

Evaluation of ACE-FTS and OSIRIS Satellite retrievals of ozone and nitric acid in the tropical upper troposphere: Application to ozone production efficiency

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[1] We evaluate climatologies of upper tropospheric ozone and nitric acid retrieved from two satellite instruments (ACE-FTS and OSIRIS) with long-term in situ measurements from aircraft (MOZAIC, CR-AVE, PRE-AVE, PEM Tropics, and TC4) and ozonesondes. A global chemical transport model (GEOS-Chem) is used to guide the evaluation and to relate sparse in situ measurements with the satellite retrievals. Both satellite retrievals generally reproduce broad ozone features in the upper troposphere such as summer enhancements in the northern subtropics and larger concentrations over the tropical Atlantic versus the tropical Pacific. These comparisons indicate biases in annual, tropical mean ozone concentrations from both ACE-FTS (10–13%) and OSIRIS (5%) relative to aircraft and ozonesonde observations. More uncertain evidence suggests that nitric acid from ACE-FTS has a positive mean bias of 15%. We demonstrate that an upper limit on the ozone production efficiency in the upper troposphere can be determined using ACE-FTS satellite measurements of O₃ and HNO₃. The resulting value of 196 (+34, –61) mol/mol is in broad agreement with model simulations. Higher OPE values inferred from ACE-FTS over the tropical Pacific (249 (+21, –68) mol/mol) than the tropical Atlantic (146 (+16, –41) mol/mol) reflect increasing ozone production efficiency with decreasing pollution. This analysis indicates a new capability of satellite observations to provide insight into ozone production in the tropical troposphere.

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1. Introduction

[2] Ozone (O₃) in the tropical troposphere is a key component in atmospheric oxidation processes and has a large radiative forcing of climate [Lacis *et al.*, 1990; Thompson, 1992]. Ozone production in the tropical troposphere is controlled by the supply of nitrogen oxides (NO_x = NO + NO₂) whose main sink is oxidation to nitric acid (HNO₃) [Murphy *et al.*, 1993; Jacob *et al.*, 1996]. Scientific understanding of upper tropospheric ozone is inhibited by sparse measurements in time and space. Well validated satellite observations of HNO₃ and O₃ in the upper troposphere could improve scientific understanding of ozone production and its impact on climate.

[3] Current understanding of upper tropospheric ozone involves a complex interaction of dynamics and photochemical production [Liu *et al.*, 2006; Nassar *et al.*, 2009]. Ozonesonde and aircraft measurements in the upper troposphere indicate low ozone concentrations over marine convective regions and enhanced concentrations over regions of persistent subsidence [Thompson *et al.*, 2003b; Sauvage

et al., 2006]. An outstanding question is the efficiency of ozone production by nitrogen oxides during transport in the upper troposphere. Models predict a high ozone production efficiency in the upper troposphere [Sauvage *et al.*, 2007a], but this result has not been tested with observations. The relationship between O₃ and HNO₃ has been exploited to infer ozone production efficiencies in the lower and middle troposphere [Trainer *et al.*, 1993; Ryerson *et al.*, 1998; Kleinman *et al.*, 2000, 2002; Hudman *et al.*, 2004]. Simultaneous observations of O₃ and HNO₃ from satellites over large spatial scales should offer similar constraints on O₃ production efficiencies in the upper troposphere.

[4] This study focuses on satellite observations of tropical upper tropospheric O₃ and HNO₃ from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) and ozone from the Optical Spectrograph and InfraRed Imaging System (OSIRIS). Previous validation experiments for both instruments have largely focused on either higher latitudes, or on the stratosphere where mixing ratios are higher and satellite retrievals are easier [Petelina *et al.*, 2004; von Savigny *et al.*, 2005; McLinden *et al.*, 2007; Hegglin *et al.*, 2008; Wolff *et al.*, 2008; Dupuy *et al.*, 2009]. No detailed validation of ACE-FTS O₃, ACE-FTS HNO₃ or OSIRIS O₃ with in situ observations throughout the tropical troposphere has been published to date.

[5] The purposes of this study are to (1) evaluate ozone and nitric acid as observed by ACE-FTS and OSIRIS with ozonesonde and aircraft data in the tropical upper troposphere, and (2) examine the information that ACE-FTS provides about the ozone production efficiency. Section 2 describes the satellite and in situ data sets used for this study. Section 3 discusses how a global chemical transport model (GEOS-Chem) is used as a validation tool. Comparisons between the satellite and in situ measurements are displayed and discussed in section 4. The ozone production efficiency is described and is calculated using ACE-FTS measurements in section 5.

2. Data Description

2.1. OSIRIS

[6] OSIRIS was launched on the Odin satellite in 2001 [Llewellyn *et al.*, 2004]. The OSIRIS spectrograph measures scattered sunlight in the limb with wavelengths ranging from ultraviolet to infrared (280 to 800 nm) with 1 nm spectral resolution [von Savigny *et al.*, 2005]. Observations are made between 6 and 60 km with a horizontal resolution of 500 to 1000 km and a vertical resolution of 2 km [McLinden *et al.*, 2007]. The polar, Sun-synchronous, near-terminator orbit of Odin allows for OSIRIS to provide year-round coverage in the tropics, but no coverage in the winter hemisphere due to large solar zenith angles.

[7] This study uses the SaskMART ozone product version 5 for orbits occurring between October 2001 to March 2010 [Degenstein *et al.*, 2009]. Individual sources of error are less than 5% throughout most of the stratosphere, but high altitude clouds may cause larger retrieval errors in the tropical upper troposphere and lower stratosphere [von Savigny *et al.*, 2005]. OSIRIS ozone retrievals have been found to be accurate to within 4–8% in the stratosphere between 15 and 32 km with a total error of 10% [Petelina *et al.*, 2004;

von Savigny *et al.*, 2005], however uncertainties increase at lower altitudes, up to 25–30% at 10 km [McLinden *et al.*, 2007].

2.2. ACE-FTS

[8] ACE is a Canadian-led mission on the SCISAT satellite [Bernath *et al.*, 2005]. The main instrument is the ACE-FTS which measures infrared radiation (750 to 4400 cm^{−1}) at a high spectral resolution (0.02 cm^{−1}). ACE-FTS is a solar occultation instrument; the instrument takes a series of measurements while observing the sun rise and set over Earth as it orbits, where each measurement represents a different raypath [Boone and Bernath, 2002]. The orbit of SCISAT is such that it observes up to 15 sunrises and sunsets per day, allowing for global coverage over several years. SCISAT's circular low-Earth orbit is optimized for high latitudes and thus provides only medium coverage in the tropics [Bernath, 2006]. Retrievals of more than 30 atmospheric species extend from cloud top to 100–150 km altitude with a maximum vertical resolution better than 3 km [Hegglin *et al.*, 2008]. Retrieval version 3 is used here for both ozone and nitric acid measurements spanning January 2004 to August 2010. We exclude all HNO₃ data more than two standard deviations from the median, as a small percentage of the retrievals produced unrealistically high concentrations; this eliminated less than 8% of the data and reduced the bias in section 4. Excluding outliers for O₃ had no significant effect; we retained all O₃ data. ACE-FTS retrievals of NO, NO₂ and CO are also used in this study.

[9] ACE-FTS stratospheric ozone measurements agree to within 10% with ozonesondes and other satellite instruments, including OSIRIS, with ACE-FTS retrievals typically reporting higher values [Dupuy *et al.*, 2009]. These differences increase below 16 km due to increased ozone variability, cloud contamination, and decreased instrument sensitivity [Dupuy *et al.*, 2009]. Comparisons with aircraft measurements between 5 km and the tropopause over Europe indicate a high bias in ACE-FTS O₃ of 18–25% [Hegglin *et al.*, 2008]. ACE-FTS HNO₃ profiles agree with satellite, aircraft, ground-based and balloon observations to within ±1 ppbv in the stratosphere [Wolff *et al.*, 2008].

2.3. In Situ Data

[10] Sources of in situ data used in this study include ozonesondes and aircraft campaigns. Ozonesondes used here are part of the Southern Hemisphere Additional Ozonesondes (SHADOZ, <http://croc.gsfc.nasa.gov/shadoz/>) network, a group of 16 ozonesonde sites in the southern tropics [Thompson *et al.*, 2003a, 2003b]. Additional ozonesonde data were provided by the World Ozone and Ultraviolet Radiation Data Center (WOUDC, <http://www.woudc.org>). Given that ozonesondes are launched only 2–3 times a month, seasonal mean values over multiple years provide sufficient observations for accurate climatologies [Logan, 1999]. Table 1 lists ozonesonde sites used in this study. Additional ozone and total odd nitrogen (NO_y = NO_x + HNO₃ + PAN + other organic nitrates) observations are provided by the Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC) program [Marenco

Table 1. List of Ozonesonde Sites Used

Site	Location	Years Included	Count
American Samoa	170°W/14°S	1998–2008	384
Ascension Island	14°W/8°S	1998–2008	493
Costa Rica	84°W/10°N	2005–2008	167
Fiji	178°E/18°S	1998–2005, 2007–2008	275
Hilo, Hawaii	155°W/19°N	1998–2008	545
Hong Kong	114°E/22°N	2000–2009	403
Huntsville, Alabama	87°W/35°N	1999–2007	110
Irene, South Africa	28°E/26°S	2002–2007	141
Kagoshima	131°E/32°N	1969–2005	257
Kuala Lumpur	101°E/2°N	1998–2007	235
Nairobi	36°E/1°S	1998–2008	472
Natal	35°W/5°S	1998–2008	380
New Delhi	77°E/28°N	1969–1976, 1982–1986, 1994–2009	82
Paramaribo	55°W/6°N	1999–2007	323
Poona, India	73°E/18°N	1969–1976, 1982–1986, 1996–2009	77
La Reunion	55°E/21°S	1998–2008	270
San Cristobal	89°W/1°S	1998–2008	379
Santa Cruz	16°W/28°N	1996, 1999–2003	124
Watukosek, Java	112°E/7°S	1998–2008	257

et al., 1998; Volz-Thomas *et al.*, 2005]. The MOZAIC program places instruments onboard commercial aircraft to measure water vapor, ozone, NO_y and CO at cruising altitudes between 9 and 12 km. Measurement precision is estimated to be 2 ppbv ± 2% or better for each 4 s measurement for tropospheric ozone concentrations, and ozone climatologies produced from MOZAIC observations agree with ozonesondes to within their uncertainties [Thouret *et al.*, 1998a, 1998b]. NO_y measurement precision is given as better than 50 pptv for a 4 s integration time, however the overall statistical error can be up to 200 pptv for measurements in the tropical upper troposphere [Volz-Thomas *et al.*, 2005]. Ozone measurements from 1500 flights in the tropics (20°N–20°S) between 1994 and 2006 and NO_y measurements from 160 flights from 2001 to 2005 are used here.

[11] Measurements of O₃ and HNO₃ from several aircraft campaigns are used in this study. Data from the NASA WB-57F high-altitude research aircraft were collected for the NOAA Pre-Aura Validation Experiment (PRE-AVE) in January and February 2004 and the Costa Rica Aura Validation Experiment (CR-AVE) in February 2006 [Popp *et al.*, 2009]. Additional flights originating in Costa Rica and Panama were part of the Tropical Composition, Cloud and Climate Coupling (TC4) in July and August 2007 [Toon *et al.*, 2010]. HNO₃ measurement accuracy for a 10 s interval is reported as 25% with a precision of 40 pptv or better, and O₃ measurements are accurate to within 5% [Popp *et al.*, 2009]. TC4, CR-AVE and PRE-AVE data are available at the NASA Earth Science Project Office Archives (<http://espoarchive.nasa.gov>). Measurements across the tropical Pacific were taken by instruments onboard the NASA DC-8 as part of the Pacific Exploratory Mission in the Tropical Pacific (PEM-Tropics) [Hoell *et al.*, 1999; Raper *et al.*, 2001]. Phase A of the mission occurred August–September 1996 while Phase B followed in March–April 1999. HNO₃ measurement accuracy is reported as 30–35% and O₃ measurement accuracy is reported at 3% [Hoell *et al.*, 1999]. PEM-Tropics data are available at the NASA Global

Tropospheric Experiment Field Missions archive (http://www-gte.larc.nasa.gov/gte_fld.htm).

2.4. Tropopause Altitude

[12] Knowledge of the tropopause altitude is useful when comparing measurements in the upper troposphere as large vertical gradients may occur in the tropopause region [Liu *et al.*, 2006]. A thermal tropopause is often appropriate in the tropics, while a dynamic tropopause based on potential vorticity may be more appropriate at midlatitudes [Hoinka, 1998]. For ACE-FTS we use the combined thermal-dynamic tropopause that is already available as one of the Derived Meteorological Products [Manney *et al.*, 2007]. For OSIRIS, MOZAIC, ozonesondes and GEOS-Chem, we calculate the tropopause as the lowest altitude from either the thermal or dynamic definition. The thermal tropopause is obtained from the NCEP Reanalysis data provided by the NOAA/OAR/ESRL PSD, which defines the tropopause as the lowest level where the temperature lapse rate is less than 2 K/km [Kalnay *et al.*, 1996] (<http://www.esrl.noaa.gov/psd>). The dynamic tropopause is defined as the lowest level where potential vorticity exceeds $2.5 \times 10^{-6} \text{ K m}^2 \text{ kg}^{-1} \text{ s}^{-1}$ following Liu *et al.* [2006]. Potential vorticity profiles were obtained from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim data, provided by ECMWF. We reject all data within 2 km of the tropopause to account for the satellite vertical resolution and avoid stratospheric air.

3. Using a Model as an Evaluation Tool

[13] Tropospheric ozone concentrations are subject to substantial geophysical variability. As both the ozonesonde and aircraft observation networks have restricted spatial distributions and sampling times, coincident measurements between in situ and satellite data can be infrequent.

[14] A global 3-D model can help bridge the gap between localized in situ measurements and the global coverage provided by the satellite instruments. This study utilizes the GEOS-Chem model which is described in the Appendix. A seasonal mean simulated ozone profile was produced by sampling the GEOS-Chem model at the ozonesonde or MOZAIC flight path locations. These profiles were then compared to simulated seasonal mean ozone profiles over larger domains surrounding the measurement sites. Domain boundaries for comparison of satellite and in situ data were chosen to maximize the area of each region while ensuring that the simulated seasonal mean domain average profile agreed with the locally sampled simulated seasonal mean profiles to within 5 ppbv for all altitudes between 7 and 14 km. This method maximizes the number of satellite observations that fall in each domain while limiting errors due to spatial variations between flight paths, ozonesonde locations and satellite observation locations. This method also allows comparisons to be made using noncoincident measurements by comparing seasonal mean profiles for each region.

[15] The satellite measurements can also be indirectly compared with the in situ observations using a model as a transfer function. This approach is of particular value for comparing short duration aircraft campaigns with satellite observations, as is done here for the evaluation of ACE-FTS HNO₃. GEOS-Chem has been previously used as an

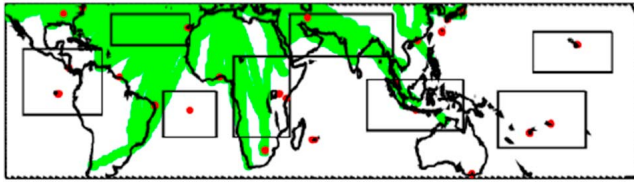


Figure 1. Boxes defining the domains used to calculate seasonal mean ozone profiles. Also displayed are aircraft flight paths (green) and ozonesonde site locations (red).

intermediary step for evaluation of satellite retrievals [Zhang *et al.*, 2010].

4. Evaluation Results

4.1. Ozone Evaluation

[16] Figure 1 shows the eight regions used for our global evaluation of ACE-FTS and OSIRIS measurements. The boundaries of these regions were chosen following the method outlined in section 3. MOZAIC data are used in

the boxes over Central Asia, Africa and the North Atlantic, and ozonesondes are used in the Tropical Atlantic (Ascension), Africa (Nairobi), Oceania (Kuala Lumpur, Java) and three Pacific regions (Hilo in North Pacific, San Cristobal and Costa Rica in East Pacific, Fiji and Samoa in South Pacific).

[17] Figure 2 shows seasonal mean ozone profiles and their standard errors within each region. Seasonal mean ozone concentrations from in situ measurements in the upper troposphere range from 30 ppbv over the tropical Pacific in December–February due to persistent deep convection [Folkins *et al.*, 2002] to 70 ppbv over Africa in September–November due to a combination of lightning and biomass burning [Thompson *et al.*, 1996]. The small standard errors indicate sufficient observations to assess bias, with the exception of some ACE-FTS mean profiles that were calculated using a small number of observations. As described in section 3, we estimate the uncertainty in the comparison of point observations from ozonesondes and flight paths with satellite observations over the eight larger domains to be less than 5 ppbv.

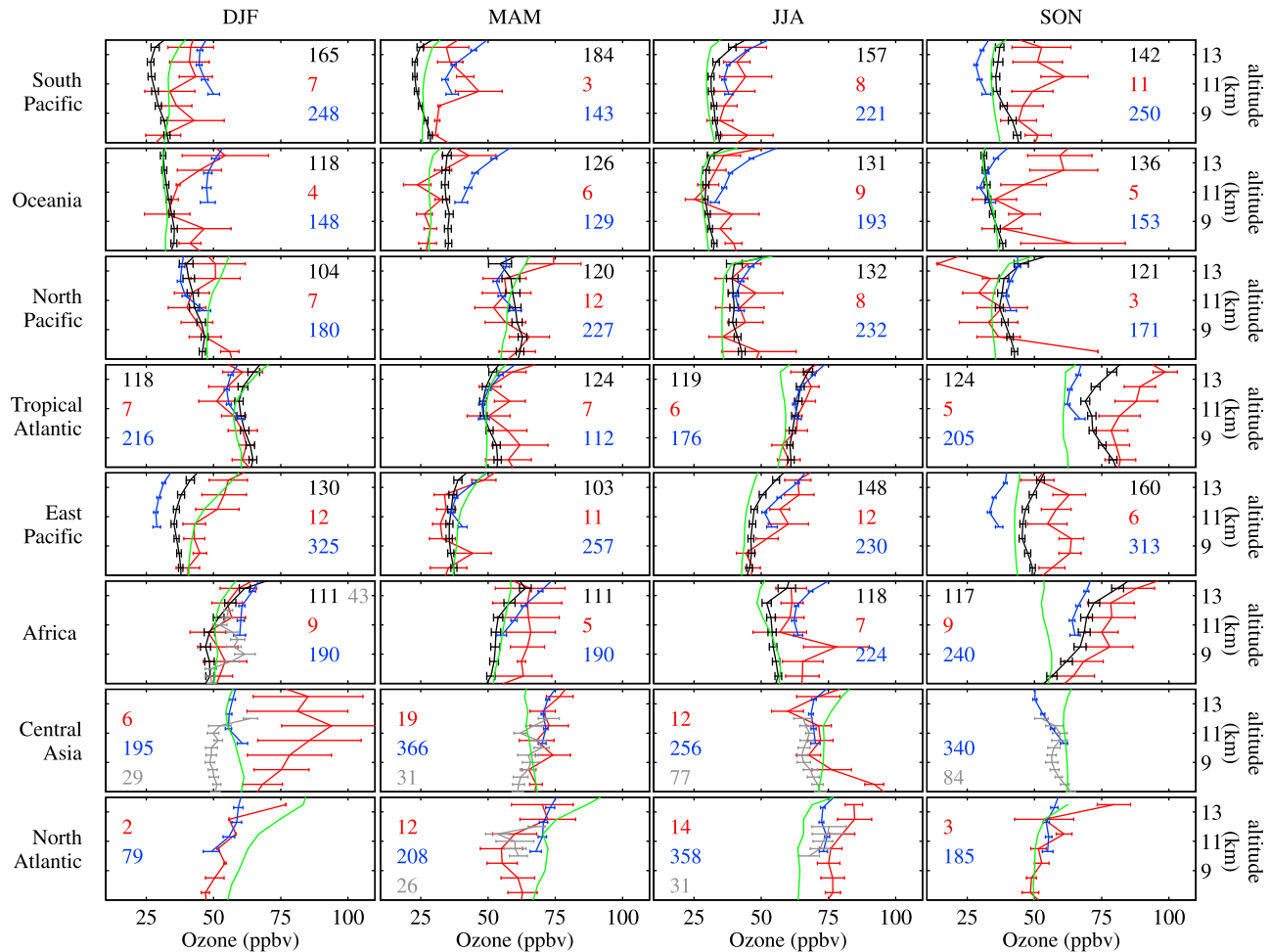


Figure 2. Seasonal mean ozone profiles from GEOS-Chem (green), ozonesondes (black), aircraft (grey), OSIRIS (blue), and ACE-FTS (red). Numbers indicate the number of ozonesonde launches, flight paths, or satellite observations used to calculate the averages. Error bars represent ± 1 standard error of the mean. Regions are defined in Figure 1. DJF, December–February; MAM, March–May; JJA, June–August; SON, September–November.

Table 2. Annual Mean Absolute and Percent Differences Between Satellite and in Situ Ozone Profiles

Region	ACE-FTS – Ozonesondes		ACE-FTS – MOZAIC		OSIRIS – Ozonesondes		OSIRIS – MOZAIC	
	ppbv	Percent	ppbv	Percent	ppbv	Percent	ppbv	Percent
South Pacific	12	41	N/A	N/A	8	27	N/A	N/A
Indonesia	4	12	N/A	N/A	7	23	N/A	N/A
Africa	8	14	–4	–7	4	8	4	7
Central Asia	N/A	N/A	10	16	N/A	N/A	3	5
North Atlantic	N/A	N/A	1	2	N/A	N/A	3	4
North Pacific	–1	–2	N/A	N/A	0.1	0.2	N/A	N/A
East Pacific	8	19	N/A	N/A	–3	–7	N/A	N/A
Tropical Atlantic	4	7	N/A	N/A	–3	–4	N/A	N/A
Global	5	13	6	10	2	5	3	5

[18] The agreement between seasonal mean satellite profiles and the in situ observations is variable. In some cases, such as the East Pacific in MAM, the observational data sets agree well. In other cases, such as the East Pacific in DJF, significant differences exist. Regional differences are summarized in Table 2. In the global annual mean, both OSIRIS and ACE-FTS tend to be biased high. OSIRIS ozone concentrations are on average 5% higher (RMSE = 4 ppbv) than the MOZAIC profiles and 5% higher (RMSE = 8 ppbv) than the ozonesondes. This is an improvement compared to the retrieval version 2.1 evaluation in the lower stratosphere by *McLinden et al.* [2007]. Although the relatively lower number of ACE-FTS measurements in each region increases scatter, the ACE-FTS profiles have significant mean biases

of 10% versus MOZAIC (RMSE = 18 ppbv) and 13% versus ozonesondes (RMSE = 10 ppbv). This is an improvement compared with previous ACE-FTS validation efforts over Europe, which found a positive bias of 25% in ACE-FTS O₃ in the upper troposphere [*Hegglin et al.*, 2008]. Excluding satellite data outside three standard deviations of the median changed annual mean ozone profiles by less than 3% for OSIRIS and less than 1% for ACE-FTS.

[19] Seasonal mean simulated O₃ profiles from GEOS-Chem generally agree with the in situ observations to within 10 ppbv (mean bias 4% for MOZAIC, 3% for ozonesondes), the most prominent discrepancy is over Central Asia during DJF when the simulated ozone is higher than MOZAIC by

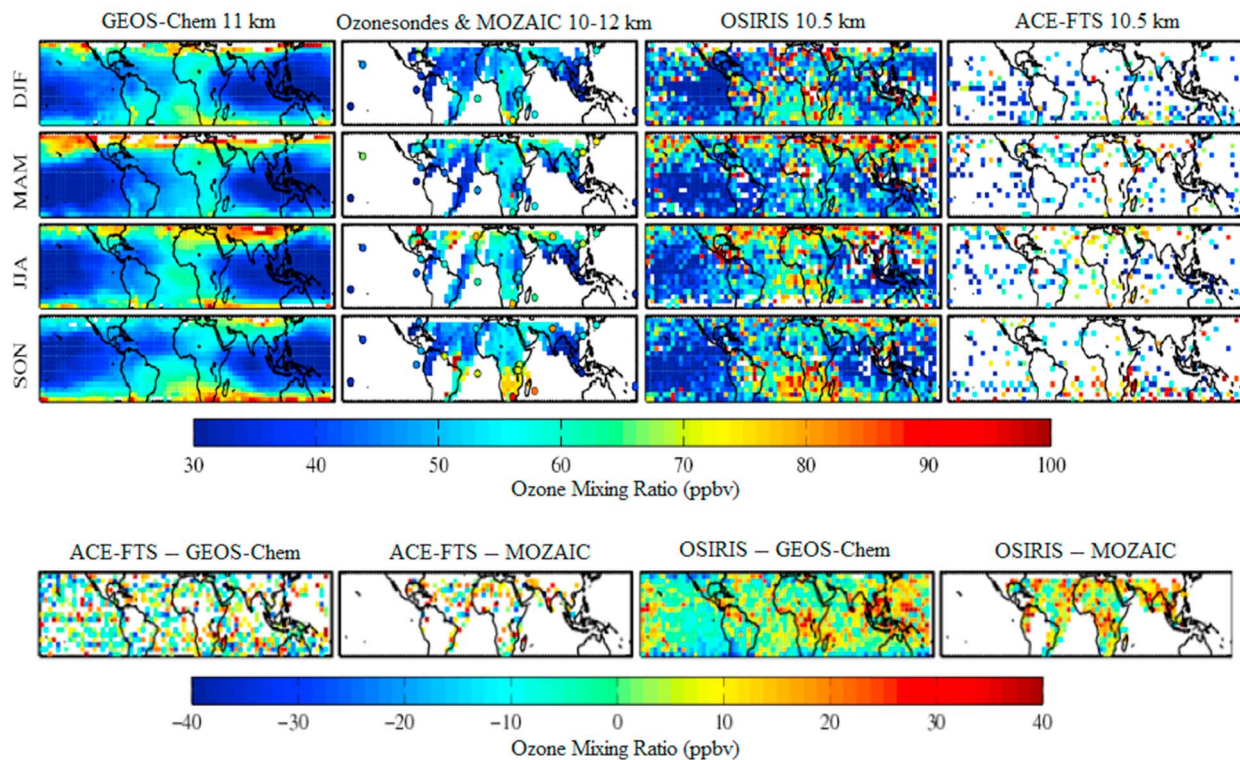


Figure 3. (top) Seasonal mean ozone concentrations from GEOS-Chem, MOZAIC, OSIRIS, and ACE-FTS in the upper troposphere (10–12 km). Circles on MOZAIC maps represent seasonal mean ozone-sonde observations. (bottom) Annual mean differences between the satellite, MOZAIC, and GEOS-Chem data sets.

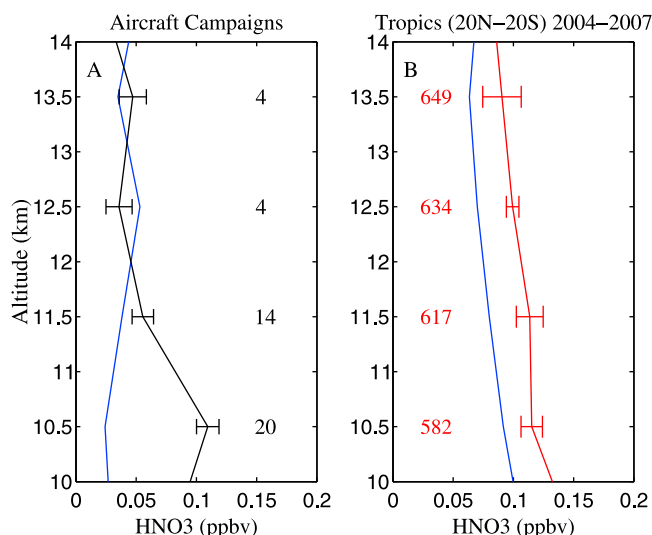


Figure 4. Mean nitric acid (HNO₃) vertical profiles. (a) Aircraft data (black) with GEOS-Chem simulation sampled along the flight path (blue) for CR-AVE, PRE-AVE, and PEM Tropics A and B campaigns. (b) Annual (2004–2007) mean tropical HNO₃ profile from ACE-FTS (red) and GEOS-Chem sampled at the month and location of the ACE-FTS observations (blue). Numbers indicate the number of data points used for comparison.

20%, perhaps reflecting issues in representing stratosphere-troposphere exchange [Zhang *et al.*, 2010].

[20] Figure 3 shows maps of seasonal mean upper tropospheric (10–12 km) ozone concentrations from GEOS-Chem, MOZAIC and both satellite instruments. Ozonesondes listed in Table 1 are also displayed. All maps broadly indicate the wave-one pattern of higher O₃ concentrations over the tropical Atlantic Ocean than the Pacific [Thompson *et al.*, 2003b]. This pattern reflects ozone production from lightning and persistent subsidence over the tropical Atlantic [Martin *et al.*, 2002]. We compare the tropical seasonal mean ozone concentrations from GEOS-Chem and MOZAIC with the seasonal mean concentrations from the satellite retrievals. MOZAIC and GEOS-Chem show good agreement throughout the tropics ($r = 0.5$, mean bias 7%, RMSE = 11 ppbv) although GEOS-Chem ozone concentrations in the northern subtropics are higher than MOZAIC particularly during March–May. Zhang *et al.* [2010] also found indications of a model overestimation versus ozonesondes at midlatitudes, which may be related to excessive stratospheric influx. Both ACE-FTS and OSIRIS have modest agreement with MOZAIC ($r = 0.4$, RMSE = 22 ppbv, mean bias 15% for ACE-FTS, $r = 0.2$, RMSE = 24 ppbv, mean bias 20% for OSIRIS) and GEOS-Chem ($r = 0.5$, RMSE = 7 ppbv, mean bias 7% for ACE-FTS, $r = 0.4$, RMSE = 20 ppbv, mean bias 10% for OSIRIS). The differences between the satellites, MOZAIC and GEOS-Chem are also displayed in Figure 3.

4.2. Nitric Acid Evaluation

[21] While SHADOZ and MOZAIC provide sufficient observations for ozone comparisons, a comprehensive set of

in situ HNO₃ measurements is not available. Instead, aircraft measurements of HNO₃ from aircraft campaigns (CR-AVE, PRE-AVE, TC4, PEM Tropics) and of NO_y from MOZAIC are used to evaluate GEOS-Chem, which is in turn compared with ACE-FTS HNO₃ retrievals.

[22] Aircraft measurements were used to evaluate GEOS-Chem by sampling the simulation along the flight paths. Figure 4a shows mean HNO₃ concentrations over the four campaigns. Mean HNO₃ concentrations are typically less than 0.1 ppbv throughout the upper troposphere. The average simulated profile shows HNO₃ concentrations that agree with the aircraft measurements above 11.5 km, however the simulated HNO₃ concentrations are 50% lower than the aircraft measurements between 10 and 11.5 km. Direct comparison of ACE-FTS versus aircraft measurements is inhibited by their lack of coincidence during their short campaigns, and by the high HNO₃ variability. For further insight, we compared ACE-FTS to GEOS-Chem by sampling a monthly mean model simulation at the ACE occultation locations in Figure 4b. ACE-FTS measurements are 38% higher than the modeled profile between 10 and 14 km. Some of this difference may be due to large spatial and temporal variations of HNO₃ that are not captured by the model.

[23] MOZAIC total odd nitrogen (NO_y) measurements are also used to evaluate ACE-FTS and GEOS-Chem as HNO₃ can represent up to 50% of NO_y in the tropical troposphere [Kasibhatla *et al.*, 1993; Folkins *et al.*, 2006]. We approximate NO_y as NO + NO₂ + HNO₃, as these species provide the largest contributions to NO_y and are regularly retrieved by ACE-FTS. PAN can provide a significant contribution to NO_y, however it is not regularly retrieved by ACE-FTS. Therefore we exclude regions where simulated PAN represents more than 30% of the total simulated NO_y.

[24] Figure 5 shows maps of annual mean NO_y concentrations in the tropical upper troposphere from MOZAIC, ACE-FTS and GEOS-Chem. The spatial distribution of ACE-FTS and GEOS-Chem NO_y exhibit a wave-1 pattern showing a maximum over Africa and a minimum over the Pacific, similar to that found by Martin *et al.* [2007] for HNO₃. Simulated NO_y concentrations show some similarities in spatial structure with a mean negative bias versus MOZAIC of 9%. The largest discrepancies are found in regions with few MOZAIC flights, such as Southeast Asia. However, both ACE-FTS NO_y and HNO₃ are significantly larger than the simulated values (mean bias 29% for HNO₃, mean bias 23% for NO_y). Adding simulated PAN to the ACE-FTS NO_y would increase the mean bias to 55%. Including data lying outside two standard deviations of the median would increase the mean bias to 50%.

[25] In summary, both the comparisons with CR-AVE and MOZAIC provide evidence of a positive bias in ACE-FTS. The larger spatial and temporal domain of the comparison with MOZAIC yields a more quantitative estimate. Considering the negative bias in the simulated NO_y versus MOZAIC, we find evidence of a positive mean bias in ACE-FTS HNO₃ of 15%. This bias is greater than the error found in stratospheric validations [Wolff *et al.*, 2008], but consistent with the validation over Europe by Hegglin *et al.* [2008]. This evaluation shows improvement in the ACE-FTS version 3 retrievals, especially in the middle troposphere, when compared to previous studies of ACE-FTS

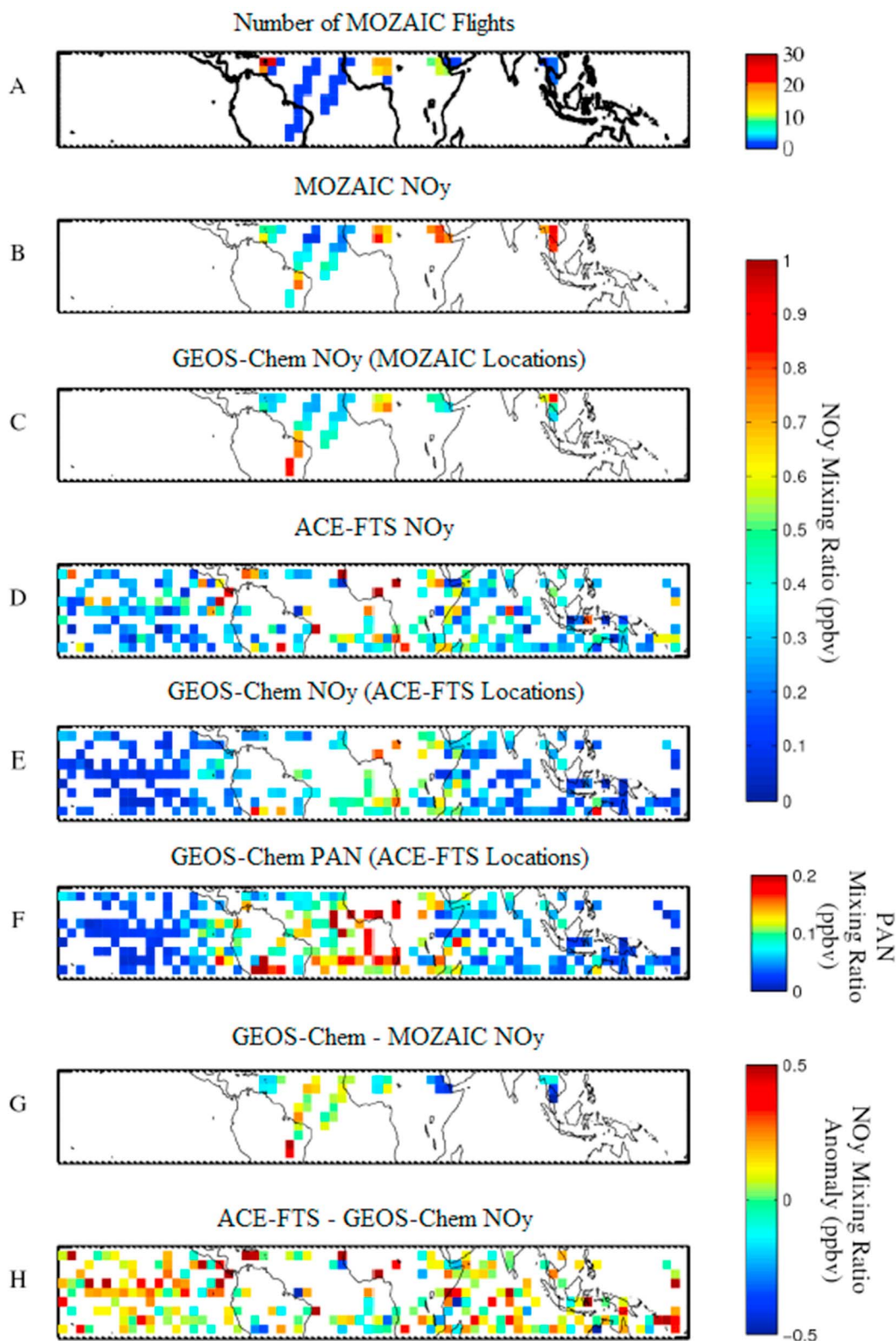


Figure 5. (a) Number of MOZAIC flights where NO_y is measured. Annual mean NO_y concentrations from (b) MOZAIC, (c) GEOS-Chem sampled along MOZAIC flight paths, (d) ACE-FTS, and (e) GEOS-Chem sampled at ACE-FTS locations and months. Data in Figures 5b–5e are excluded in regions where the contribution of PAN to simulated NO_y concentrations exceeds 30%. (f) Annual mean PAN concentrations from GEOS-Chem sampled at ACE-FTS locations and months. Annual mean differences between (g) MOZAIC and GEOS-Chem NO_y, and (h) ACE-FTS and GEOS-Chem NO_y.

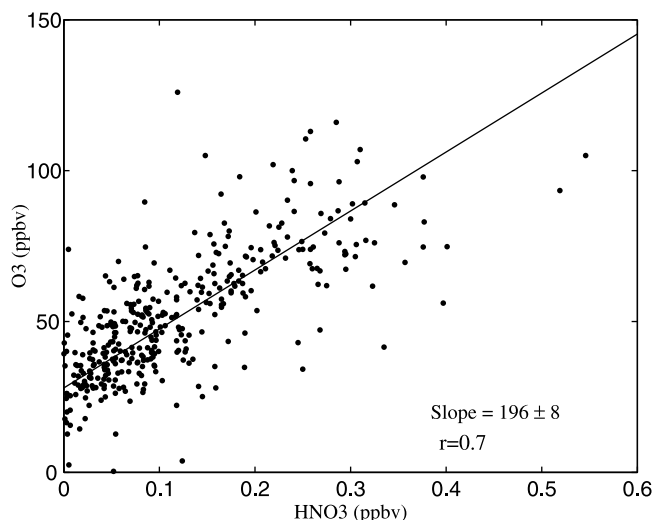


Figure 6. Scatterplot of ACE-FTS O₃ versus HNO₃ used to infer ozone production efficiency (OPE) at 11.5 km. Each point represents a monthly mean of ACE-FTS measurements on a 2° latitude by 2.5° longitude grid in the tropics (20°N–20°S). The line of best fit is determined by reduced major-axis linear regression [Miller and Kahn, 1962].

version 2.2 versus GEOS-Chem [Folkins *et al.*, 2006]. In the next section, we will use the biases inferred here.

5. Ozone Production Efficiency

5.1. Estimating Ozone Production Efficiency

[26] We go on to develop a method to interpret the ACE-FTS observations for insight into the ozone production efficiency (OPE). OPE can be defined as the number of O₃ molecules produced per NO_x molecule consumed [Liu *et al.*, 1987]. Several studies have calculated OPE using aircraft or surface measurements of O₃ and HNO₃. Near-surface OPE has been found to range from 2 mol/mol in polluted urban regions [Kleinman *et al.*, 2000] to 10 mol/mol in rural areas [Trainer *et al.*, 1993]. These studies show that OPE increases with decreasing NO_x [Kleinman *et al.*, 2002]. OPE is greater in the free troposphere than at the surface due to low NO_x concentrations as well as low humidity and more intense solar radiation [Sauvage *et al.*, 2007a]. Hudman *et al.* [2004] used aircraft observations of a pollution plume crossing the Pacific Ocean to estimate the OPE in the middle troposphere as 53 mol/mol.

[27] ACE-FTS measurements of upper tropospheric O₃ and HNO₃ can be used to estimate OPE. Convective outflow in the upper troposphere contains some initial ozone and NO_x concentration but is depleted of HNO₃ due to its high solubility [Mari *et al.*, 2000]. Ozone is produced in the presence of NO_x during transport until the cycle is broken by oxidation of NO_x to HNO₃. The loss of NO_x is therefore nearly equivalent to HNO₃ production, and the OPE can be inferred by the ratio of O₃ production to HNO₃ production.

$$OPE = \frac{P(O_3)}{L(NO_x)} \approx \frac{\Delta O_3}{\Delta HNO_3} \quad (1)$$

This expression assumes that O₃ and HNO₃ losses are small. The assumption is reasonable in the tropical upper troposphere, given the long lifetimes of O₃ and HNO₃ in this region. However, the lifetime of the O₃ family (O_x) is longer (90 days in GEOS-Chem) than that of HNO₃ scavenging (75 days in GEOS-Chem). This lifetime difference lowers HNO₃ concentrations and causes an overestimation of OPE. For this reason, the OPE calculation presented here should be considered an upper limit.

[28] We tested the method by comparing a GEOS-Chem calculation of OPE based on O₃ and HNO₃ production rates with an estimate of OPE using a scatterplot of annual mean simulated O₃ and HNO₃. OPE calculated from O₃ and HNO₃ production rates is 26% lower than that estimated from O₃ and HNO₃ concentrations, confirming our expectations of an upper limit. Sampling the model at ACE-FTS measurement locations did not change the tropical mean OPE, indicating that the OPE estimate is not sensitive to ACE-FTS sampling. We also tested the sensitivity to dynamics of the OPE estimated from HNO₃ and O₃ concentrations. We estimated the OPE for two different assimilation systems (GEOS-4 and GEOS-5) that use different convective parameterizations, which lead to variations in the height and intensity of convective outflow in the upper troposphere [Folkins *et al.*, 2006; Wu *et al.*, 2007]. The OPE estimates differed by <2%, indicating this method has little sensitivity to dynamics.

[29] We go on to apply our method to the ACE-FTS data. Figure 6 shows a scatterplot of ACE-FTS O₃ and HNO₃ data between 20°N and 20°S at 11.5 km in the tropical upper troposphere. Each point represents an average of ACE-FTS O₃ and HNO₃ over 2° latitude and 2.5° longitude. The

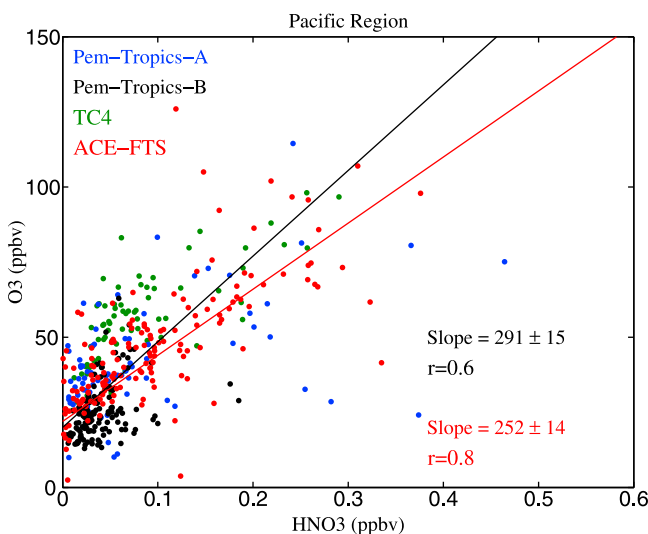


Figure 7. Scatterplot of O₃ versus HNO₃ from ACE-FTS (red), PEM-Tropics A (blue) and B (black), and TC4 (green). Only ACE-FTS measurements over the tropical Pacific (20°N–20°S, 150°E–50°W) at 11.5 km are shown here. The vertical range for aircraft measurements is 8–12 km. Each point represents an average measurement on a 2° latitude by 2.5° longitude grid. Lines of best fit for ACE-FTS (red) and all aircraft (black) data in this region are determined by reduced major-axis linear regression [Miller and Kahn, 1962].

Table 3. Regional Ozone Production Efficiency Variations as Estimated From ACE-FTS Measurements^a

Region	Longitude Range	OPE (mol/mol)	Measurements Count	r (HNO ₃ Versus O ₃)	Mean CO (ppbv)	δ_p (mol/mol)	δ_r (mol/mol)
Whole Tropics	180°W–180°E	196 (+34, –61)	368	0.71	85	32	7
Tropical Pacific	160°E–130°W	249 (+21, –68)	65	0.80	71	4	19
Tropical Atlantic	50°W–30°E	146 (+16, –41)	62	0.68	100	6	14

^aHere δ_p is the error in the OPE estimate due to sensitivity to polluted outflow and δ_r is the uncertainty in the OPE estimate from the standard error of the reduced major axis regression.

significant correlation (0.7) between the two species implies a single chemical system. As demonstrated in equation (1), OPE is given by the slope of the line of best fit for this plot, which is found by a reduced major axis regression [Miller and Kahn, 1962] to be 196 (+34, –61) mol/mol. The method for determining the uncertainty is described below. While 11.5 km was chosen here, OPE estimations from ACE-FTS were consistent between 8 and 12 km. Above 12 km, OPE increases with altitude ($\Delta\text{OPE}/\Delta z = 40 \pm 10$ mol/mol/km).

[30] O₃ and HNO₃ measurements from ACE-FTS and aircraft campaigns over the tropical Pacific are shown in Figure 7. Both data sets show similar correlation, and a line fitted to the aircraft data shows a tropical mean in situ OPE estimate that is within 15% of the one found using satellite observations. Differences may reflect different sampling domains. The higher correlation in ACE-FTS (0.8) versus the aircraft data (0.6) could indicate the benefit of sampling a larger air mass.

[31] We explore the horizontal variation in the estimate. Table 3 contains OPE calculated from ACE-FTS separately for the tropical Atlantic and tropical Pacific. OPE values over the tropical Pacific are 67% larger than those over the tropical Atlantic, reflecting increased OPE in less polluted regions. Higher OPE in regions of lower NO_x is consistent with previous OPE calculations [Liu et al., 1987; Lin et al., 1988; Trainer et al., 1993; Kleinman et al., 2002].

[32] We compare the OPE estimate from ACE-FTS with OPE calculated from GEOS-Chem O₃ and HNO₃ production rates, which are shown in Figure 8. OPE ranges from 100 to 150 mol/mol or higher throughout the middle and upper troposphere over the tropical South Atlantic [Savage et al., 2007a], and over the tropical Pacific can exceed 200 mol/mol. These values are lower than those from ACE-FTS, but agree within their uncertainty. Satellite measurements of O₃ and HNO₃ with higher measurement density could yield a spatially resolved OPE estimate.

5.2. Uncertainty in the OPE Estimate

[33] Here we examine sources of error in the ACE-FTS OPE estimate. The estimate is based on the assumption that the O₃ and HNO₃ concentrations in air exiting a convective updraft are constant throughout the tropics. In practice, higher O₃ concentrations in convective outflow can occur over polluted regions. We examine this issue using ACE-FTS CO measurements as a tracer for convective outflow of pollution. As the convective outflow from a cloud will have little HNO₃ due to wet deposition, the intercept of Figure 6 (O₃ = 25 ± 1 ppbv when HNO₃ = 0) is an estimate of the average O₃ concentration of the convective outflow. The intercept increases with increasing CO ($\Delta\text{intercept}/\Delta\text{CO} = 0.32 \pm 0.04$ ppbv O₃ per ppbv CO, $r = 0.96$) indicating that convective outflow in the tropical upper troposphere has higher O₃ concentrations over polluted regions. A similar relationship was found between CO concentrations and the intercept from PEM-Tropics measurements ($\Delta\text{intercept}/\Delta\text{CO} = 0.43 \pm 0.02$ ppbv O₃ per ppbv CO, $r = 0.99$).

[34] We estimate the OPE uncertainty due to the initial conditions of the convective outflow as the change in OPE due to a 1 σ perturbation of CO. The OPE calculation decreases with increasing CO concentrations ($\Delta\text{OPE}/\Delta\text{CO} = -1.5 \pm 0.1$, $r = -0.99$), indicating that OPE is lower over regions with enhanced pollution outflow into the upper troposphere. An inverse relationship between CO and OPE is also found in calculations using measurements from PEM-Tropics ($\Delta\text{OPE}/\Delta\text{CO} = -2.9 \pm 0.5$, $r = -0.94$). This does not imply that OPE is inversely related to CO concentrations themselves, as CO is used here only as a tracer for pollution. Using the mean ACE-FTS tropical upper tropospheric CO (85 ± 23 ppbv) and the value of $\Delta\text{OPE}/\Delta\text{CO}$ we estimate that perturbing the initial CO conditions by one standard deviation would cause an OPE change of 33 mol/mol.

[35] In addition to errors from sensitivity to pollution outflow ($\delta_p = 33$ mol/mol), the uncertainty of our OPE

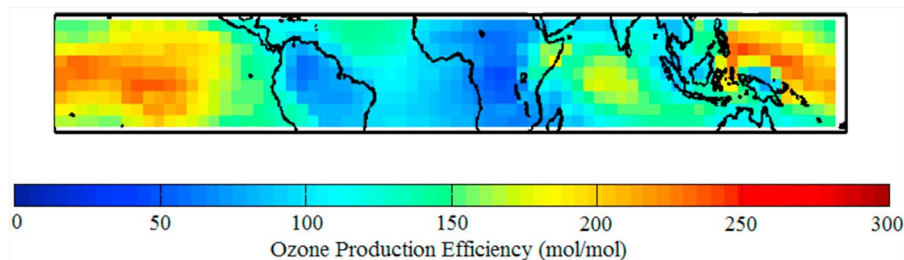


Figure 8. Simulated annual mean ozone production efficiency at 11 km, determined from GEOS-Chem simulated O₃ and HNO₃ production rates.

estimation contains contributions from the standard error of the reduced major axis regression (δ_r) as well as biases in the ACE-FTS measurements (δ_b). The standard error of the slope in Figure 6 as defined by *Miller and Kahn* [1962] is $\delta_r = 8$ mol/mol. The uncertainty due to ACE-FTS biases was calculated by reducing the O₃ and HNO₃ by their respective mean biases (assuming 12% bias for O₃, 15% bias for HNO₃) and recalculating OPE. As OPE is estimated by a ratio of O₃ and HNO₃ and the biases are of similar magnitude, the biases partly cancel resulting in an uncertainty of $\delta_b = 5$ mol/mol. Section 5.1 found that OPE estimated from the slope of O₃ and HNO₃ was biased high by 26%. Combining these errors in quadrature yields a combined global error of (+34, −61) mol/mol.

6. Conclusion

[36] This study evaluates OSIRIS O₃, ACE-FTS O₃, and ACE-FTS HNO₃ retrievals. Our focus was on the tropical troposphere, as these instruments had not been thoroughly evaluated in this region. Seasonal mean ozone profiles over eight regions were compared with measurements from the MOZAIC aircraft program and from ozonesondes. These regions were defined using the GEOS-Chem model to minimize sampling errors. Both satellite retrievals generally reproduce major ozone features in the upper troposphere such as summer enhancements at northern midlatitudes, and enhanced ozone concentrations over the tropical Atlantic versus the tropical Pacific. Annual mean O₃ concentrations in the upper troposphere from ACE-FTS are 10–13% higher than seasonal mean MOZAIC and ozonesonde profiles, while those from OSIRIS are higher by 5%. We indirectly evaluated ACE-FTS HNO₃ retrievals by comparing GEOS-Chem HNO₃ and NO_y concentrations with aircraft measurements and ACE-FTS. GEOS-Chem HNO₃ mixing ratios generally agreed with aircraft measurements above 12 km and were 9% lower than MOZAIC NO_y. Mean ACE-FTS measurements of HNO₃ are 29% higher on average than simulated values.

[37] Simultaneous measurements of HNO₃ and O₃ by ACE-FTS allowed for a calculation of an upper limit on the annual mean ozone production efficiency in the tropical troposphere. The ACE-FTS biases in O₃ and HNO₃ partially cancel in their ratio. A value of 196 (+34, −61) moles of O₃ produced per mole NO_x consumed was found and is consistent with the range of values seen in GEOS-Chem simulations. The ozone production efficiency of 249 (+21, −68) mol/mol inferred from ACE-FTS over the tropical Pacific is considerably larger than that of 146 (+16, −41) mol/mol over the tropical Atlantic, reflecting a decreased ozone production efficiency in a region where convective outflow is more polluted. Future improvement of satellite retrievals could yield a more refined estimate of the ozone production efficiency.

Appendix A: The GEOS-Chem Model

[38] The GEOS-Chem global 3-D chemical transport model [*Bey et al.*, 2001] is used in this study as a tool to aid comparisons between in situ and satellite comparisons. The simulation is driven by assimilated meteorological data from the Goddard Earth Observing System (GEOS) at the NASA

Global Modeling and Assimilation Office (GMAO). Version 7-02-04 (<http://geos-chem.org>) is used here at 4° × 5° resolution with GEOS-4 meteorological fields for the year 2000. The tropical tropospheric ozone simulation for this version has been thoroughly evaluated by *Sauvage et al.* [2007b]. GEOS-4 data extend from the surface to 0.1 hPa including approximately 16 levels in the troposphere.

[39] The model includes a detailed simulation of tropospheric ozone-NO_x-hydrocarbon chemistry as well as of aerosols and their precursors. NO_x emissions from biomass burning, soils, lightning and anthropogenic sources included in the model have been recently described by *Sauvage et al.* [2007b]. The lightning parameterization is based on work by *Price and Rind* [1992] with vertical profiles from *Pickering et al.* [1998]. The lightning NO_x source is 5 Tg N/yr globally with 3 Tg occurring in the tropics between ±20° latitude. The spatial distribution of lightning is scaled to match the seasonal mean lightning flash rates as observed by the OTD and LIS satellite instruments [*Sauvage et al.*, 2007b]. HNO₃ scavenging by precipitation includes in-cloud and below-cloud scavenging by cloud droplets and ice crystals as described by *Jacob et al.* [2000].

[40] GEOS-Chem has been used in several recent studies to interpret tropospheric ozone measurements from satellite instruments such as TES [*Jourdain et al.*, 2007; *Bowman et al.*, 2008; *Zhang et al.*, 2008; *Nassar et al.*, 2009], OMI [*Martin et al.*, 2007; *Stajner et al.*, 2008; *Zhang et al.*, 2010], GOME [*Liu et al.*, 2006; *Sauvage et al.*, 2007a, 2007b], and TOMS and SAGE II [*Choi et al.*, 2008]. The O₃ simulation has been extensively evaluated against in situ measurements [*Jaeglé et al.*, 2003; *Hudman et al.*, 2004, 2007; *Li et al.*, 2004; *Auvray et al.*, 2007; *Sauvage et al.*, 2007b; *Zhang et al.*, 2008; *Nassar et al.* 2009].

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References

- Auvray, M., I. Bey, E. Lllull, M. Schultz, and S. Rast (2007), A model investigation of tropospheric ozone chemical tendencies in long-range transported pollution plumes, *J. Geophys. Res.*, **112**, D05304, doi:10.1029/2006JD007137.
- Bernath, P. F. (2006), Atmospheric Chemistry Experiment: Analytical chemistry from orbit, *Trends Analyt. Chem.*, **25**, 647–654, doi:10.1016/j.trac.2006.05.001.
- Bernath, P. F., et al. (2005), Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, **32**, L15S01, doi:10.1029/2005GL022386.
- Bey, I., D. J. Jacob, R. M. Yantosca, J. A. Logan, B. D. Field, A. M. Fiore, Q. Li, H. Liu, L. J. Mickley, and M. G. Schultz (2001), Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, **106**(D19), 23,073–23,095, doi:10.1029/2001JD000807.
- Boone, C., and P. F. Bernath (2002), Pressure/temperature and volume mixing ratio retrievals for the Atmospheric Chemistry Experiment

- (ACE), *Proc. SPIE Int. Soc. Opt. Eng.*, 4814, 50–61, doi:10.1117/12.451526.
- Bowman, K. W., D. Jones, J. Logan, H. Worden, F. Boersma, R. Chang, S. Kulawik, G. Osterman, and J. Worden (2008), Impact of surface emissions to the zonal variability of tropical tropospheric ozone and carbon monoxide for November 2004, *Atmos. Chem. Phys. Discuss.*, 8, 1505–1548, doi:10.5194/acpd-8-1505-2008.
- Choi, Y., Y. Wang, T. Zeng, D. Cunnold, E.-S. Yang, R. Martin, K. Chance, V. Thouret, and E. Edgerton (2008), Springtime transitions of NO₂, CO, and O₃ over North America: Model evaluation and analysis, *J. Geophys. Res.*, 113, D20311, doi:10.1029/2007JD009632.
- Degenstein, D. A., A. E. Bourassa, C. Z. Roth, and E. J. Llewellyn (2009), Limb scatter ozone retrieval from 10 to 60 km using a multiplicative algebraic reconstruction technique, *Atmos. Chem. Phys.*, 9, 6521–6529, doi:10.5194/acp-9-6521-2009.
- Dupuy, E., et al. (2009), Validation of ozone measurements from the Atmospheric Chemistry Experiment (ACE), *Atmos. Chem. Phys.*, 9, 287–343, doi:10.5194/acp-9-287-2009.
- Folkens, I., C. Braum, A. M. Thompson, and J. Witte (2002), Tropical ozone as an indicator of deep convection, *J. Geophys. Res.*, 107(D13), 4184, doi:10.1029/2001JD001178.
- Folkens, I., P. Bernath, C. Boone, L. J. Donner, A. Eldering, G. Lesins, R. V. Martin, B.-M. Sinnhuber, and K. Walker (2006), Testing convective parameterizations with tropical measurements of HNO₃, CO, H₂O, and O₃: Implications for the water vapor budget, *J. Geophys. Res.*, 111, D23304, doi:10.1029/2006JD007325.
- Hegglin, M. I., C. D. Boone, G. L. Manney, T. G. Shepherd, K. A. Walker, P. F. Bernath, W. H. Daffer, P. Hoor, and C. Schiller (2008), Validation of ACE-FTS satellite data in the upper troposphere/lower stratosphere (UTLS) using non-coincident measurements, *Atmos. Chem. Phys.*, 8, 1483–1499, doi:10.5194/acp-8-1483-2008.
- Hoell, J. M., D. D. Davis, D. J. Jacob, M. O. Rodgers, R. E. Newell, H. E. Fuelberg, R. J. McNeal, J. L. Raper, and R. J. Bendura (1999), Pacific Exploratory Mission in the tropical Pacific: PEM-Tropics A, August–September 1996, *J. Geophys. Res.*, 104(D5), 5567–5583, doi:10.1029/1998JD100074.
- Hoinka, K. P. (1998), Statistics of the Global Tropopause Pressure, *Mon. Weather Rev.*, 126, 3303–3325, doi:10.1175/1520-0493(1998)126<3303:SOTGTP>2.0.CO;2.
- Hudman, R. C., et al. (2004), Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California, *J. Geophys. Res.*, 109, D23S10, doi:10.1029/2004JD004974.
- Hudman, R. C., et al. (2007), Surface and lightning sources of nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow, *J. Geophys. Res.*, 112, D12S05, doi:10.1029/2006JD007912.
- Jacob, D. J., et al. (1996), Origin of ozone and NO_x in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic Basin, *J. Geophys. Res.*, 101(D19), 24,235–24,250, doi:10.1029/96JD00336.
- Jacob, D. J., H. Liu, C. Mari, and R. M. Yantosca (2000), Harvard wet deposition scheme for GMI, report, Harvard Univ. Atmos. Chem. Modeling Group, Cambridge, Mass.
- Jaeglé, L., D. Jaffe, H. U. Price, P. Weiss-Penzias, P. I. Palmer, M. J. Evans, D. J. Jacob, and I. Bey (2003), Sources and Budgets for CO and O₃ in the northeastern Pacific during the spring of 2001: Results from the PHOBEA-II Experiment, *J. Geophys. Res.*, 108(D20), 8802, doi:10.1029/2002JD003121.
- Jourdain, L., S. S. Kulawik, H. M. Worden, K. E. Pickering, J. Worden, and A. M. Thompson (2007), Tropospheric vertical distribution of tropical Atlantic ozone observed by TES during the northern African biomass burning season, *Geophys. Res. Lett.*, 34, L04810, doi:10.1029/2006GL028284.
- Kalnay, E., et al. (1996), The NCEP/NCAR 40-year reanalysis project, *Bull. Am. Meteorol. Soc.*, 77, 437–470, doi:10.1175/1520-0477(1996)077<0437:TNYRP>2.0.CO;2.
- Kasibhatla, P. S., H. Levey II, and W. J. Moxim (1993), Global NO_x, HNO₃, PAN, and NO_y distributions from fossil fuel combustion emissions: A model study, *J. Geophys. Res.*, 98(D4), 7165–7180, doi:10.1029/92JD02845.
- Kleinman, L. I., P. H. Daum, D. G. Imre, J. H. Lee, Y.-N. Lee, L. J. Nunnermacker, S. R. Springston, J. Weinstein-Lloyd, and L. Newman (2000), Ozone production in the New York City urban plume, *J. Geophys. Res.*, 105(D11), 14,495–14,511, doi:10.1029/2000JD900011.
- Kleinman, L. I., P. H. Daum, Y.-N. Lee, L. J. Nunnermacker, and S. R. Springston (2002), Ozone production efficiency in an urban area, *J. Geophys. Res.*, 107(D23), 4733, doi:10.1029/2002JD002529.
- Lacis, A. A., D. J. Wuebbles, and J. A. Logan (1990), Radiative forcing of climate by changes in the vertical distribution of ozone, *J. Geophys. Res.*, 95(D7), 9971–9981, doi:10.1029/JD095iD07p09971.
- Li, Q. B., D. J. Jacob, W. Munger, R. M. Yantosca, and D. D. Parrish (2004), Export of NO_y from the North American boundary layer: Reconciling aircraft observations and global model budgets, *J. Geophys. Res.*, 109, D02313, doi:10.1029/2003JD004086.
- Lin, X., M. Trainer, and S. C. Liu (1988), On the nonlinearity of the tropospheric ozone production, *J. Geophys. Res.*, 93(D12), 15,879–15,888, doi:10.1029/JD093iD12p15879.
- Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hübner, and P. C. Murphy (1987), Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res.*, 92(D4), 4191–4207, doi:10.1029/JD092iD04p04191.
- Liu, X., et al. (2006), First directly retrieved global distribution of tropospheric column ozone from GOME: Comparison with the GEOS-Chem model, *J. Geophys. Res.*, 111, D02308, doi:10.1029/2005JD006564.
- Llewellyn, E. J., et al. (2004), The OSIRIS instrument on the Odin spacecraft, *Can. J. Phys.*, 82, 411–422.
- Logan, J. (1999), An analysis of ozonesonde data for the troposphere: Recommendations for testing 3-D models and development of a gridded climatology for tropospheric ozone, *J. Geophys. Res.*, 104(D13), 16,115–16,149, doi:10.1029/1998JD100096.
- Manney, G. L., et al. (2007), Solar occultation satellite data and derived meteorological products: Sampling issues and comparisons with Aura microwave limb sounder, *J. Geophys. Res.*, 112, D24S50, doi:10.1029/2007JD008709.
- Marenco, A., et al. (1998), Measurement of ozone and water vapor by Airbus in-service aircraft: The MOZAIK airborne program, An overview, *J. Geophys. Res.*, 103(D19), 25,631–25,642, doi:10.1029/98JD00977.
- Mari, C., D. J. Jacob, and P. Bechtold (2000), Transport and scavenging of soluble gases in a deep convective cloud, *J. Geophys. Res.*, 105(D17), 22,255–22,267, doi:10.1029/2000JD900211.
- Martin, R. V., et al. (2002), Interpretation of TOMS observations of tropical tropospheric ozone with a global model and in situ observations, *J. Geophys. Res.*, 107(D18), 4351, doi:10.1029/2001JD001480.
- Martin, R. V., B. Sauvage, I. Folkens, C. E. Sioris, C. Boone, P. Bernath, and J. Ziemke (2007), Space-based constraints on the production of nitric oxide by lightning, *J. Geophys. Res.*, 112, D09309, doi:10.1029/2006JD007831.
- McLinden, C. A., V. E. Fioletov, C. S. Haley, N. Lloyd, C. Roth, D. Degenstein, A. Bourassa, C. T. McElroy, and E. J. Llewellyn (2007), An evaluation of Odin/OSIRIS limb pointing and stratospheric ozone through comparisons with ozonesondes, *Can. J. Phys.*, 85, 1125–1141.
- Miller, R. L., and J. S. Kahn (1962), *Statistical Analysis in the Geological Sciences*, 205 pp., John Wiley and Sons, New York, New York.
- Murphy, D. M., D. W. Fahey, M. H. Proffitt, S. C. Liu, K. R. Chan, C. S. Eubank, S. R. Kawa, and K. K. Kelly (1993), Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, 98(D5), 8751–8773, doi:10.1029/92JD00681.
- Nassar, R., J. A. Logan, I. A. Megretskaya, L. T. Murray, L. Zhang, and D. B. A. Jones (2009), Analysis of tropical tropospheric ozone, carbon monoxide, and water vapor during the 2006 El Niño using TES observations and the GEOS-Chem model, *J. Geophys. Res.*, 114, D17304, doi:10.1029/2009JD011760.
- Petelina, S. V., et al. (2004), Comparison of the Odin/OSIRIS stratospheric ozone profiles with coincident POAM III and ozonesonde measurements, *Geophys. Res. Lett.*, 31, L07104, doi:10.1029/2003GL019299.
- Pickering, K. E., Y. S. Wang, W. K. Tao, C. Prince, and J. F. Muller (1998), Vertical distribution of lightning NO_x for use in regional and global chemical transport models, *J. Geophys. Res.*, 103(D23), 31,203–31,216, doi:10.1029/98JD02651.
- Popp, P. J., et al. (2009), Stratospheric correlation between nitric acid and ozone, *J. Geophys. Res.*, 114, D03305, doi:10.1029/2008JD010875.
- Price, C., and D. Rind (1992), A simple lightning parameterization for calculating global lightning distributions, *J. Geophys. Res.*, 97(D9), 9919–9933, doi:10.1029/92JD00719.
- Raper, J. L., M. M. Kleb, D. J. Jacob, D. D. Davis, R. E. Newell, H. E. Fuelberg, R. J. Bendura, J. M. Hoell, and R. J. McNeal (2001), Pacific Exploratory Mission in the Tropical Pacific: PEM-Tropics B, March–April 1999, *J. Geophys. Res.*, 106(D23), 32,401–32,425, doi:10.1029/2000JD900833.
- Ryerson, T. B., et al. (1998), Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, 103(D17), 22,569–22,583, doi:10.1029/98JD01620.
- Sauvage, B., V. Thouret, A. M. Thompson, J. C. Witte, J.-P. Cammas, P. Nedelec, and G. Athier (2006), Enhanced view of the “Tropical Atlantic Ozone Paradox” and “Zonal Wave-one” from the in situ

- MOZAIC and SHADOZ data, *J. Geophys. Res.*, **111**, D01301, doi:10.1029/2005JD006241.
- Sauvage, B., R. V. Martin, A. van Donkelaar, and J. R. Ziemke (2007a), Quantification of the factors controlling tropical tropospheric ozone and the South Atlantic maximum, *J. Geophys. Res.*, **112**, D11309, doi:10.1029/2006JD008008.
- Sauvage, B., R. V. Martin, A. van Donkelaar, X. Liu, K. Chance, L. Jaeglé, P. I. Palmer, S. Wu, and T.-M. Fu (2007b), Remote sensed and in situ constraints on processes affecting tropical tropospheric ozone, *Atmos. Chem. Phys.*, **7**, 815–838, doi:10.5194/acp-7-815-2007.
- Stajner, I., et al. (2008), Assimilated ozone from EOS-Aura: Evaluation of the tropopause region and tropospheric columns, *J. Geophys. Res.*, **113**, D16S32, doi:10.1029/2007JD008863.
- Thompson, A. M. (1992), The oxidizing capacity of the Earth's atmosphere: Probable past and future changes, *Science*, **256**, 1157–1165, doi:10.1126/science.256.5060.1157.
- Thompson, A. M., K. E. Pickering, D. P. McNamara, M. R. Schoeberl, R. D. Hudson, J. H. Kim, E. V. Browell, V. W. J. H. Kirchhoff, and D. Nganga (1996), Where did tropospheric ozone over southern Africa and the tropical Atlantic come from in October 1992? Insights from TOMS, GTE TRACE A, and SAFARI 1992, *J. Geophys. Res.*, **101** (D19), 24,251–24,278, doi:10.1029/96JD01463.
- Thompson, A. M., et al. (2003a), Southern Hemisphere Additional Ozone-sondes (SHADOZ) 1998–2000 tropical ozone climatology: 1. Comparison with Total Ozone Mapping Spectrometer (TOMS) and ground-based measurements, *J. Geophys. Res.*, **108**(D2), 8238, doi:10.1029/2001JD000967.
- Thompson, A. M., et al. (2003b), Southern Hemisphere Additional Ozone-sondes (SHADOZ) 1998–2000 tropical ozone climatology: 2. Tropospheric variability and the zonal wave-one, *J. Geophys. Res.*, **108**(D2), 8241, doi:10.1029/2002JD002241.
- Thouret, V., A. Marenco, P. Nédélec, and C. Grouhel (1998a), Ozone climatologies at 9–12 km altitude as seen by the MOZAIC airborne program between September 1994 and August 1996, *J. Geophys. Res.*, **103**(D19), 25,653–25,679, doi:10.1029/98JD01807.
- Thouret, V., A. Marenco, J. Logan, P. Nédélec, and C. Grouhel (1998b), Comparisons of ozone measurements from the MOZAIC airborne program and the ozone sounding network at eight locations, *J. Geophys. Res.*, **103**(D19), 25,695–25,720, doi:10.1029/98JD02243.
- Toon, O. B., et al. (2010), Planning, implementation, and first results of the Tropical Composition, Cloud and Climate Coupling Experiment (TC4), *J. Geophys. Res.*, **115**, D00J04, doi:10.1029/2009JD013073.
- Trainer, M., et al. (1993), Correlation of ozone with NO_y in photochemically aged air, *J. Geophys. Res.*, **98**(D2), 2917–2925, doi:10.1029/92JD01910.
- Volz-Thomas, A., M. Berg, T. Heil, N. Houben, A. Lerner, W. Petrick, D. Raak, and H.-W. Pätz (2005), Measurements of total odd nitrogen (NO_y) aboard MOZAIC in-service aircraft: Instrument design, operation and performance, *Atmos. Chem. Phys.*, **5**, 583–595, doi:10.5194/acp-5-583-2005.
- von Savigny, C., I. C. McDade, E. Griffioen, C. S. Haley, C. E. Sioris, and E. J. Llewellyn (2005), Sensitivity studies and first validation of stratospheric ozone profile retrievals from Odin/OSIRIS observations of limb-scattered solar radiation, *Can. J. Phys.*, **83**, 957–972.
- Wolff, M. A., et al. (2008), Validation of HNO₃, ClONO₂, and N₂O₅ from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS), *Atmos. Chem. Phys.*, **8**, 3529–3562, doi:10.5194/acp-8-3529-2008.
- Wu, S., L. J. Mickley, D. J. Jacob, J. A. Logan, R. M. Yantosca, and D. Rind (2007), Why are there large differences between models in global budgets of tropospheric ozone?, *J. Geophys. Res.*, **112**, D05302, doi:10.1029/2006JD007801.
- Zhang, L., et al. (2008), Transpacific transport of ozone pollution and the effect of recent Asian emission increases on air quality in North America: An integrated analysis using satellite, aircraft, ozonesonde, and surface observations, *Atmos. Chem. Phys.*, **8**, 6117–6136, doi:10.5194/acp-8-6117-2008.
- Zhang, L., D. J. Jacob, X. Liu, J. A. Logan, K. Chance, A. Eldering, and B. R. Bojkov (2010), Intercomparison methods for satellite measurements of atmospheric composition: Application to tropospheric ozone from TES and OMI, *Atmos. Chem. Phys. Discuss.*, **10**, 1417–1456, doi:10.5194/acpd-10-1417-2010.
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