl), washout or photo-dissociate to form inorganic bromine species as end product (Krysztofiak et al., 2012).

The implementation of the complex chemistry of very short-lived species in current models like the Community Atmospheric Model with Chemistry (CAM-Chem) has been simplified by assuming that inorganic bromine is immediately
10  formed from photo-oxidised $VSL_{org}$ (Ordóñez et al., 2012).  However, the challenge to simulate $VSL_{org}$ observations and quantify their degradation products ($Br_y = Br + BrO + HOBr + BrONO_2 + HBr + BrCl + 2Br_2 + BrNO_2 + IBr$) relies on other atmospheric processes that could modify this chemistry. For example, the location and timing of emissions, the transport dynamics and dehydration processes in the tropical tropopause layer (TTL) (Liang et al., 2010), and the occurrence of heterogeneous recycling reactions on sea-salt aerosol and ice-crystals (Fernandez et al., 2014). A recent study by Navarro et
15  al. (2015), carried out in the TTL over the Pacific Ocean, showed the impact of strong convective events on the chemistry of brominated species. The estimates of the contribution of very short-lived substances to total stratospheric bromine over the tropical eastern and western Pacific, showed a similar amount of $VSL_{org}$ over both regions. Nevertheless, a smaller amount of $Br_y$ was observed over the western Pacific due to the influence of the South Pacific Convection Zone (SPCZ) and the path of typhoon Faxai in 2014.

20  As the tropical circulation, assisted by convection, could enhance the vertical transport of $VSL_{org}$, the $VSL_{org}$ degradation products could reflect changes in their abundances and chemical speciation.  A previous study by Fernandez et al. (2014) calculated that $VSL_{org}$ provided an annual average tropical stratospheric injection of total bromine of approximately 5 ppt (parts per trillion), where ~ 3 ppt entered the stratosphere as a product gas, while ~2 ppt did so as a source gas. In this study, the distribution of inorganic bromine species showed Br and BrO to be the dominant inorganic species during daytime,
25  particularly over the tropical western Pacific, which was suggested to be a hot spot with increased stratospheric bromine injection (~3.8 ppt $Br_y$ and ~3.8 ppt $VSL_{org}$). Similarly, the estimates of stratospheric $Br_y$ inferred from atmospheric measurements of BrO during the NASA- Airborne Tropical TRopopause EXperiment (ATTREX) deployment over eastern Pacific, showed approximately 3 to 5 ppt for potential temperatures between 350 and 400 K in the TTL (Werner et al., 2016).

30  Our study focuses on the difference in modelled $Br_y$ concentrations in the TTL over the Pacific throughout the ATTREX campaign flight tracks, and examines its temporal and spatial distributions.  Based on the reliable representation of the observed $VSL_{org}$ by the CAM-Chem model, we estimated the partitioning of inorganic bromine over the tropical eastern and western Pacific during 2013 and 2014, respectively. This paper is organized as follows: Section 2 briefly describes the campaign, the methods used for the observations of trace gases, and the characteristics of the model simulations.  Section 3

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discusses the major findings regarding the amount of inorganic bromine and its partitioning within the TTL, as well as its relevance for the formation of the proposed tropical ring of atomic bromine (Fernandez et al., 2014;Saiz-Lopez and Fernandez, 2016). In addition, section 3 discusses the results of a sensitivity test in the model where water-ice aerosol reactions are deactivated. Section 4 summarizes and concludes this study.

## 2 Methods: Observations and Simulations

ATTREX, an airborne campaign focused on the chemical and physical processes in the TTL (~13-18 km), took place over the Pacific Ocean during boreal winter (Jensen et al., 2015). In 2013, six flights were conducted over the eastern and central Pacific, targeting the area between 187 and 268 °E and 11 °S to 34 °N (hereafter referred to as the eastern Pacific (EP)). In 2014, eight flights were carried out over the western Pacific, covering the area between 120 and 165 °E and 11 °S to 35 °N (hereafter referred to as the western Pacific (WP)). On board the NASA Global Hawk, the University of Miami deployed the Global Hawk Whole Air Sampler (GWAS) to collect more than 900 samples at different locations along the flight tracks. Measurements of brominated very short-lived organic substances, like bromoform ($CHBr_3$), dibromomethane ($CH_2Br_2$), bromochloromethane ($CH_2BrCl$), dibromochloromethane ($CHBr_2Cl$) and bromodichloromethane ($CHBrCl_2$), were carried out during the deployments and were used here to evaluate the model. The $VSL_{org}$ bromine budget and the vertical distribution of these species were presented in a previous publication (Navarro et al., 2015) which also included estimates of the organic *vs.* inorganic bromine fraction over the EP and WP.

At the tropopause level (~17 km), the modelling estimates of the organic bromine fractions were similar for the entire Pacific ($3.84 \pm 0.64$ and $3.18 \pm 1.49$ ppt from WP and EP, respectively). However, the inorganic fraction inferred from $VSL_{org}$ measurements showed $3.02 \pm 1.90$ ppt of $Br_y$ over the EP and $1.97 \pm 0.21$ ppt over WP (Navarro et al., 2015). Based on these results, we performed model simulations to look into the variability and distribution of the inorganic bromine partitioning, and used ozone concentrations measured with the National Oceanic & Atmospheric Administration's Ozone system (NOAA-$O_3$) during ATTREX 2013, and the Unmanned aircraft system Chromatograph for Atmospheric Trace Species (UCATS-$O_3$) during ATTREX 2014 to also evaluate the model.

Measurements of ozone were carried out with dual-beam UV photometers. These instruments utilize two identical absorption cells, a mercury lamp, an ozone scrubbing catalyst, and two detectors that measure 253.7-nm UV radiation transmitted through the absorption cell. At this wavelength, the ozone absorption cross-section is well known, and thus the ozone number density can be readily calculated by Beer's Law. Since the two absorption cells are identical, virtually continuous measurements of ozone are made by alternating the ambient air sample and ozone scrubbed sample between the two of them. At a fast collection rate (from 2 Hz at < 200hPa to 0.5 Hz at 500hPa for NOAA- $O_3$ and 0.2 Hz for UCATS-$O_3$), the minimum detectable concentration of ozone corresponds to 1 ppb or less at STP. Based on an intercomparison between the two instruments during ATTREX 2013, the UCATS-$O_3$ instrument was $4.8\pm0.8$ ppb higher than NOAA-$O_3$ in the regions of interest between 50 and 250 ppb, and approached zero near 500 ppb. The NOAA-$O_3$ instrument was unavailable on

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ATTREX-2014. These continuous measurements of ozone were averaged to match the location where GWAS samples were collected, and then compared to CAM-Chem outputs.

The estimations of VSL$_{org}$, O$_3$ and the Br$_y$ partitioning were carried out with the Community Atmosphere Model with Chemistry (CAM-Chem), a 3-D chemistry climate model included into the CESM framework (Community Earth System

5  Model, version 1.1.1) (Lamarque et al., 2012). This model includes a complete photochemistry, wet and dry deposition and heterogeneous chemistry on sea-salt aerosols and ice particles (Fernandez et al., 2014; Lamarque et al., 2012; Ordóñez et al., 2012). Model simulations were run in specified dynamics mode (SD) using meteorological fields prevailing at the time of the campaigns. Model output was sampled at exactly the same times and locations as the ATTREX measurements. A spatial resolution of 1° (longitude) x 1° (latitude) with 56 vertical levels (from the surface to ~ 3.5 hPa) and a temporal resolution of

10  30 min were used.

The chemistry of inorganic bromine species between the daytime and night-time was distinguished by disregarding the samples collected during twilight (total solar zenith angle between 80° and 100°). In addition, local estimations of ozone, nitrogen dioxide and inorganic chlorine concentrations were carried out over the EP and WP along the flight tracks to understand the chemistry that leads to the specific bromine partitioning.

15  **3 Results and discussion**

The first step of this study was to evaluate the CAM-Chem model to substantiate that its chemistry and other components show a satisfactory performance, and that its results are consistent with the intended application. We used the NOAA-O$_3$, UCATS-O$_3$, and organic bromine species from GWAS measurements taken during the ATTREX campaign, since BrO and NO$_2$ measurements from the ATTREX mission were still under examination by the time of this analysis. Figure 1 shows the

20  measurements and model mixing ratios of O$_3$ in the Upper Troposphere-Lower Stratosphere (UTLS) for both, the WP and EP respectively. The NOAA and UCATS O$_3$ mixing ratios averaged into 1 km altitude bins ranged from 46 ppb at 14 km to 166 ppb at 18km over the WP, and 46 ppb to 179 ppb from 14 to 18 km over EP; while CAM-Chem simulations estimated 67 ppb to 196 ppb from 14 to 18 km over WP, and 100 ppb at 14 km and 243 ppb at 18 km over EP. The model reproduces well the variability of measured ozone with altitude in both the WP and EP. However, the different convective processes are

25  not accurately represented for in both regions, leading to an offset in the EP between measurements and simulated ozone values. The vertical profile of organic bromine species from GWAS measurements can be found in a previous publication (Navarro et al., 2015).

Figure 2 shows the correlation between average measurements and model outputs of the 1 km of altitude bins for O$_3$, CHBr$_3$ and CH$_2$Br$_2$ over the WP and EP. Excellent correlation (R$^2$ > 0.97) between O$_3$ measurements and CAM-Chem estimates for

30  both EP and WP were observed, with slopes not differing significantly from unity. However, small vertical offsets in the "y" axis (27.1 ppb in WP and 54.5 ppb in EP) reflect the simulated bias in the model. In addition, good agreement was observed

between GWAS measurements and model simulations of $CHBr_3$ ($R^2 = 0.84$ for WP, $R^2 = 0.81$ for EP), and $CH_2Br_2$ ($R^2 = 0.95$ for WP, $R^2 = 0.90$ for EP), as shown in figure 2 and the previous work of Navarro et al., (2015).

After reaching satisfactory results in the model evaluation, 436 observations along the flight track (388 during the day and 48 at night) over the WP and 309 flight points (152 during the day and 157 at night) over the EP were used to simulate

5  inorganic bromine partitioning during NASA ATTREX campaigns (Fig 3). Due to the logistics of the missions, the distribution of sample points according to solar zenith angle (SZA) was different between WP and EP. During ATTREX 2014 (WP), flights occurred mostly during daylight hours, as the plane took off at early local morning (~17:00 UTC, 3:00 am local time). Also, flights lasted approximately 20 hours reducing the amount of night-time samples, particularly at high SZA. The legs went in different directions, mostly west-east, north-south, and even a local circle flight, following a different path

10  from and to Andersen Air Force Base (13.5 °N, 144.9 °E). For these reasons, samples showed a high density of observations at 50° SZA, and no samples beyond 130° SZA for WP. On contrast, during ATTREX 2013 (EP), flights also took off during early local morning (~15:00 UTC, 7:00 am local time), but lasted between 22 to 24 hours. In addition, the legs went in southern and south-western direction and came back to Edwards Air Force Base (34.9 °N, 243.8 °E) over the same path. Hence, for the EP, the number of samples was evenly distributed along the entire range of SZAs.

15  The vertical distribution of inorganic species showed a slight variability with altitude (Fig 4). Over both the WP and the EP, BrO and Br prevail at daytime hours from 14 to 18 km. However, below 16 km, the amount of HBr present over the EP tends to be slightly larger than that of atomic Br. For the WP and the EP during night-time hours, BrCl and $BrONO_2$ are the dominant species in agreement with Fernandez et al. (2014). Mixing ratios of BrCl closely compete with $BrONO_2$, particularly at 15 and 18 km over the WP. Over the EP, $BrONO_2$ dominates the entire range of altitude from 14 to 18 km.

20  The total $Br_y$ burden during daylight hours increases from 1.49 to 2.43 ppt between 14 km and 18 km over the WP and from 1.82 to 2.97 ppt over the EP within the same altitude range. On the other hand, night-time $Br_y$ ranges from 1.40 to 2.27 ppt and 1.82 to 2.99 ppt for the WP and EP, respectively. This indicates that the total $Br_y$ atmospheric burden is equivalent within the diurnal cycle. Note that within the same altitude range, the model output for total $VSL_{org}$ decreases from 5.72 ppt at 14 km to 2.53 ppt at 18 km over the WP, and from 3.90 ppt at 14 km to 1.97 ppt at 18 km over the EP, indicating the

25  dominant role played by VSL photodecomposition in controlling the $Br_y$ loading in the tropical UTLS (Navarro et al., 2015). At the tropopause level (~17 km) and integrated over all flights and SZAs, the inorganic partitioning showed ~ 43 % (0.79 ppt) of abundance of BrO during daylight and ~61 % of BrCl (0.94 ppt) during night-time over WP. On the other hand, 48 % (1.43 ppt) of inorganic bromine is presented as BrO during daylight and 56 % (1.41 ppt) as $BrONO_2$ at night time over EP (Fig 4). Atomic bromine is the second most abundant species during the day, with mean daytime values of 0.64 ppt and 0.57

30  ppt for the WP and EP, respectively. During the night, $BrONO_2$ (0.29 ppt) and BrCl (0.34 ppt) are the 2nd most abundant species over the WP and EP, respectively.

In order to understand the chemistry that led to these abundances, the concentrations of inorganic bromine products (Br, BrO, HOBr, $BrONO_2$, HBr, and BrCl), as well as modelled mixing ratios of the dominant reactants: ozone ($O_3$), nitrogen dioxide ($NO_2$), and inorganic chlorine ($Cl_y$), were studied as a function of the SZA for the entire range of altitude (14 to 18

km) (Fig 5). According to the results, during the daylight hours, the high abundance of average $O_3$ (up to ~ 190 ppb), compared to average $NO_2$ and $Cl_y$ ($Cl_y$ up to ~ 84 ppt, $NO_2$ up to ~ 33 ppt) (Fig 5b), led to the rapid formation of BrO over the WP (Fig 5a). As the SZA keeps on increasing, a decrease on photolysis as well as ozone concentrations (particularly at SZA ~ 100-120°, Fig 5b) allow the heterogeneous reaction of the inorganic chlorine (mostly HCl) and bromine reservoirs

5    (HOBr and $BrONO_2$) to increase the production of BrCl during the night time hours. Note that the accumulation of night-time BrCl is more evident during ATTREX 2014 due to the larger ice-crystals surface areas and lower $NO_x$ levels prevailing over the WP (Fig 5a).

The scenario over the EP is slightly different as levels of $NO_2$ and $O_3$ define a high $NO_x$ regime. A statistical analysis of CAM-Chem $NO_2$ model estimations during daylight over the EP is presented in Fig 6. Our average range of $NO_2$ mixing

10    ratios is approximately $15 \pm 6$ ppt at 14 km, with slightly higher values over the tropopause, $22 \pm 24$ ppt at 17 km. These estimates within 1 standard deviation agree with the $NO_2$ values presented by Stutz et al. (2016) and Werner et al. (2016) from observations made during ATTREX 2013 over the EP. As they report in their manuscript, their $O_3$ scaling technique allowed retrieval of $NO_2$ concentrations of $15 \pm 15$ ppt in the TTL, and a range of 70 up to 170 ppt in the mid-latitude lower stratosphere. However, previous studies have shown large associated uncertainties in TTL $NO_2$ measurements based on

15    remote sensing instruments (Weidner et al., 2005;Butz et al., 2006;Bauer et al., 2012).

Hence, the EP daytime average concentrations of ozone (up to ~ 300 ppb), $Cl_y$ (max $Cl_y$ ~ 181 ppt) and $NO_2$ (max $NO_2$ ~ 48 ppt) are almost twice as high as those over the WP (Fig 5d). Higher concentrations of ozone were associated with enhanced production of BrO (Fig 5c). Meanwhile, during dark hours, the high concentrations of $NO_2$ (up to ~ 210 ppt) (Fig 5d), lead to the predominant formation of $BrONO_2$ over the EP (Fig 5c). These results are in good agreement with the partitioning of

20    inorganic bromine found by Werner et al. (2016) where BrO is the daylight dominant species over EP, and the estimates of Fernandez et al. (2014), which suggested BrO and $BrONO_2$ as the dominant species in the TTL over the entire tropics during daytime and midnight, respectively.

Our results also indicate that, integrated over all SZAs, the second most abundant species over both EP and WP during daytime is atomic Br. This species plays a fundamental role in the formation of the proposed inhomogeneous tropical ring of

25    atomic Br, a natural atmospheric phenomenon that comes from the rapid photochemical equilibrium between BrO and Br under low $O_3$ and temperatures (Fernandez et al., 2014;Saiz-Lopez and Fernandez, 2016). According to our estimations, during daytime hours, the average mixing ratios of Br remain below 0.75 ppt over the EP and WP along the entire range of altitudes (i.e., between 14 to 18 km) (Fig 4). Note, however, that atomic Br abundances surpass BrO mixing ratios at low SZA (close to noontime) and low ozone abundances (below 100 ppb, Fig 5b and 5d). These observations contrast with the

30    variability observed in BrO, whose mixing ratios vary from 0.61 ppt up to 1.19 ppt over WP and from 0.72 ppt to 1.43 ppt over EP (Fig 4), depending on $O_3$ and $NO_2$ background levels. Also note that Br shows a smooth variation during the day, slightly decreasing its abundance as the SZA increases, while the temporal evolution of BrO is more variable, mostly under the high $NO_x$ regime prevailing in the EP (Fig. 5).

In contrast to the study of Werner et al., (2016), which focused on ATTREX measurements taken exclusively over the EP and used an $O_3$-scaling techniques to retrieve their results, our model calculations support the fact that the Br/BrO ratio could become larger than the unity, particularly in the tropical UT and TTL of both, Eastern and Western Pacific Ocean during daylight hours, particularly at low SZA. Nevertheless, the combination of ozone concentrations and temperatures plays a fundamental role in the distribution of both species, thus it is expected to find a spatially irregular pattern in the conditions that favour Br/BrO > 1.

Figure 7 shows the distribution of the Br/BrO ratio over the WP and EP, and its correlation with ozone concentrations and temperatures. Over the EP, Br/BrO > 1 are observed as discrete masses, particularly at SZA between 40° and local noon. Note that cold temperatures and low $O_3$ concentrations enhance the prevalence of atomic Br for those times and locations. Indeed, Saiz-Lopez and Fernandez (2016), determined that Br becomes the dominant species for $O_3$ < 100 ppb and T < 200 K. Br/BrO ratios lower than 1 are observed near the tropopause for SZA between 40° and 55° under higher concentrations of ozone and warmer temperatures. The Br/BrO distribution over the WP seems to be more inhomogeneous with an overall higher Br/BrO ratio than over the EP. This overall lower ratio Br/BrO in the EP compared to WP could be due to the higher levels of $O_3$ modelled in this region (Fig. 1). In any case, the presence of the tropical rings of Br occurs as a spotted/patchy stamp of bromine atoms superposed on top of a background BrO curtain. In general, the Br/BrO ratio peaks at 17 km, very close to the upper limit of the TTL, highlighting the importance of determining Br abundances in order to address the total amount of inorganic bromine injected to the stratosphere.

As the magnitude of the inorganic bromine reactive species (Br and BrO) depends on changes in the oceanic sources and vertical transport, the Br/BrO ratio will vary according to the seasons and geographical regions. Hence, during strong convective events over the WP (e.g., air masses tracked from the SPCZ) the amount of Br and BrO remained similar to each other. These results are in good agreement with the statements of Fernandez et al. (2014), which suggested Br/BrO > 1 during strong convective periods over the WP warm pool region.

Reservoir species like HBr and HOBr were the third most dominant substances. These two species contribute to the formation of BrCl through heterogeneous recycling reactions (see Ordóñez et al., 2012), particularly at night due to the absence of photolysis reactions and the presence of trace chlorine. As suggested by Fernandez et al. (2014), higher abundances of $Cl_y$, could result from the decomposition of very short-lived chlorocarbons or the subsidence of HCl from the stratosphere to the TTL, driving the night-time chemistry in areas where $Cl_y > Br_y$.

Heterogeneous reactions of reservoir species on ice-crystals are relevant at UTLS levels, thus, a sensitivity test was carried out to determine the influence of water-ice aerosols on the distribution of the inorganic species. Figure 8 shows mixing ratios at different altitudes when water-ice aerosol reactions were deactivated simultaneously (see Table S1 in supplementary online material of Fernandez at al., 2014 for a complete list of heterogeneous reactions included in CAM-Chem). Relative to the results from the complete mechanism (Fig. 4), at 17 km, the absence of ice-crystal reactions increases the total inorganic fraction by 7% and 12% over the EP during the day and night, respectively. On the other hand, $Br_y$ increases by 29% and 40% over the WP during day and night, respectively. This relative increase of total $Br_y$ is mainly due to changes in the

amount of HBr and BrCl. Note that the mixing ratio of all species, except for HBr (and BrONO$_2$ during night-time) remain similar when comparing Figure 4 and Figure 8. As explained by Aschmann et al. (2011) the increment in the amount of HBr at high altitude levels could be due to a slowly sedimentation following by evaporation as the adsorbed HBr is not washed out right away.

5   Another characteristic of the sensitivity test is the clear absence of BrCl during night-time as water-ice aerosol reactions of HOBr and HCl are suppressed. Comparing to the base case, the absence of BrCl makes BrONO$_2$ the dominant species at night over the WP, with 53% at 17 km, compared to 61% BrCl in the base case. However, the heterogeneous chemistry of bromine species with water-ice aerosols still requires further research as their atmospheric surfaces are highly dynamic. The presence of cirrus ice clouds, at the cold temperatures of the equatorial and mid-latitude UTLS, facilitates the conversion of

10  bromine reservoir species to more photochemically active forms, which play an important role in the oxidative capacity of this region of the atmosphere.


## 4 Summary and Conclusions

Our estimates of the inorganic bromine partitioning at the tropical tropopause over the Pacific Ocean showed BrO and atomic Br to be the dominant species during daytime hours, while BrCl and BrONO$_2$ were found as the night-time dominant

15  species over the WP and EP, respectively. The difference in the partitioning of inorganic bromine during the diurnal cycle could be explained by the changes in the abundance of O$_3$, NO$_2$ and Cl$_y$ in these two regions of the Pacific, as well as the efficiency of heterogeneous reactions that could modify this chemistry, mostly during the night. Table 1 show a summary of the results found at 17 km.

Reactive species like atomic Br become the dominant inorganic bromine species in large regions of the TTL during daylight,

20  following the large variation of ozone abundance within these regions strongly influenced by deep convection. The low ozone and cold conditions, in combination with the rapid photochemical equilibrium between BrO and Br, favour Br/BrO > 1 and support previous results about the proposed tropical ring of atomic bromine. Within the ATTREX flights, both Br and BrO alternate as the dominant daytime species, indicating a large inhomogeneity for the tropical ring of Br, mainly due to the large ozone/T variability of the air parcels within the convective tropical WP and EP. Nevertheless, improved field data for

25  the speciation of bromine are evidently needed to continue evaluating this hypothesis.

The degradation of VSL$_{org}$, their transport into the TTL, as well as the efficiency of heterogeneous reactions involving ice aerosols, play an important role in the overall atmospheric loading of inorganic bromine, both reactive and reservoir species. This model study contributes to the growing database of reactive halogen estimates based on halocarbon observations. However, further research on the organic/inorganic bromine fraction, as well as its distribution between reactive and

30  reservoir species, is needed in different areas of the globe and at different heights to diminish the uncertainty of the amount of Br$_y$ that reaches the stratosphere, and properly constraint the global bromine budget.

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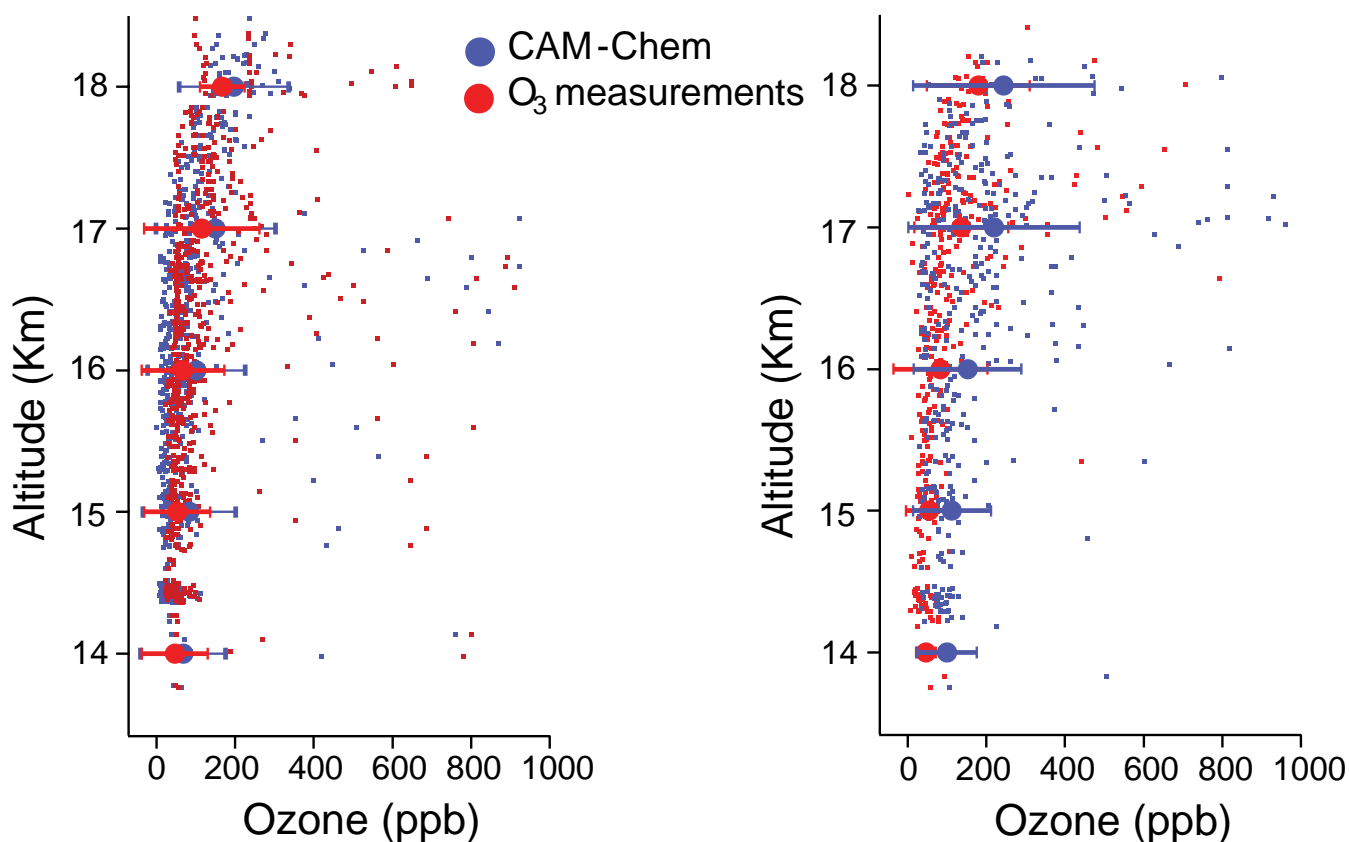
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**Figure 1: NOAA-UCATS O₃ observations for all flights (blue dots) and CAM-Chem simulations along ATTREX flight tracks (red dots). Filled circles represent the mixing ratios averaged into 1 km altitude bins ± 1 sd over WP and EP to observe the tendency of the mixing ratios as the altitude increases. Range of the bins are: 14 km= 13.5 to 14.5 km, 15 km= 14.5 to 15.5 km, 16 km= 15.5 to 16.5 km, 17 km= 16.5 to 17.5 km, 18 km= 17.5 to 18.5 km. Similar figures for CH₂Br₂ and CHBr₃ are in Navarro et al., (2015).**
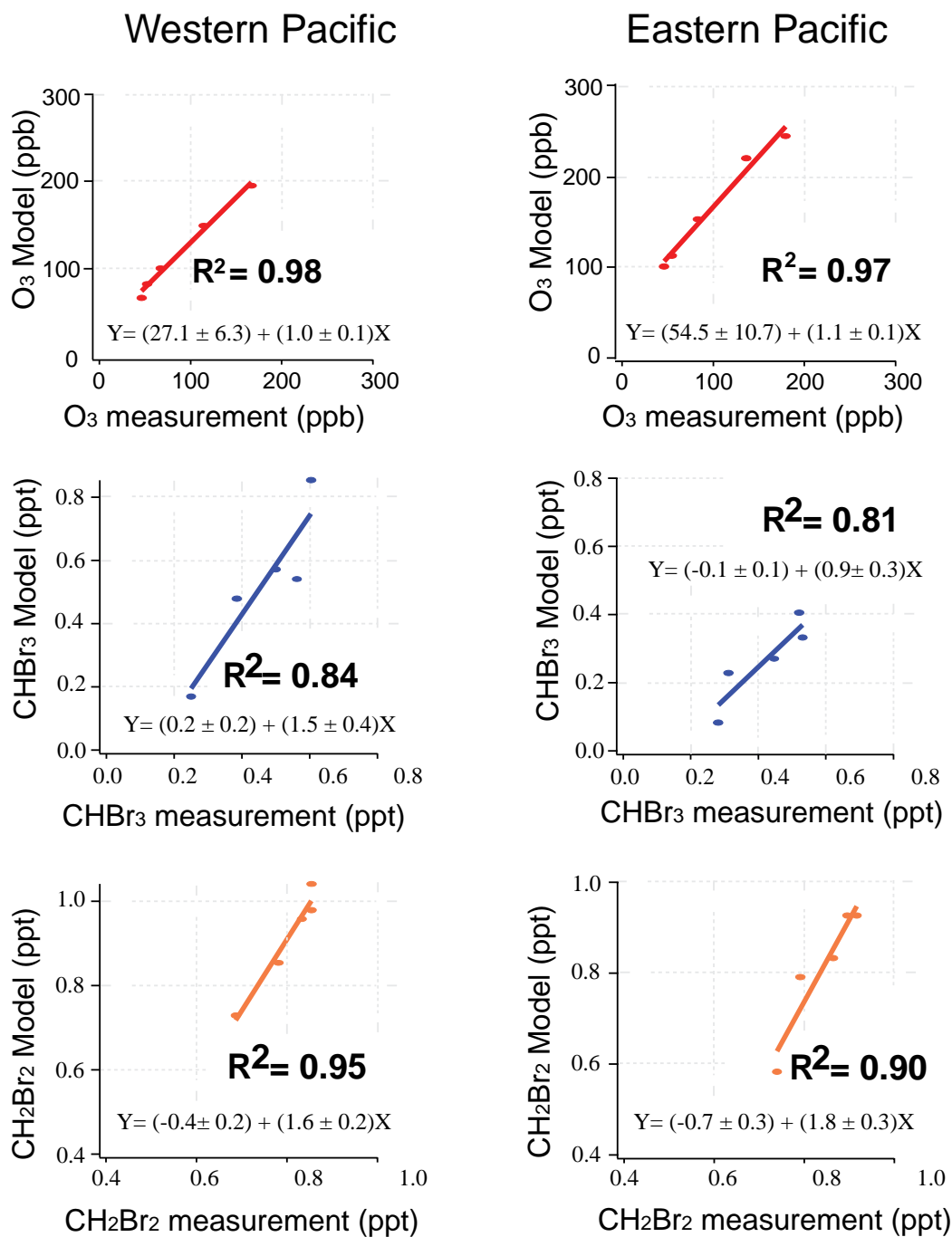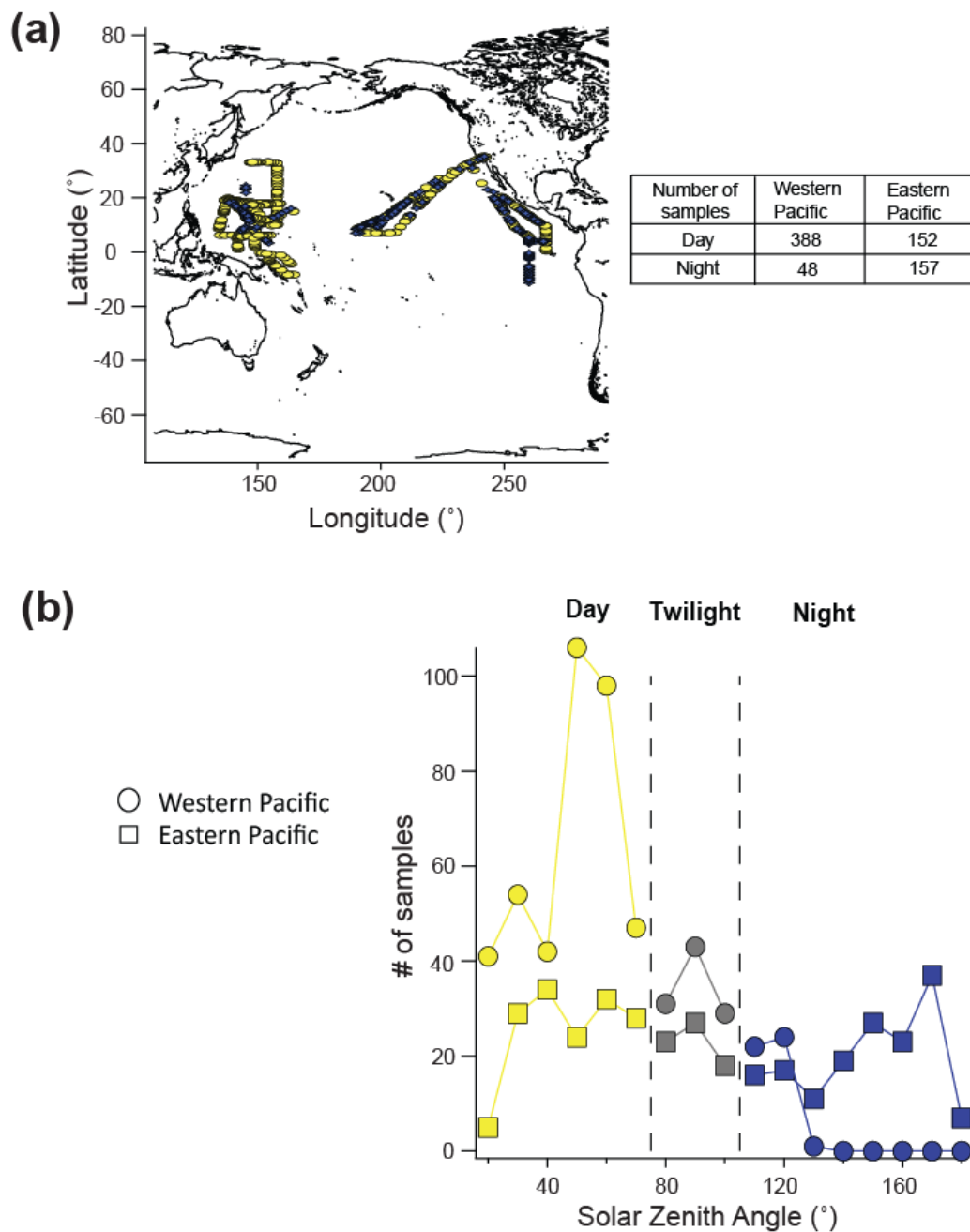
**Figure 2: Correlations between measured and modelled mixing ratios of $O_3$, $CHBr_3$ and $CH_2Br_2$ over the WP and EP, respectively, using the 1 km average bins. Filled circles are the mixing ratios averaged into 1 km altitude bins (same as in figure 1 for $O_3$, and figure 1 in Navarro et al., (2015) for $CHBr_3$ and $CH_2Br_2$). Solid lines represent the linear regression analysis of the 1 km average bins including coefficient of determination ($R^2$) and regression equation (Y).**

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| Number of samples | Western Pacific | Eastern Pacific |
|---|---|---|
| Day | 388 | 152 |
| Night | 48 | 157 |



**Figure 3: (a) Location of GWAS observations along ATTREX flight tracks taken at different altitudes over WP and EP. Yellow filled circles represent the samples taken during the day and blue filled circles the samples taken at night. (b) Sample density of GWAS observations arranged by solar zenith angle over the western and eastern Pacific. Yellow filled circles represent samples taken over WP during daylight, while blue filled circles are the samples taken over WP during night-time. Yellow filled squares represent the samples taken over EP during daylight, while blue filled squares are the samples taken over EP during night-time. Grey circles and squares are the samples taken during twilight over WP and EP, respectively.**

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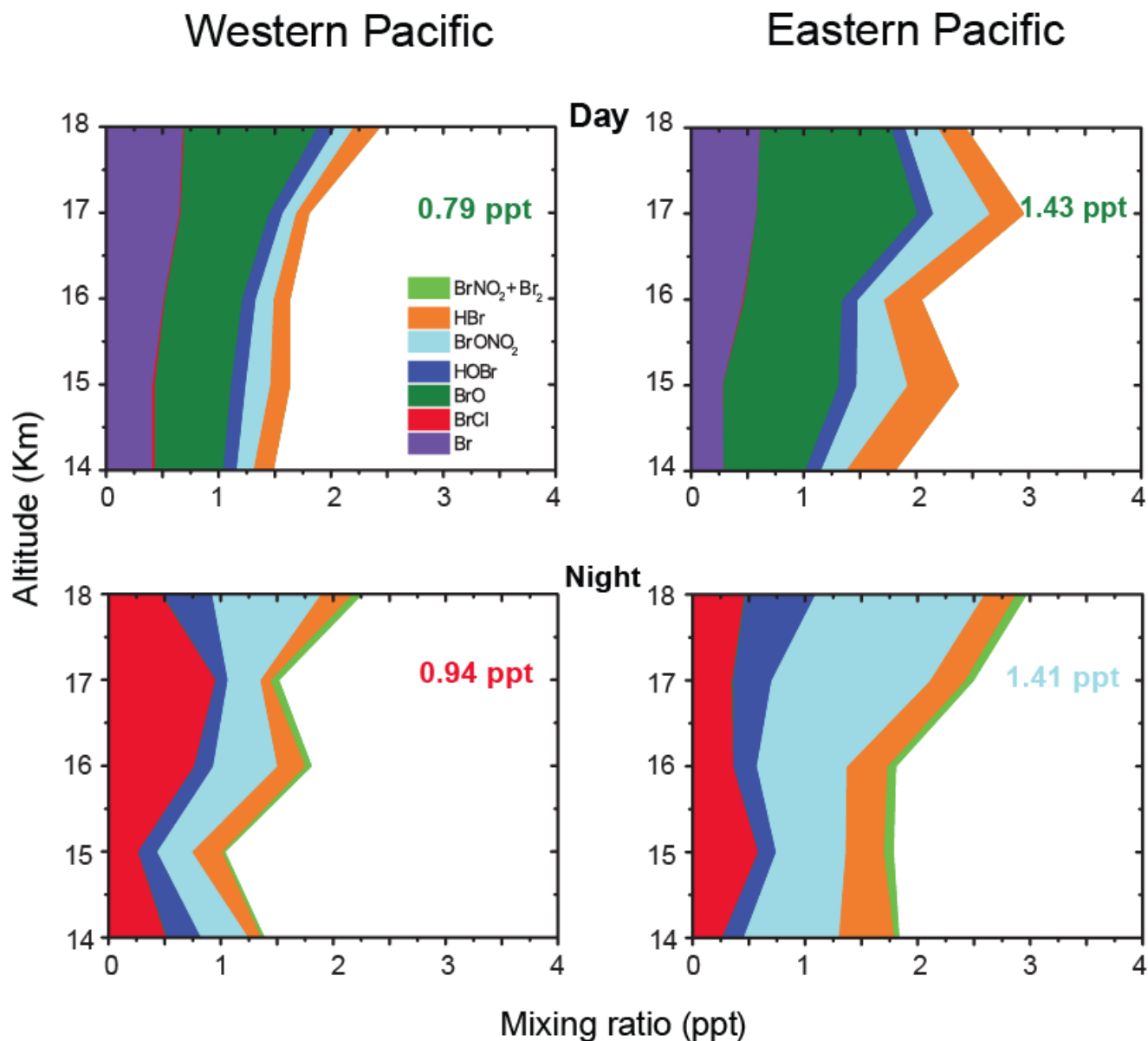
Figure 4: Model calculations of inorganic bromine partitioning along ATTREX flight tracks over the WP and EP using CAM-Chem with prevailing atmospheric conditions (specified meteorology) during the ATTREX campaign. Numbers inside the boxes represent the mixing ratios of BrO (green), BrCl (red) and BrONO₂ (light blue) at 17 km.
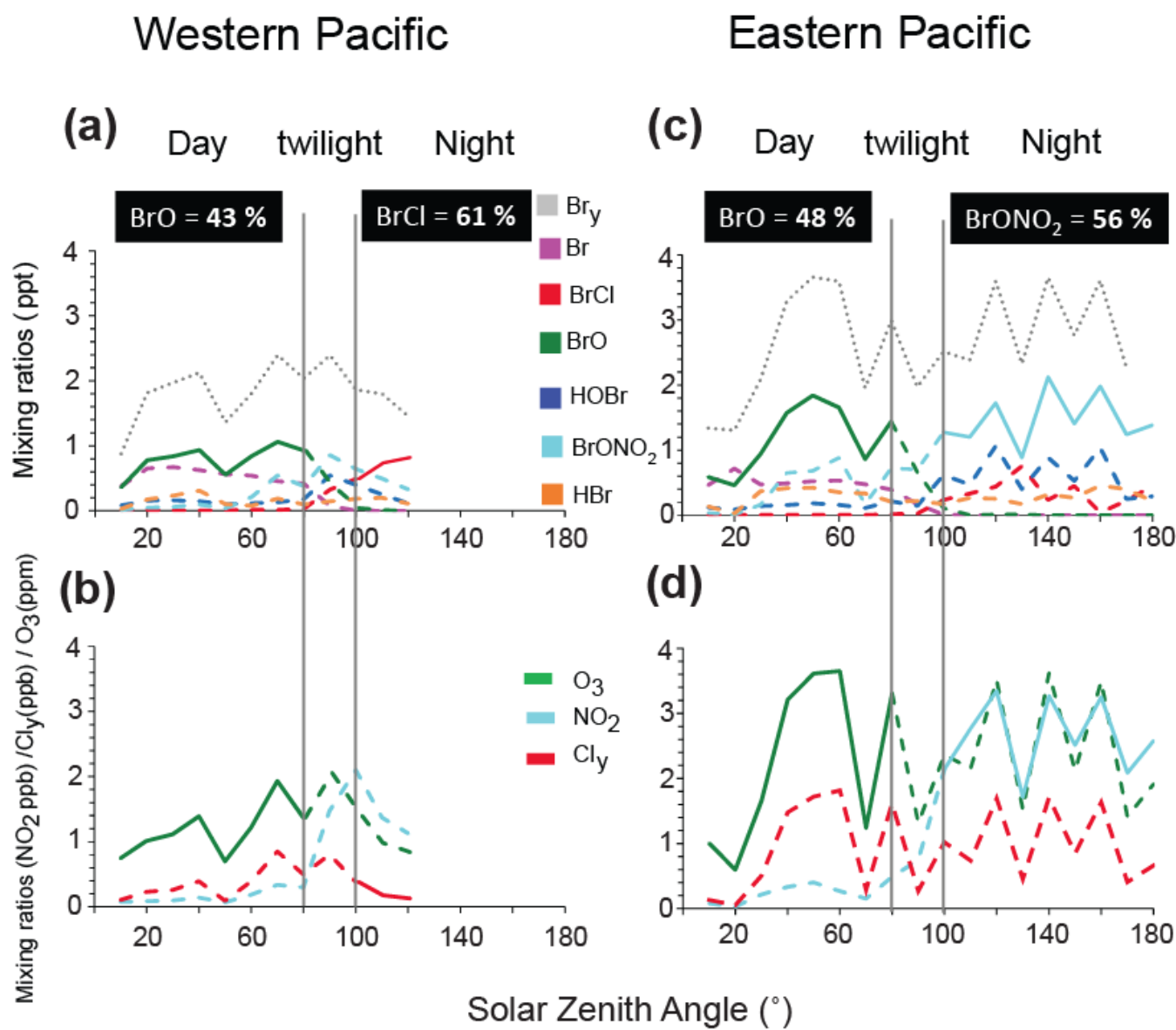
**Figure 5: Average of inorganic bromine species (top panel) and main reactants of the inorganic chemistry (bottom panel) using the entire range of altitudes (14 to 18 km) over the western Pacific (a and b) and eastern Pacific (c and d). Black boxes indicate the percentage of the dominant $Br_y$ species for day and night at 17 km.**
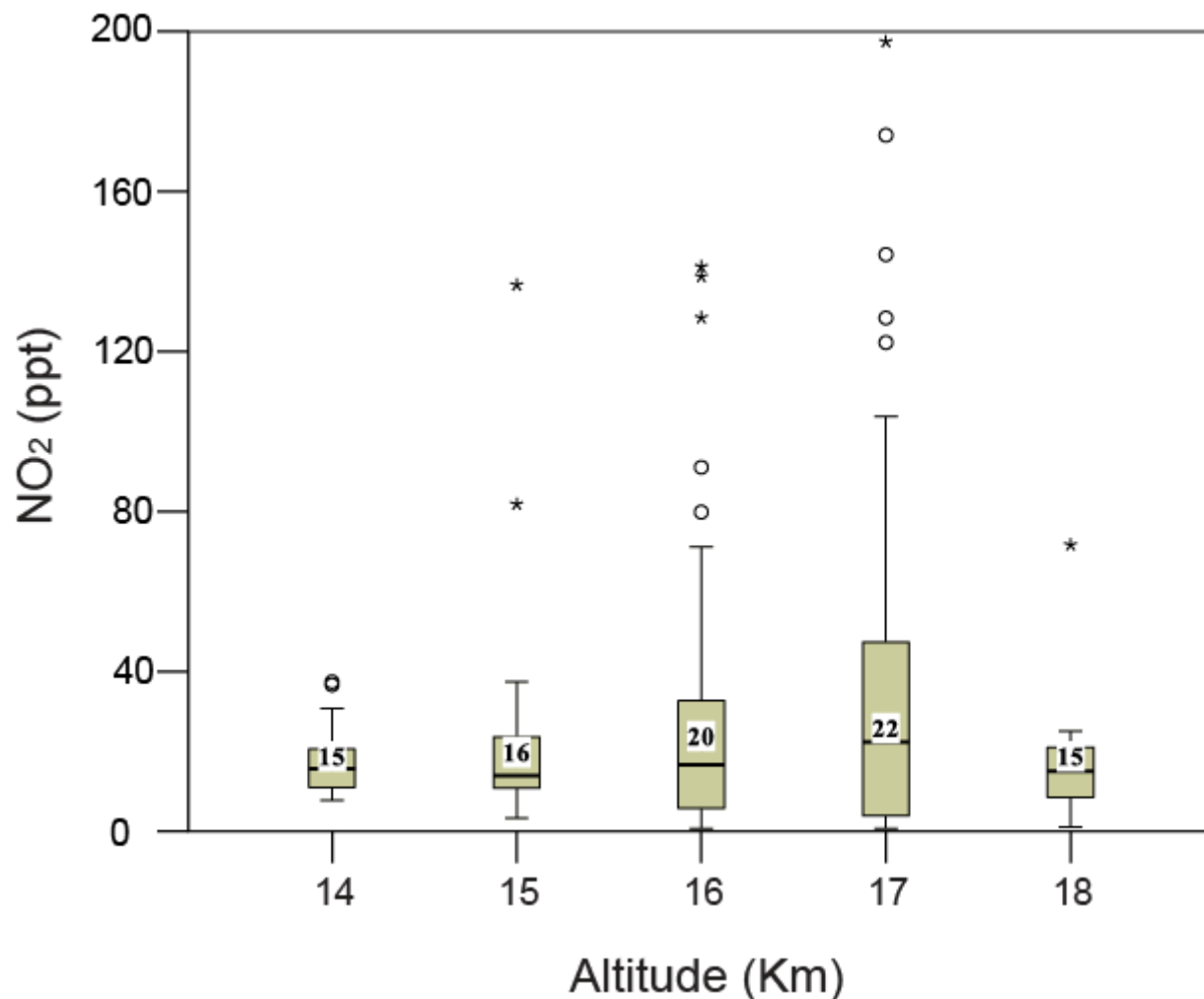
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**Figure 6: Boxplot of CAM-Chem NO₂ estimations as a function of altitude during daylight over Eastern Pacific. The filled boxes display the minimum, first quartile (Q1), median (Q2), third quartile (Q3), and maximum values. Black line across the interior of the box represent the median (Q2) of NO₂ for the corresponding altitude. The bottom of the box is the first quartile (Q1) or the 25th percentile (the middle value between the smallest number and the median of the data set), while the top of the box is the third quartile (Q3) or the 75th percentile (the middle value between the median and the highest value of the data). T-bars extended from the boxes represent the whiskers (the largest and the smallest non-outlier value, respectively). Circles and stars are the outliers defined according to the interquartile range (IQR = Q3-Q1): Circles are the "out values" or the NO₂ mixing ratios greater than 1.5 times the interquartile range, and starts are "the extreme values" or the NO₂ mixing ratios greater than 3 times the interquartile range. The numbers inside the box represent the average NO₂.**
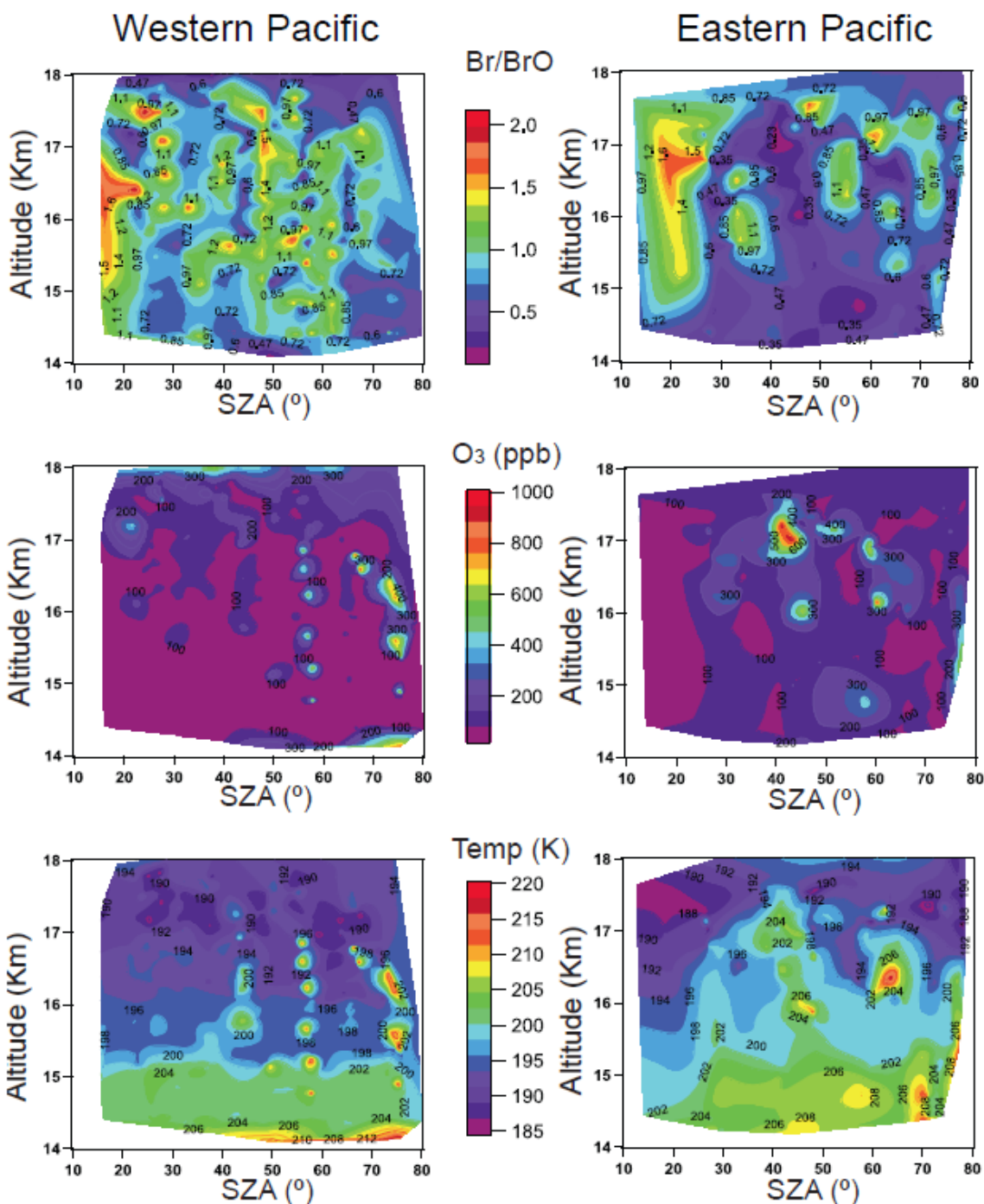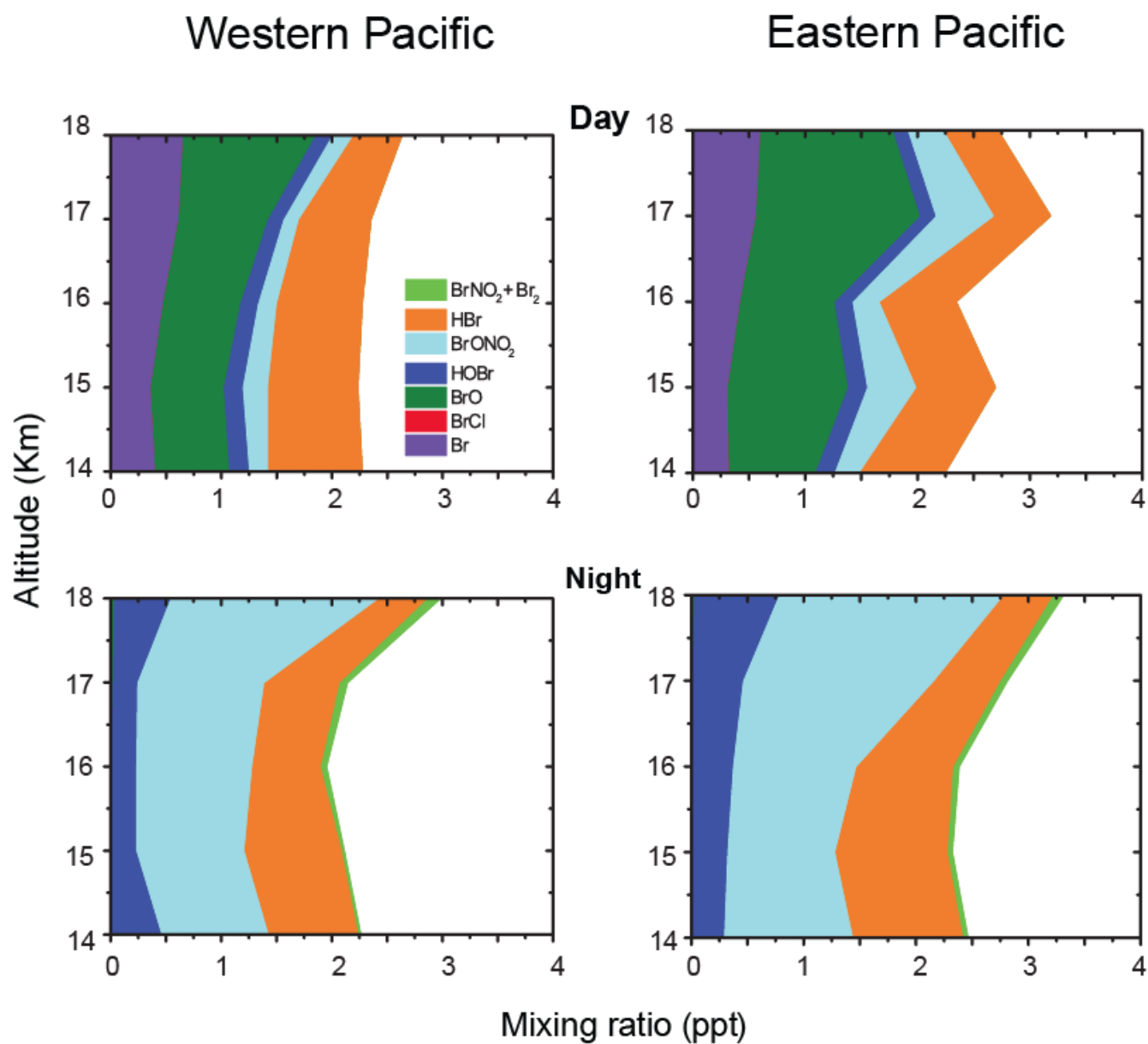
**Figure 7: Modelled estimations of the daylight Br/BrO ratio (top panel), ozone (middle panel) and temperature (bottom panel) as function of SZA over the WP and EP using CAM-Chem.**

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**Figure 8: Inorganic bromine partitioning along ATTREX flight tracks over the Western and Eastern Pacific. Similar to Fig 4, but turning off the ice aerosol recycling reactions in the CAM-Chem chemical mechanism.**

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**Table 1: Summary of the results found at the Tropical Tropopause level (~17km)**

|  | **Specie (time)** | **WP (ppt)** | **EP (ppt)** |
|---|---|---|---|
| Mean | BrO (day) | 0.79 | 1.43 |
|  | Br (day) | 0.64 | 0.57 |
|  | BrCl (night) | 0.94 | 0.34 |
|  | BrONO2 (night) | 0.29 | 1.41 |
| #Range | $O_3$ (day)* | 35-500 | 35-900 |
|  | $NO_2$ (day) | 1-227 | 0.7-343 |
|  | $Cl_y$ (day) | 1-515 | 1-969 |
|  | Temp (day)** | 188-192 | 188-206 |

# Range defined as min and max values, *units in ppb, **units in K.