Atmos. Chem. Phys. Discuss., 11, 32003–32029, 2011
www.atmos-chem-phys-discuss.net/11/32003/2011/
doi:10.5194/acpd-11-32003-2011

Atmospheric Chemistry and Physics Discussions

Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere

A. Saiz-Lopez[1], J.-F. Lamarque[2], D. E. Kinnison[2], S. Tilmes[2], C. Ordóñez[1], J. J. Orlando[2], A. J. Conley[2], J. M. C. Plane[3], A. S. Mahajan[1], G. Sousa Santos[4], E. L. Atlas[5], D. R. Blake[6], S. P. Sander[7], S. Schauffler[8], A. M. Thompson[9], and G. Brasseur[10]

[1]Laboratory for Atmospheric and Climate Science, CSIC, Toledo, Spain
[2]Atmospheric Chemistry Division, NCAR, Boulder, CO, USA
[3]School of Chemistry, University of Leeds, Leeds, UK
[4]Institute for Atmospheric and Climate Science, ETH, Zurich, Switzerland
[5]Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL, USA
[6]Department of Chemistry, University of California, Irvine, CA, USA
[7]Jet Propulsion Laboratory, California Institute of Technology, CA, USA
[8]Earth Observing Laboratory, NCAR, Boulder, CO, USA

[9]Department of Meteorology, Pennsylvania State University, Pennsylvania, USA
[10]Climate Service Center, Hamburg, Germany

Received: 2 September 2011 – Accepted: 28 November 2011 – Published: 6 December 2011

Correspondence to: A. Saiz-Lopez (a.saiz-lopez@ciac.jccm-csic.es)

ACPD
11, 32003–32029, 2011

Abstract

We have integrated observations of tropospheric ozone, very short-lived (VSL) halocarbons and reactive iodine and bromine species from a wide variety of tropical data sources with the global CAM-Chem chemistry-climate model and offline radiative transfer calculations to compute the contribution of halogen chemistry to ozone loss and associated radiative impact in the tropical marine troposphere. The inclusion of tropospheric halogen chemistry in CAM-Chem leads to an annually averaged depletion of around 10 % (∼2.5 Dobson units) of the tropical tropospheric ozone column, with largest effects in the middle to upper troposphere.This depletion contributes approximately $-0.10\,\mathrm{W\,m^{-2}}$ to the radiative flux at the tropical tropopause. This negative flux is of similar magnitude to the $\sim 0.33\,\mathrm{W\,m^{-2}}$ contribution of tropospheric ozone to present-day radiative balance as recently estimated from satellite observations. We find that the implementation of oceanic halogen sources and chemistry in climate models is an important component of the natural background ozone budget and we suggest that it needs to be considered when estimating both preindustrial ozone baseline levels and long term changes in tropospheric ozone.

1 Introduction

Tropospheric ozone (O_3) is one of the most important short-lived gases contributing to greenhouse radiative forcing (RF) (Forster et al., 2007). It is produced by photochemical oxidation of carbon monoxide (CO), methane (CH_4) and non-methane volatile organic compounds (NMVOC) in the presence of nitrogen oxides (NO_x). A large fraction of the tropospheric ozone loss occurs within the tropical marine boundary layer (TMBL) via photolysis to excited oxygen atoms $O(^1D)$, followed by reaction with water vapour, reactions with odd hydrogen radicals (HO_x), and surface deposition (Horowitz et al., 2003). However, since conventional HO_x chemistry and ozone photochemistry cannot account for the observed ozone variability in the TMBL, it has been suggested

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

ACPD

11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

that reactive halogen species released into the atmosphere by the photodecomposition of organohalogens and via autocatalytic recycling on sea-salt aerosols may also contribute to ozone destruction in this environment (e.g. Dickerson et al., 1999; Read et al., 2008).

Measurements of low ozone levels (< 10 ppbv) and large diurnal variability of surface ozone have been reported over the tropical regions of the Atlantic Ocean (Oltmans and Levy II, 1992; Dickerson et al., 1999), Pacific Ocean (Johnson et al., 1990; Kley et al., 1996; Nagao et al., 1999; Shiotani et al., 2002; Takashima et al., 2008), and Indian Ocean (Johnson et al., 1990; Bremaud et al., 1998; Dickerson et al., 1999; de Laat et al., 1999; Burket et al., 2003). Tropical ozonesonde data also show events of substantially reduced ozone levels in the upper troposphere at different locations throughout the tropics (Solomon et al., 2005), although Vömel and Diaz (2010) claim that such events might be caused by artefacts in the measurement procedures. Despite the considerable number of low ozone events reported, only recently has halogen-induced ozone destruction been unambiguously demonstrated over the tropical oceans (Read et al., 2008).

The reduction in tropospheric ozone due to bromine chemistry has been previously studied with 3-dimensional global chemistry transport models (CTMs) (von Glasow et al., 2004; Yang et al., 2005), but those studies did not include the combined effect of bromine and iodine sources. Moreover, the resulting radiative impact of halogen-driven ozone loss in the tropical marine troposphere has not been quantified so far. In this study we integrate observations of tropospheric ozone, very short-lived (VSL) halocarbons – halogenated organic compounds with atmospheric lifetimes of less than 6 months (WMO, 2011), and reactive iodine and bromine species from a wide variety of tropical data sources with the global CAM-Chem chemistry-climate model and radiative transfer calculations to estimate the impact of halogen chemistry on ozone loss and radiative balance in the tropical marine troposphere.

2 Description of the chemistry-climate model

CAM-Chem is the global three-dimensional Community Atmosphere Model (CAM) (Gent et al., 2010), modified to include interactive chemistry (i.e. with feedback to the radiation calculation in the atmosphere) and calculate distributions of gases and aerosols (Lamarque et al., 2011). Here we use CAM-Chem with a horizontal resolution of 1.9° (latitude) × 2.5° (longitude) and 26 hybrid vertical levels from the surface to approximately 40 km, with a model timestep of 30 min. The model has a full representation of tropospheric (Emmons et al., 2010) and stratospheric (Kinnison et al., 2007) chemistry. CAM-Chem has been used here with the same configuration as in a variety of applications with a focus both on the troposphere (e.g. Lamarque et al., 2010) and the lower stratosphere (e.g. Lamarque and Solomon, 2010). Details on the bulk aerosol parameterizations are given elsewhere (e.g. Lamarque et al., 2011; Ordóñez et al., 2011).

The scope of CAM-Chem has been extended to include natural sources of VSL halocarbons from the ocean; reactive chlorine, bromine and iodine species; related photochemical, gas-phase and heterogeneous reactions, as well as dry and wet deposition for relevant species. A detailed description of the new halogen sources and chemistry scheme implemented in CAM-Chem can be found in the companion paper (Ordóñez et al., 2011). Briefly, the tropospheric halogen chemical scheme follows that of the 1-dimensional Tropospheric HAlogen chemistry MOdel (THAMO) (Saiz-Lopez et al., 2008), which has recently been used to model reactive halogen species over the tropical Atlantic Ocean (Mahajan et al., 2010). To determine the emissions of VSL bromocarbons ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$, and $CHBrCl_2$) and iodocarbons (CH_2I_2, CH_2IBr and CH_2ICl), Ordóñez et al. (2011) used a compilation of aircraft campaigns and some observations available in the marine boundary layer. Over the tropical oceans (20° S–20° N) these emission fields follow the geographical distribution of the Phytoplankton Pigment Concentration (PPC) retrieved from SeaWIFS satellite data, while they consist of constant oceanic fluxes with a fixed 2.5 coast to ocean emission

ACPD
11, 32003–32029, 2011

ratio in the extratropics (Sousa Santos, 2008; Ordóñez et al., 2011). Unlike in Ordóñez et al. (2011), the emission sources used for this study have only been extended to the mid-latitude oceans (up to 50° in both hemispheres). Emissions for methyl iodide (CH_3I) are based on the inventory from a previous modelling study (Bell et al., 2002), while the longer-lived methyl bromide (CH_3Br) concentration is set as a lower boundary condition (see below). We assume that the emission of all VSL halocarbons is photosynthetically driven and depends on the actinic flux, with a diurnal variation described by a Gaussian profile peaking at noon and null at night. The model predictions for these species compare reasonably well against observations (Ordóñez et al., 2011).

One-dimensional model analyses constrained with observed iodocarbon fluxes (Mahajan et al., 2010; Jones et al., 2010) suggest that a substantial source of iodine is required to support the observed iodine oxide (IO) levels over the tropical Atlantic Ocean. From observations at different coastal locations there is evidence that this additional source may be in the form of molecular iodine (I_2) (Saiz-Lopez and Plane, 2004). Laboratory studies (Garland and Curtis, 1981; Sakamoto et al., 2009) have shown that deposition of O_3 on the sea surface may lead to the emission of I_2. Similarly, there are reports on the photosensitised production of volatile halogen species at the sea surface (Reeser et al., 2009). Therefore, we use a flux of inorganic iodine (i.e. I_2) along with the iodocarbon flux to reproduce the observed IO at the different tropical locations where IO has been observed at pptv levels (e.g. Eastern Pacific, Tropical Atlantic and Indian Ocean). In the simulation presented here, this is accounted for by a global total I_2 emission field of ~1200 Gg yr^{-1}, with the same geographical distribution as that of the above mentioned VSL halocarbons but with a flat diurnal cycle. The average I_2 flux over the tropical oceans in CAM-Chem (including open oceans, upwelling regions and coastal areas within 20° N–20° S) is 4.9×10^7 molecule cm^{-2} s^{-1}, very close to the constant day and night I_2 flux of 5.0×10^7 molecule cm^{-2} s^{-1} considered in Mahajan et al. (2010) for the tropical Atlantic Ocean around Cape Verde. Note that the lifetime of I_2 is too short (i.e. seconds) to be transported to the mid-upper troposphere. As a consequence, the model results for that region of the atmosphere are not expected

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |
ACPD
11, 32003–32029, 2011

to be very sensitive to the I_2 flux. However the emission of I_2, subsequent photolysis and further halogen-HO_x-ozone reactions in the TMBL may have an impact on the amount of ozone transported to the mid- and upper troposphere.

At the lower boundary, the time-varying (monthly values) zonal-averaged distributions of CO_2, CH_4, H_2, N_2O, and long-lived halocarbons (CFC-11, CFC-12, CFC-113, HCFC-22, H-1211, H-1301, CCl_4, CH_3CCl_3, CH_3Cl, CH_3Br) are specified following their observed surface concentrations for 2000. Emissions from anthropogenic activities and biomass burning (natural and anthropogenically-forced) are equivalent to those from a MOZART-4 simulation for the year 2004 (Emmons et al., 2010).

Two 10-yr simulations of CAM-Chem, with and without VSL halocarbons, were conducted. For these model runs, climatological sea surface temperatures and sea-ice extent (Rayner et al., 2003) were set as lower boundary conditions. Hence CAM-Chem only solved for the atmospheric and land portions of the climate system, and the simulations do not pertain to any specific meteorological year. The model output shown here corresponds to the last year of those simulations. We only present results from the simulation with VSL halogenated species unless otherwise stated.

3 Results of the chemistry-climate model

3.1 Halocarbons and halogen radicals

Bromoform ($CHBr_3$) and CH_3I are the main VSL halocarbons contributing to the total tropospheric bromine and iodine burden, respectively (WMO, 2011). Their tropospheric lifetimes are long enough – local lifetime (calculated using an average tropospheric OH concentration of 1×10^6 molecule cm^{-3} and the OH reaction rate constant at $T = 275$ K) of ~24 days for $CHBr_3$ and ~7 days for CH_3I (WMO, 2011) – for them to be transported to the upper troposphere within deep convection areas. By contrast, emissions of other iodocarbons (e.g. CH_2ICl, CH_2IBr and CH_2I_2), which have shorter lifetimes on the order of a few hours to minutes, and catalytic bromine release from sea-salt aerosols

ACPD
11, 32003–32029, 2011

provide a source of reactive halogens in the TMBL. The simulated vertical profiles of $CHBr_3$ and CH_3I in the tropical troposphere are in good agreement, both in magnitude and vertical distribution, with a composite of aircraft observations from three field campaigns: PEM-Tropics A (Hoell at al., 1999), PEM-Tropics B (Raper et al., 2001), and TRACE-P (Jacob et al., 2003) (Fig. 1). For two longer lived bromocarbons, CH_3Br and CH_2Br_2 – total lifetime (considering not only photochemical loss in the atmosphere but also uptake to oceans and soil) of ∼0.8 yr and local lifetime of ∼123 days, respectively (WMO, 2011) –, that additionally contribute to the tropospheric halogen burden, the average modelled profiles throughout the tropical troposphere are also comparable to the observations (Fig. 1). The slight overestimation of CH_3Br by the model for PEM-Tropics B (1999) and TRACE-P (2001) may be partly related to the decline in the industrial production of this compound since the mid/end of the 1990 s (WMO, 2011). More details on the evaluation of CH_3Br and VSL halocarbon species, including the most short-lived iodocarbons which are not shown here (i.e. CH_2ICl, CH_2IBr and CH_2I_2), can be found in Ordóñez et al. (2011).

The reactive species bromine oxide (BrO) and IO have been observed over the Atlantic, Indian and Pacific Oceans from a variety of measuring platforms. The computed daytime average boundary layer distribution of these species in the model lies within 0.5–2 pptv, in good accord with a compilation of reported observations in the tropical regions (Fig. 2). In the tropical upper troposphere there are only two studies from balloon-based platforms reporting observations of BrO and IO over Northern Brasil (Dorf et al., 2008; Butz et al., 2009). The simulated mixing ratios of BrO (∼0.5 pptv) and IO (∼0.02 pptv) are below the ∼1 pptv BrO (Dorf et al., 2008) and the upper limit of ∼0.2 pptv IO (Butz et al., 2009) reported for that location in the upper troposphere.

3.2 Tropical tropospheric ozone

Simulated vertical profiles of ozone are compared with Southern Hemisphere Additional Ozonesonde Network (SHADOZ; Thompson et al., 2003a,b) and World Ozone and Ultraviolet Radiation Data Centre (WOUDC, ftp://ftp.tor.ec.gc.ca/) ozone profiles

ACPD
11, 32003–32029, 2011

at three marine locations (San Cristobal – Galapagos, Fiji, and Naha – Japan), where long-term measurements are available in the vicinity of the above mentioned airborne field measurement campaigns (Fig. 3). The tropical SHADOZ sites San Cristobal and Fiji are located within the regions covered by PEM-Tropics A and PEM-Tropics B, respectively, while Naha is a sub-tropical site sampled during Trace-P. The model reproduces well the observed magnitude and structure of ozone throughout the tropospheric column. Despite the underestimation of the measurements in the lower and mid-troposphere over Fiji, the modelled ozone mixing ratios are within the variability of the observations. Additionally, the multi-year seasonal variation of simulated ozone mixing ratios at the surface (1000 hPa) and in the upper troposphere (300 hPa) also agrees reasonably well with observations at the three sites (Fig. 4). A good match between model and surface observations is found for Naha while the model overestimates the ozone mixing ratios measured at San Cristobal and underestimates them at Fiji; note that in the case of the low ozone events the deviations between model and observations are magnified by the logarithmic scale used. No significant over- or underestimation is found for the model results at 300 hPa.

3.3 Chemical ozone loss

In the TMBL (20° S–20° N), the annually integrated rate of surface ozone loss due to halogen chemistry is ~6×10^5 molecule cm^{-3} s^{-1} (~0.15 ppbv h^{-1} at daytime) (Fig. 5, left). The integrated contribution of iodine-mediated reactions to the total rate of surface ozone loss is three times larger than that of bromine chemistry alone. When both chemistries are combined via the reaction of IO + BrO to Br + OIO (75 %) and Br + I (25 %), the ozone loss rate is fourfold that of bromine chemistry alone. On an annual average basis, in the absence of halogens, the model sampled at Cape Verde predicts a diurnal loss of 2.5 ppbv by mid-afternoon (Fig. 5, right). However, in the presence of halogens the loss is ~3.2 ppbv, shifting the timing of the minimum ozone level. This is in agreement with observed diurnal ozone loss and previous zero- and one-dimensional model analyses at this location (Read et al., 2008; Mahajan et al., 2010).

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |
ACPD
11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

In the tropical troposphere the contribution to chemical ozone loss is dominated by ozone and HO_x photochemistry (Fig. 6, middle and top panels). However, we find that the integrated loss due to halogen-catalysed ozone destruction cycles is 15–30 % of the total ozone chemical loss throughout the tropospheric column (Fig. 6, bottom). Halogen-induced ozone loss is enhanced in the 400–150 hPa pressure range. From a climate perspective, this finding is particularly relevant because the sensitivity of long-wave absorption by ozone is the largest in the upper troposphere (e.g. Lacis et al., 1990; Kiehl et al., 1999; Worden et al., 2008). The halogen precursor source region and rapid vertical transport of air determine the contribution of halogen chemistry to ozone depletion and the extent of ozone-poor air in the tropical upper troposphere. Within deep convection zones, this can proceed via efficient uplift of: (i) air that has been ozone-depleted through chemical processing in the clean TMBL, and ii) VSL organic iodine and bromine species whose breakdown in the upper troposphere initiates ozone depletion cycles. Our results indicate that vertical transport and efficient photochemical breakdown of VSL halocarbons contribute at least to 80 % of the halogen-driven ozone loss in the upper troposphere. The combination of these processes leads to an average reduction of 2.5 Dobson Units (DU), more than 10 % of the tropospheric ozone column, over large regions of the tropics (Fig. 7, top). Most of the ozone loss (measured in DU) occurs in the mid- to upper-troposphere (pressure range between 850 hPa and 200 hPa), above the TMBL (Fig. 7, middle). There is high regional variability, with the largest ozone loss found in the upper troposphere of the western tropical Pacific, Indian and Atlantic Oceans, within areas with efficient vertical transport.

4 Radiative impact of halogen-driven ozone loss

The climate significance of halogen-mediated ozone loss in the troposphere can be determined by the tropical annually integrated radiative impact from the tropospheric ozone depletion associated with the atmospheric processing of natural oceanic halogen sources. The radiative impact of halogen chemistry in the troposphere is com-

ACPD
11, 32003–32029, 2011

puted using the CAMRT radiative transfer scheme (Collins et al., 2006). For that purpose, we calculate the radiative fluxes (shortwave and longwave, all sky) at the tropopause, after stratospheric temperature adjustment (Forster et al., 2007). These fluxes are computed using identical present-day environmental conditions (temperature, humidity, clouds, aerosols and surface albedo), except for tropospheric ozone, which is set to its distribution from the simulations with and without halogen chemistry. On an annual basis, the tropical difference (halogen *minus* no halogen) between those fluxes is $\approx -0.1\,W\,m^{-2}$, defining the size of the contribution of the effect of tropospheric halogen chemistry on ozone alone to the radiative balance of the atmosphere. This estimate is quite reasonable considering that our tropical tropospheric ozone column is estimated to decrease by about 2.5 DU, leading to a $0.1\,W\,m^{-2}$ imbalance when scaled by the $0.042\,W\,m^{-2}\,DU^{-1}$ estimated for all-sky conditions in Ramaswamy et al. (2001). The difference in the longwave fluxes from both simulations (-0.138 and $-0.104\,W\,m^{-2}\,DU^{-1}$ under clear-sky and all-sky conditions, respectively; see Table 1) can also be compared with recent satellite estimates of the longwave radiative effect (LWRE) of tropospheric ozone, i.e. the reduction in outgoing longwave radiation (OLR) at the top of the atmosphere (TOA) due to tropospheric ozone. This enables us to put into a broader context the significance of the radiative effect associated with the destruction of tropospheric ozone by VSL halogens over the tropics. Worden et al. (2008) estimated the LWRE of tropospheric ozone to be $0.48\,W\,m^{-2}$ by using clear-sky ocean observations of the TES sensor in the upper troposphere (200–500 hPa) for 45° S–45° N during the year 2006. Worden et al. (2011) developed a new approach to improve the accuracy of their LWRE estimate during August 2006. Interferences with water vapour were removed, which yields lower estimates of the OLR sensitivity to ozone, and results were computed for all observations over the full troposphere. They obtained a global average LWRE from tropospheric ozone of $0.50\,W\,m^{-2}$ under clear-sky conditions and $0.33\,W\,m^{-2}$ under all-sky conditions. This suggests that the negative contribution of halogen-driven ozone loss to the longwave radiative flux at the tropical tropopause is significant since it is around 30 % of the positive contribution to the TOA radiation flux associated with infrared ozone absorption. Note, however, that our results are not directly comparable to the previous satellite estimates because the latter (i) exclude the stratospheric temperature adjustment and therefore represent instantaneous radiative forcings and (ii) are extended to areas outside the tropics.

5 Concluding remarks

According to the IPCC Fourth Assessment Report (AR4) Chapt. 2 (Forster et al., 2007), the global estimate of the direct RF resulting from the increase in tropospheric ozone since 1750 (on average +0.35 W m^{-2}) has a medium level of scientific understanding which originates from the uncertainties in the model formulations used and the inability of the models to reproduce the low ozone concentrations indicated by the very uncertain semi-quantitative observations during the late 19th century (see e.g. Volz and Kley, 1988; Marenco et al., 1994; Pavelin et al., 1999; Mickley et al., 2001; Shindell et al., 2003; Lamarque et al., 2005). This study shows that accounting for oceanic halogen sources and their chemistry the natural rate of chemical ozone removal in the tropical marine troposphere is up to ~30 % larger than previously assumed in global chemistry-climate models, and that the associated contribution to the TOA radiation flux is of similar magnitude (i.e. about 30 %) as the long-wave absorption by tropospheric ozone. The inclusion of this natural component of the ozone budget has the potential to improve simulations of preindustrial ozone baseline levels, and therefore estimates of anthropogenically-influenced increase in tropospheric ozone concentrations and its associated RF. Note that reactive bromine and iodine not only deplete O_3 through efficient catalytic cycles but are also coupled with HO_x and NO_x chemistry. Even though halogens have been present since preindustrial times, they may have altered ozone concentrations in a different way under changing NO_x regimes. Finally, fluxes of natural halogenated VSL species from the ocean surface are controlled by biological, physical and photochemical mechanisms that may respond to future changes in climate processes (WMO, 2011). Therefore, further field and laboratory work is needed to assess

ACPD
11, 32003–32029, 2011

how climate variability may influence ocean-atmosphere exchange of reactive halogen precursors and its associated impact on the radiation balance in the tropical marine troposphere.

Acknowledgements. The authors are grateful to S. Solomon for valuable discussions and comments on this manuscript. We thank the University of York for making available the ozone data at the Cape Verde Atmospheric Observatory. Ozonesonde data at Naha were obtained from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) operated by Environment Canada, Toronto, Ontario, Canada under the auspices of the World Meteorological Organization. This work was supported by the Department of Energy under the SciDAC program. The CESM project is supported by the National Science Foundation and the Office of Science (BER) of the US Department of Energy. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under sponsorship of the National Science Foundation.

References

Allan, B. J., McFiggans, G., Plane, J. M. C., and Coe, H.: Observations of iodine monoxide in the remote marine boundary layer, J. Geophys. Res., 105(D11), 14363–14369, 2000.

Bell, N., Hsu, L., Jacob, D. J., Schultz, M. G., Blake, D. R., Butler, J. H., King, D. B., Lobert, J. M., and Maier-Reimer, E.: Methyl iodide: atmospheric budget and use as a tracer of marine convection in global models, J. Geophys. Res., 107(D17), 4340, doi:10.1029/2001JD001151, 2002.

Bremaud, P. J., Taupin, F., Thompson, A. M., and Chaumerliac, N.: Ozone nighttime recovery in the marine boundary layer: Measurement and simulation of the ozone diurnal cycle at Reunion Island, J. Geophys. Res., 103, 3463–3473, doi:10.1029/97JD01972, 1998.

Burkert, J., Andrés-Hernández, M. D., Reichert, L., Meyer-Arnek, J., Doddridge, B., Dickerson, R. R., Mühle, J., Zahn, A., Carsey, T., and Burrows, J. P.: Trace gas and radical diurnal behavior in the marine boundary layer during INDOEX 1999, J. Geophys. Res., 108, 8000, doi:10.1029/2002JD002790, 2003.

Butz, A., Bösch, H., Camy-Peyret, C., Chipperfield, M. P., Dorf, M., Kreycy, S., Kritten, L., Prados-Román, C., Schwärzle, J., and Pfeilsticker, K.: Constraints on inorganic gaseous io-

ACPD

11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

dine in the tropical upper troposphere and stratosphere inferred from balloon-borne solar occultation observations, Atmos. Chem. Phys., 9, 7229–7242, doi:10.5194/acp-9-7229-2009, 2009.
Colllins, W. D., Rasch, P. J., Boville, B. A., Hack, J. J., McCaa, J. R., Williamson, D. L., Briegleb, B. P., Bitz, C. M., Lin, S.-J., and Zhang, M.: The formulation and atmospheric simulation of the Community Atmosphere Model version 3 (CAM3), J. Clim., 19, 2144–2161, 2006.
de Laat, A. T. J., Zachariasse, M., Roelofs, G. J., van Velthoven, P., Dickerson, R. R., Rhoads, K. P., Oltmans, S. J., and Lelieveld, J.: Tropospheric O_3 distribution over the Indian Ocean during spring 1995 evaluated with a chemistry-climate model, J. Geophys. Res., 104, 13881–13893, 1999.
Dickerson, R. R., Rhoads, K. P., Carsey, T. C., Oltmans, S. J., Burrows, J. P., and Crutzen, P. J.: Ozone in the remote marine boundary layer: a possible role for halogens, J. Geophys. Res., 104, 21385–21395, doi:10.1029/1999JD900023, 1999.
Dorf, M., Butz, A., Camy-Peyret, C., Chipperfield, M. P., Kritten, L., and Pfeilsticker, K.: Bromine in the tropical troposphere and stratosphere as derived from balloon-borne BrO observations, Atmos. Chem. Phys., 8, 7265–7271, doi:10.5194/acp-8-7265-2008, 2008.
Emmons, L. K., Walters, S., Hess, P. G., Lamarque, J.-F., Pfister, G. G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X., Tyndall, G., Wiedinmyer, C., Baughcum, S. L., and Kloster, S.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), Geosci. Model Dev., 3, 43–67, doi:10.5194/gmd-3-43-2010, 2010.
Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R.: Changes in Atmospheric Constituents and in Radiative Forcing, in Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, NY, USA., 129–234, 2007.
Garland, J. A. and Curtis, H.: Emission of Iodine From the Sea Surface in the Presence of Ozone, J. Geophys. Res. Oc., 86, 3183–3186, 1981.
Gent, P. R., Yeager, S. G., Neale, R. B., Levis, S., and Bailey, D. A.: Improvements in a half degree atmosphere/land version of the CCSM, Clim. Dynam., 34, 819–833, 10.1007/s00382–

ACPD
11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

009-0614–8, 2010.

Hoell, J. M., Davis, D. D., Jacob, D. J., Rodgers, M. O., Newell, R. E., Fuelberg, H. E., McNeal, R. J., Raper, J. L., and Bendura, R. J.: Pacific exploratory mission in the tropical pacific: PEM-tropics A, August–September 1996, J. Geophys. Res., 104(D5), 5567–5583, 1999.

Horowitz, L. W., Walters, S., Mauzerall, D. L., Emmons, L. K., Rasch, P. J., Granier, C., Tie, X., Lamarque, J.-F., Schultz, M. G., Tyndall, G. S., Orlando, J. J., and Brasseur, G. P.: A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART version 2, J. Geophys. Res., 108, 4784, doi:10.1029/2002JD002853, 2003.

Jacob, D. J., Crawford, J. H., Kleb, M. M., Connors, V. S., Bendura, R. J., Raper, J. L., Sachse, G. W., Gille, J. C., Emmons, L., and Heald, C. L: Transport and Chemical Evolution over the Pacific (TRACE-P) aircraft mission: design, execution, and first results, J. Geophys. Res., 108, 9000, doi:10.1029/2002JD003276, 2003.

Johnson, J. E., Gammon, R. H., Larsen, J., Bates, T. S., Oltmans, S. J., and Farmer, J. C.: Ozone in the marine boundary layer over the Pacific and Indian Oceans: latitudinal gradients and diurnal cycles, J. Geophys. Res., 95, 11847–11856, 1990.

Jones, C. E., Hornsby, K. E., Sommariva, R., Dunk, R. M., von Glasow, R., McFiggans, G., and Carpenter, L. J.: Quantifying the contribution of marine organic gases to atmospheric iodine, Geophys. Res. Lett., 37, L18804, doi:10.1029/2010GL043990, 2010.

Kiehl, J. T., Schneider, T. L., Portmann, R. W., and Solomon, S.: Climate forcing due to tropospheric and stratospheric ozone, J. Geophys. Res., 104, 31239–31254, 1999.

Kinnison, D. E., Brasseur, G. P., Walters, S., Garcia, R. R., Marsh, D. R., and Sassi, F., Harvey, V. L., Randall, C. E., Emmons, L., Lamarque, J. F., Hess, P., Orlando, J. J., Tie, X. X., Randel, W., Pan, L. L., Gettelman, A., Granier, C., Diehl, T., Niemeier, U., and Simmons, A. J.: Sensitivity of chemical tracers to meteorological parameters in the MOZART-3 chemical transport model, J. Geophys. Res. 112, D20302, doi:10.1029/2006JD007879, 2007.

Kley, D., Crutzen, P. J., Smit, H. G. J., Vömel, H., Oltmans, S. J., Grassl, H., and Ramanathan, V: Observations of near-zero ozone concentrations over the convective Pacific: effects on air chemistry, Science, 274, 230–233, 1996.

Lacis, A. A., Wuebbles, D. J., and Logan, J. A.: Radiative forcing of climate by changes in the vertical distribution of ozone, J. Geophys. Res., 95, 9971–9981, 1990.

Lamarque, J.-F. and Solomon, S.: Impact of changes in climate and halocarbons on recent lower stratosphere ozone and temperature trends, J. Climate, 23, 2599–2611, 2010.

ACPD
11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

Lamarque, J.-F., Hess, P., Emmons, L., Buja, L., Washington, W., and Granier, C.: Tropospheric ozone evolution between 1890 and 1990, J. Geophys. Res., 110, D08304, doi:10.1029/2004JD005537, 2005.

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren, D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmos. Chem. Phys., 10, 7017–7039, doi:10.5194/acp-10-7017-2010, 2010.

Lamarque, J.-F., Emmons, L. K., Hess, P. G., Kinnison, D. E., Tilmes, S., Vitt, F., Heald, C. L., Holland, E. A., Lauritzen, P. H., Neu, J., Orlando, J. J., Rasch, P., and Tyndall, G.: CAM-chem: description and evaluation of interactive atmospheric chemistry in CESM, Geosci. Model Dev. Discuss., 4, 2199–2278, doi:10.5194/gmdd-4-2199-2011, 2011.

Leser, H., Hönninger, G., and Platt, U.: MAX-DOAS measurements of BrO and NO_2 in the marine boundary layer, Geophys. Res. Lett., 30, 1537, doi:10.1029/2002GL015811, 2003.

Mahajan, A. S., Plane, J. M. C., Oetjen, H., Mendes, L., Saunders, R. W., Saiz-Lopez, A., Jones, C. E., Carpenter, L. J., and McFiggans, G. B.: Measurement and modelling of tropospheric reactive halogen species over the tropical Atlantic Ocean, Atmos. Chem. Phys., 10, 4611–4624, doi:10.5194/acp-10-4611-2010, 2010.

Marenco, A., Gouget, H., Nédélec, P., Pages, J.-P., and Karcher, F.: Evidence of a long-term increase in tropospheric ozone from Pic du Midi data series: consequences: positive radiative forcing, J. Geophys. Res., 99, 16617–16632, 1994.

Martin, M., Pöhler, D., Seitz, K., Sinreich, R., and Platt, U.: BrO measurements over the Eastern North-Atlantic, Atmos. Chem. Phys., 9, 9545–9554, doi:10.5194/acp-9-9545-2009, 2009.

Mickley, L. J., Jacob, D. J., and Rind, D.: Uncertainty in preindustrial abundance of tropospheric ozone: implications for radiative forcing calculations, J. Geophys. Res., 106, 3389–3399, 2001.

Nagao, I., Matsumoto, K., and Tanaka, H.: Sunrise ozone destruction found in the sub-tropical marine boundary layer, Geophys. Res. Lett., 26, 3377–3380, 1999.

Oetjen, H.: Measurement of halogen oxides by scattered sunlight differential optical absorption spectroscopy, PhD thesis, University of Bremen, Germany, 2009.

Oltmans, S. J. and Levy II, H.: Seasonal cycle of surface ozone over the Western North Atlantic, Nature, 358, 392–394, 1992.

Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G., Brasseur, G., and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmos. Chem. Phys. Discuss., 11, 27421–27474, doi:10.5194/acpd-11-27421-2011, 2011.

Pavelin, E. G., Johnson, C. E., Rughooputh, S., and Toumi, R.: Evaluation of pre-industrial surface ozone measurements made using Schönbein's method, Atmos. Environ., 33, 919–929, 1999.

Ramaswamy, V., Boucher, O., Haigh, J., Hauglustaine, D., Haywood, J., Myhre, G., Nakajima, T., Shi, G. Y., and Solomon, S.: Radiative Forcing of Climate Change, in Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J., Dai, X., Maskell, K., and Johnson, C. A., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 349–416, 2001.

Raper, J. L., Kleb, M. M., Jacob, D. J., Davis, D. D., Newell, R. E., Fuelberg, H. E., Bendura, R. J., Hoell, J. M., and Mc-Neal, R. J.: Pacific exploratory mission in the tropical pacific: PEM-tropics B, March–April 1999, J. Geophys. Res., 106(D23), 32401–32425, 2001.

Rayner, N. A., Parker, D. E., Horton, E. B., Folland, C. K., Alexander, L. V., Rowell, D. P., Kent, E. C., and Kaplan, A.: Global analyses of sea surface temperature, sea ice, and night marine air temperature since the late nineteenth century, J. Geophys. Res. 108, 4407, doi:10.1029/2002JD002670, 2003.

Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J., and Plane, J. M. C.: Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, Nature, 453, 1232–1235, 2008.

Reeser, D. I., Jammoul, A., Clifford, D., Brigante, M., D'Anna, B., George, C., and Donaldson, D. J.: Photoenhanced Reaction of ozone with chlorophyll at the seawater surface, J. Phys. Chem. C, 113, 2071–2077, 2009.

Saiz-Lopez, A. and Plane, J. M. C.: Novel iodine chemistry in the marine boundary layer. Geophys. Res. Lett., 31, L04112, doi:10.1029/2003GL019215, 2004.

Saiz-Lopez, A., Plane, J. M. C., Mahajan, A. S., Anderson, P. S., Bauguitte, S. J.-B., Jones, A. E., Roscoe, H. K., Salmon, R. A., Bloss, W. J., Lee, J. D., and Heard, D. E.: On the vertical distribution of boundary layer halogens over coastal Antarctica: implications

for O_3, HO_x, NO_x and the Hg lifetime, Atmos. Chem. Phys., 8, 887–900, doi:10.5194/acp-8-887-2008, 2008.
Sakamoto, Y., Yabushita, A., Kawasaki, M., and Enami, S.: Direct emission of I_2 molecule and IO radical from the heterogeneous reactions of gaseous ozone with aqueous potassium iodide solution, J. Phys. Chem. A, 113, 7707–7713, 2009.
Schönhardt, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H. K., and Burrows, J. P.: Observations of iodine monoxide columns from satellite, Atmos. Chem. Phys., 8, 637-653, doi:10.5194/acp-8-637-2008, 2008.
Shindell, D. T., Faluvegi, G., and Bell, N.: Preindustrial-to-present-day radiative forcing by tropospheric ozone from improved simulations with the GISS chemistry-climate GCM, Atmos. Chem. Phys., 3, 1675–1702, doi:10.5194/acp-3-1675-2003, 2003.
Shiotani, M., Fujiwara, M., Hasebe, F., Hashizume, H., Vömel, H., Oltmans, S. J., and Watanabe, T.: Ozonesonde Observations in the Equatorial Eastern Pacific – the Shoyo-Maru Survey, J. Met. Soc. Japan, 80, 897–909, 2002.
Solomon, S., Thompson, D. W. J., Portmann, R. W., Oltmans, S. J., and Thompson, A. M.: On the distribution and variability of ozone in the tropical upper troposphere: Implications for tropical deep convection and chemical-dynamical coupling, Geophys. Res. Lett., 32, L23813, doi:10.1029/2005GL024323, 2005.
Sousa Santos, G.: The Effect of Halogens on Global Tropospheric Ozone, PhD Thesis, Max Planck Institute for Meteorology, Hamburg, Germany, 2008.
Takashima, H., Shiotani, M., Fujiwara, M., Nishi, N., and Hasebe, F.: Ozonesonde observations at Christmas Island (2° N, 157° W) in the equatorial Central Pacific, J. Geophys. Res., 113, D10112, doi:10.1029/2007JD009374, 2008.
Theys, N., Van Roozendael, M., Hendrick, F., Fayt, C., Hermans, C., Baray, J.-L., Goutail, F., Pommereau, J.-P., and De Mazière, M.: Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21° S, 56° E), Atmos. Chem. Phys., 7, 4733–4749, doi:10.5194/acp-7-4733-2007, 2007.
Thompson, A. M., Witte, J. C., McPeters, R. D., Oltmans, S. J., Schmidlin, F. J., Logan, J. A., Fujiwara, M., Kirchhoff, V. W. J. H., Posny, F., Coetzee, G. J. R., Hoegger, B., Kawakami, S., Ogawa, T., Johnson, B. J., Vömel, H., and Labow, G.: Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998–2000 tropical ozone climatology 1. Comparison with Total Ozone Mapping Spectrometer (TOMS) and ground-based measurements, J. Geophys. Res., 108, 8238, 10.1029/2001JD000967, 2003a.

Thompson, A. M., Witte, J. C., Oltmans, S. J., Schmidlin, F. J., Logan, J. A., Fujiwara, M., Kirchhoff, V. W. J. H., Posny, F., Coetzee, G. J. R., Hoegger, B., Kawakami, S., Ogawa, T., Fortuin, J. P. F., and Kelder, H. M.: Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998–2000 tropical ozone climatology 2. Tropospheric variability and the zonal wave-one, J. Geophys. Res., 108(D2), 8241, doi:10.1029/2002JD002241, 2003b.

Volkamer, R., Coburn, S. C., Dix, B. K., and Sinreich, R.: The Eastern Pacific Ocean is a source for short lived atmospheric gases: glyoxal and iodine oxide, News. Clim. Variab. Predict. Progr. (CLIVAR), 15, 30–33, 2010.

Volz, A. and Kley, D.: Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, Nature, 332, 240–242, 1988.

Vömel, H. and Diaz, K.: Ozone sonde cell current measurements and implications for observations of near-zero ozone concentrations in the tropical upper troposphere, Atmos. Meas. Tech., 3, 495–505, doi:10.5194/amt-3-495-2010, 2010.

von Glasow, R., von Kuhlmann, R., Lawrence, M. G., Platt, U., and Crutzen, P. J.: Impact of reactive bromine chemistry in the troposphere, Atmos. Chem. Phys., 4, 2481-2497, doi:10.5194/acp-4-2481-2004, 2004.

Worden, H. M., Bowman, K. W., Worden, J. R., Eldering, A., and Beer, R.: Satellite measurements of the clear-sky greenhouse effect from tropospheric ozone, Nat. Geosci., 1, 305–308, 2008.

Worden, H. M., Bowman, K. W., Kulawik, S. S., and Aghedo, A. M.: Sensitivity of outgoing longwave radiative flux to the global vertical distribution of ozone characterized by instantaneous radiative kernels from Aura-TES, J. Geophys. Res., 116, D14115, doi:10.1029/2010JD015101, 2011.

World Meteorological Organization (WMO): Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project – Report No. 52, 516 pp., Geneva, Switzerland, 2011.

Yang, X., Cox, R. A., Warwick, N. J., Pyle, J. A., Carver, G. D., O'Connor, F. M., and Savage, N. H.: Tropospheric bromine chemistry and its impacts on ozone: a model study, J. Geophys. Res., 110, D23311, doi:10.1029/2005JD006244, 2005.

ACPD

11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

Table 1. Annual average difference in the longwave and net (longwave plus shortwave) fluxes at the tropical tropopause (20° S–20° N) for two CAM-Chem simulations with and without VSL halogen sources.

	Longwave flux ($W\,m^{-2}$)	Net flux ($W\,m^{-2}$)
All-sky	–0.104	–0.103
Clear-sky	–0.138	–0.122

ACPD
11, 32003–32029, 2011

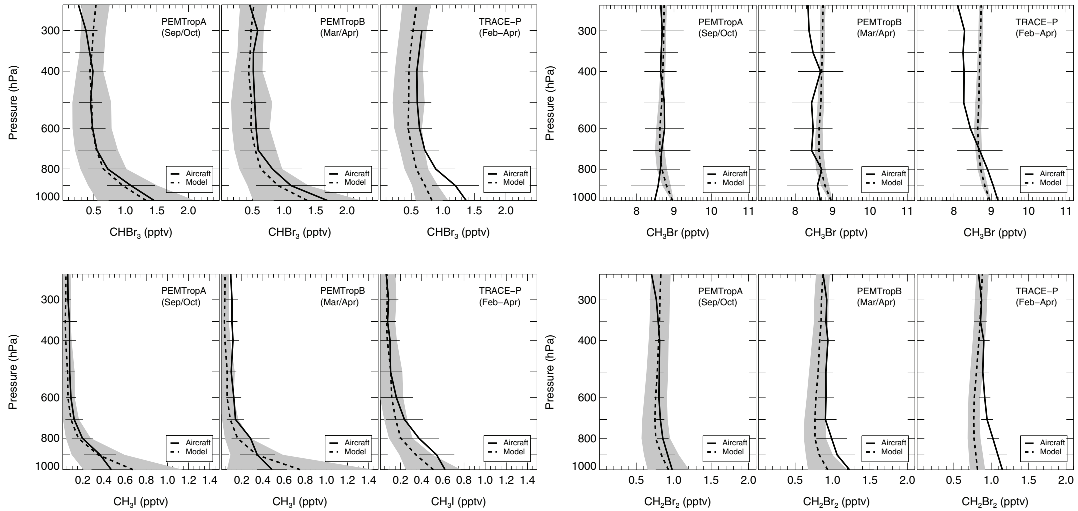
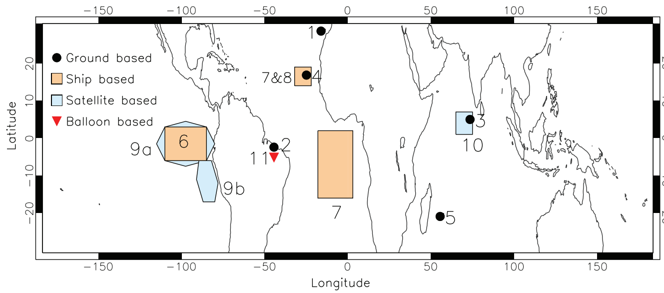


Fig. 1. Comparison of average vertical profiles of $CHBr_3$, CH_3I, CH_3Br and CH_2Br_2 as simulated by CAM-Chem for the last of a 10-yr run with a composite of aircraft observations in the tropical regions from the missions PEM-Tropics A (1996), PEM-Tropics B (1999) and TRACE-P (2001). Model results are averaged within the geographical region of each campaign considering latitudes between 30° N and 30° S and matching seasons. Shaded areas and horizontal bars represent the standard deviation of modelled fields and observations, respectively.



No. (species)	Daytime avg. mixing ratio (pptv)	
	Modelled	Observed
Ground based measurements		
1 (IO)	0.4	1.2
2 (IO)	0.7	<0.2 – 0.8
3 (IO)	1.0	∼2.4
4 (IO, BrO)	1.0, 2.0	1.0, 2.0
5 (BrO)	0.8	<0.5
Ship based measurements		
6 (IO)	1.0	∼3.5
7 (BrO)	0.8	<3.6
8 (BrO)	1.2	<3.0
Satellite based measurements		
9a (IO)	1.0	∼3.3
9b (IO)	1.0	∼3.3
10 (IO)	1.0	∼2.4
Balloon based measurements		
11 (IO)	0.02	∼0.1
11 (BrO)	0.5	∼1.0

Fig. 2. Mixing ratios of iodine oxide (IO) and bromine oxide (BrO) in the TMBL. Observations were compiled from ground-, ship-, satellite- and balloon-based platforms. Modelled mixing ratios simulated by CAM-Chem correspond to averages for the same areas and months as the observations. Daytime represents sunlit hours. Where indicated the mixing ratios are estimated from differential slant column densities (dSCD). 1: Allan et al. (2000); 2: Butz et al. (2009); 3: estimated from dSCD = 3.5×10^{13} molecule cm^{-2} (Oetjen, 2009); 4: Read et al. (2008); 5: estimated from dSCD (Theys et al., 2007); 6: peak mixing ratio, estimated from dSCD = 7×10^{13} molecule cm^{-2} (Volkamer et al., 2010); 7: Leser et al. (2003); 8: dSCD < 1.2×10^{13} molecule cm^{-2}, observations from the upwelling region around Mauritania with values up to 10 pptv are excluded for comparison with modelled data (Martin et al., 2009); 9: estimated from dSCDs = 8×10^{12} molecule cm^{-2} considering an air mass factor (AMF) of 1 and a mixed layer of 1 km at the surface (Schönhardt et al., 2008); 10: as (9) but with dSCD = 6×10^{12} molecule cm^{-2}; 11: upper limit of IO (Butz et al., 2009) and BrO (Dorf et al., 2008) in the upper troposphere.

ACPD
11, 32003–32029, 2011

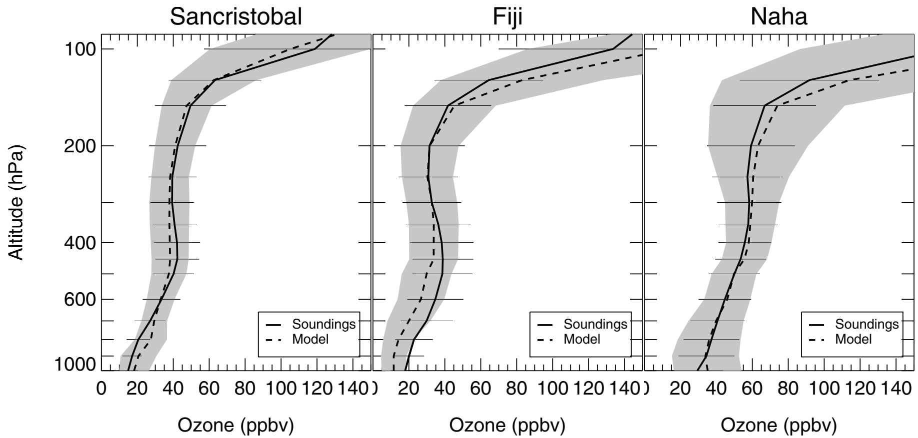


Fig. 3. Comparison of average vertical profiles for ozone as simulated by CAM-Chem for the last of a 10-yr run with observations at three sites (San Cristobal, Galapagos, 1° S–89° W; Fiji, 18° S–178° E; Naha, Japan, 26° N–127° E) of the SHADOZ and WOUDC ozonesonde networks. Shaded areas and horizontal bars represent the standard deviation of modelled fields and observations, respectively.

ACPD
11, 32003–32029, 2011

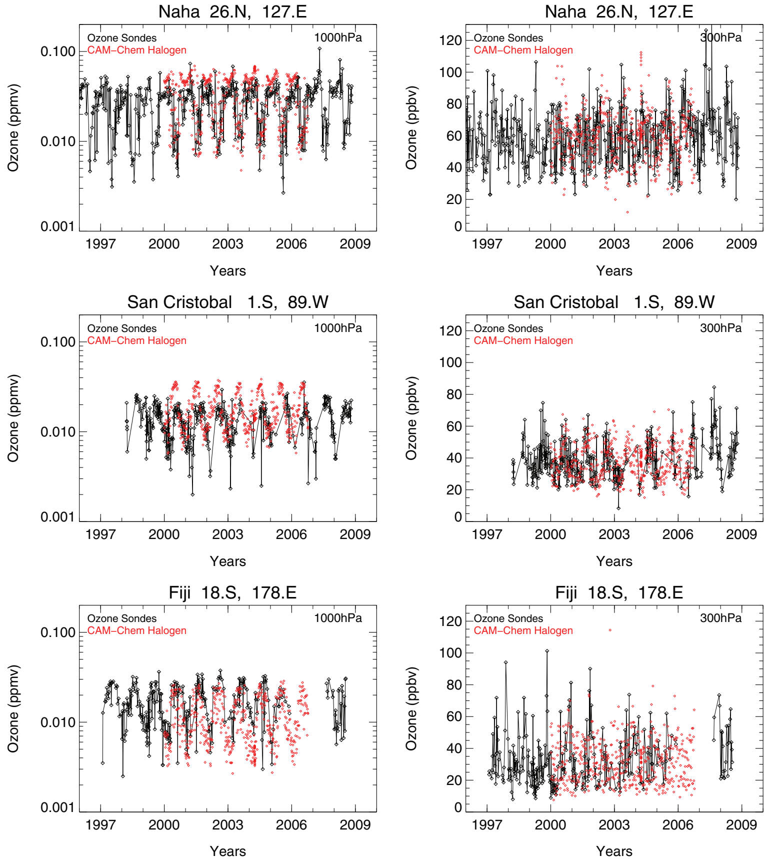


Fig. 4. Time series of observed and modelled ozone at (left) 1000 hPa and (right) 300 hPa for the location of three ozonesonde sites in the proximity of the tropics. A logarithmic vertical scale has been used for the 1000 hPa time series to draw attention to the low ozone events. The time frequency is of around 30–40 observations per year and every 10 days for modelled ozone.

ACPD
11, 32003–32029, 2011

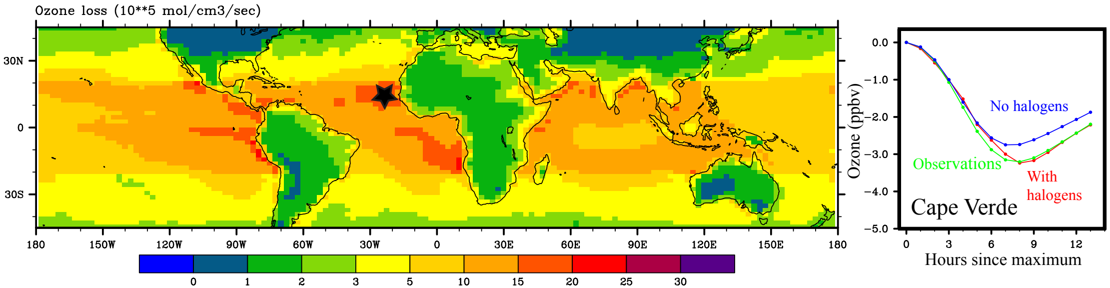


Fig. 5. (left) Surface ozone loss (in 10^5 molecule cm^{-3} s^{-1}) resulting from including tropospheric halogen chemistry in CAM-Chem. (right) Annual average of diurnal ozone loss observed and simulated by CAM-Chem (without and with tropospheric halogen chemistry) at Cape Verde.

ACPD
11, 32003–32029, 2011

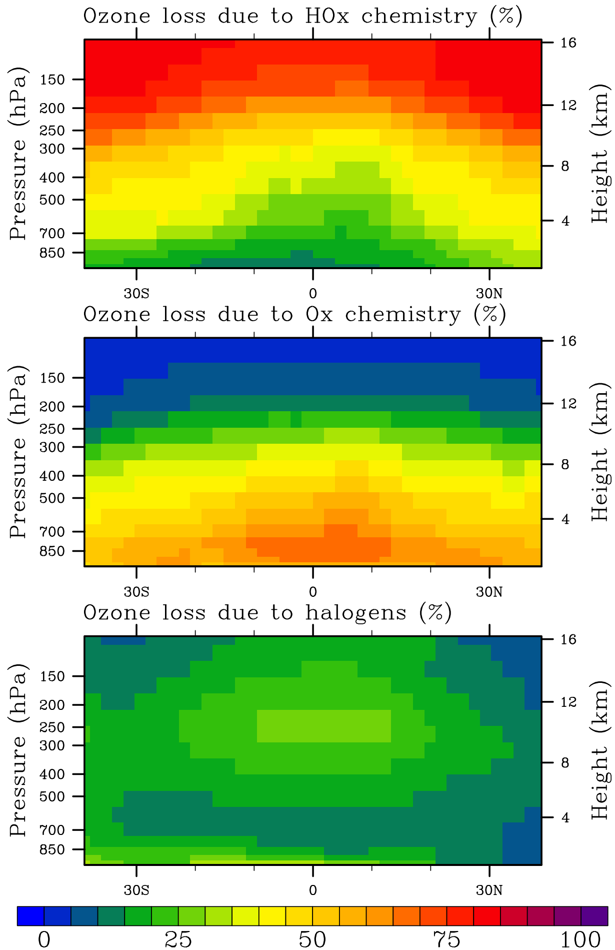


Fig. 6. Percentage of the annually integrated chemical ozone loss from HO_x, O_x and halogen photochemistry as simulated by CAM-Chem.

ACPD
11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

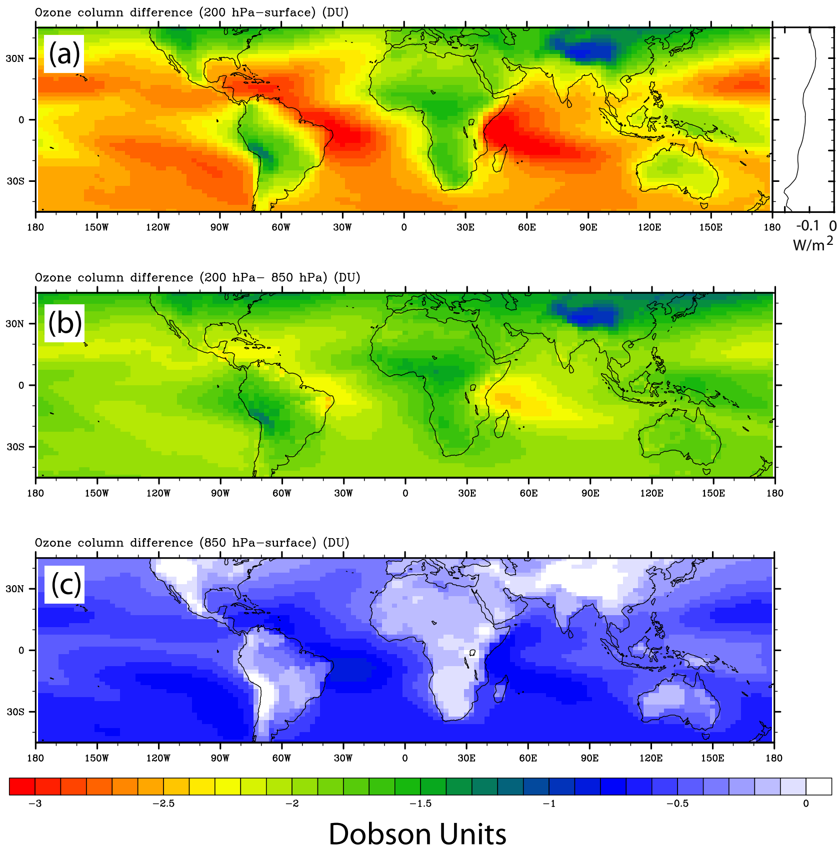


Fig. 7. Ozone column difference resulting from including tropospheric halogen chemistry in CAM-Chem for **(a)** 200 hPa–surface, **(b)** 200–850 hPa, and **(c)** 850 hPa–surface. The latitudinal dependence of the perturbation of the radiation flux at the tropopause associated with the tropospheric ozone column loss is shown on the right-hand side of the upper plot.

ACPD
11, 32003–32029, 2011

Estimating the climate significance of halogen-driven ozone loss

A. Saiz-Lopez et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◂◂ ▸▸
◂ ▸
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion