

Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998–2004 tropical ozone climatology:

3. Instrumentation, station-to-station variability, and evaluation with simulated flight profiles

Anne M. Thompson,¹ Jacquelyn C. Witte,^{2,3} Herman G. J. Smit,⁴ Samuel J. Oltmans,⁵ Bryan J. Johnson,⁵ Volker W. J. H. Kirchhoff,⁶ and F. J. Schmidlin⁷

Received 30 December 2005; revised 17 July 2006; accepted 29 September 2006; published 9 February 2007.

[1] The Southern Hemisphere Additional Ozonesondes (SHADOZ) project has collected more than 3000 ozone profiles from 14 tropical and subtropical sites using balloon-borne electrochemical concentration cell (ECC) ozonesondes flown with standard radiosondes. Published analysis of ozonesonde precision from SHADOZ profiles measured in 1998–2000 revealed that variations in ozonesonde technique might cause small station-to-station biases in the total ozone measurement. We present further evaluation of imprecisions and accuracy based on 1998–2004 SHADOZ data, results from laboratory simulations of ozonesonde flights, and a revised back-scattered ultraviolet algorithm, the TOMS version 8, 2004 release. The laboratory studies used standard ECC ozonesondes in a flight simulation chamber to evaluate techniques used at SHADOZ stations. Ozone deviations from a standard ozone instrument in the chamber tests resemble those of SHADOZ station data relative to a SHADOZ-defined climatological reference. Certain systematic variations in SHADOZ ozone profiles are accounted for by differences in solution composition, data processing, and instrument manufacturer. When SHADOZ total ozone column amounts are compared to the new TOMS algorithm, discrepancies between sonde and satellite decline 1–2 percentage points on average, compared to version 7 TOMS.

Citation: Thompson, A. M., J. C. Witte, H. G. J. Smit, S. J. Oltmans, B. J. Johnson, V. W. J. H. Kirchhoff, and F. J. Schmidlin (2007), Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998–2004 tropical ozone climatology: 3. Instrumentation, station-to-station variability, and evaluation with simulated flight profiles, *J. Geophys. Res.*, 112, D03304, doi:10.1029/2005JD007042.

1. Introduction

1.1. Tropical Ozone Profiles: Needs and Status

[2] In the past 15 years there has been interest in enhancing the number of tropical ozone soundings because important scientific issues are hard to resolve without the vertical resolution provided through these observations. There has been inadequate geographical and temporal coverage in ozone profiles for deducing ozone trends [Logan, 1994; World Meteorological Organization (WMO), 1998] in the tropics. Soundings are required to determine the vertical

structure of the zonal wave-one pattern in equatorial ozone as detected by satellite [Fishman and Larsen, 1987; Shiotani, 1992]. The wave-one feature refers to more column ozone over the Atlantic and adjacent continents (with a maximum near 0° longitude) than over the Pacific, with minimum ozone. Profiles are also needed to evaluate satellite tropospheric ozone estimates [e.g., Fishman and Balok, 1999; Thompson and Hudson, 1999; Ziemke *et al.*, 1998, 2003; Martin *et al.*, 2002; Liu *et al.*, 2005].

[3] To respond to these and other requirements, the SHADOZ project (Southern Hemisphere Additional Ozonesondes, <http://croc.gsfc.nasa.gov/shadoz> [Thompson *et al.*, 2003a, 2003b]) was initiated to augment launches at selected tropical sites. Analysis of ~1100 ozone profiles from the 1998–2000 SHADOZ record addressed some of the issues raised above. A longitudinal cross section of O₃ showed that the wave-one is predominantly in the troposphere and occurs throughout the year [Thompson *et al.*, 2003b]. The vertical structure of stratospheric ozone variations with the Quasi-biennial Oscillation was detailed with SHADOZ and satellite data [Logan *et al.*, 2003]. A SHADOZ campaign of opportunity, the Aerosols99 cruise on the *R/V Ronald H. Brown*, uncovered an “Atlantic ozone

¹Department of Meteorology, Pennsylvania State University, University Park, Pennsylvania, USA.

²Science Systems and Applications, Inc., Lanham, Maryland, USA.

³Also at NASA Goddard Space Flight Center, Greenbelt, Maryland, USA.

⁴Research Centre Jülich, Institute for Chemistry and Dynamics of the Geosphere: Troposphere, Jülich, Germany.

⁵Global Monitoring Division, NOAA, Boulder, Colorado, USA.

⁶Laboratório De Ozônio/INPE-CP 515, Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brazil.

⁷NASA Wallops Flight Facility, Wallops Island, Virginia, USA.

Table 1. SHADOZ Sites and Method, With Parameters During JOSIE-2000 Tests

SHADOZ Sites	Latitude, deg	Longitude, deg	Station Method, PCF	Station Instrument	JOSIE Method ^a	JOSIE Instrument
Suva, Fiji	−18.13	178.4	2% KI, N ^b	SPC	2% KI	SPC
Pago Pago, American Samoa	−14.23	−170.6	2% KI, N	SPC	2% KI	SPC
Papeete, Tahiti	−18	−149	2% KI, N	SPC	2% KI	SPC
San Cristóbal, Galapagos	−0.92	−89.6	2% KI, N	SPC	2% KI	SPC
Paramaribo, Surinam	5.81	−55.2	1% KI, K ^b	SPC
Natal, Brazil	−5.42	−35.38	1% KI, W ^b	SPC, ^c ENSCI	1% KI	SPC
Ascension Island	−7.98	−14.42	1% KI, W	SPC, ^c ENSCI	1% KI	SPC
Cotonou, Benin (started 2005)	6.21	2.23	1% KI, K	SPC
Irene, South Africa	−25.25	28.22	1% KI, K	SPC
Nairobi, Kenya	−1.27	36.8	1% KI, K	ENSCI	1% KI	ENSCI
Malindi, Kenya	−2.99	40.19	1% KI, K	SPC
Kuala Lumpur, Malaysia	2.73	101.7	1% KI, K	SPC
La Réunion	−21.06	55.48	0.5, 1% KI	SPC, ^c ENSCI	.5, 2% KI	ENSCI
Watukosek, Indonesia	−7.57	112.7	2% KI, N	ENSCI
Kaashidhoo, Maldives ^d	5	73.5	2% KI, N	ENSCI
Aerosols99 Cruise ^d	2% KI, N	ENSCI

^aResponsible Co-I JOSIE participant: NOAA/CMDL for Fiji, Samoa, San Cristobal, and Tahiti; NASA Wallops Flight Facility (WFF) for Natal and Ascension; Météosuisse for Nairobi; Univ. Réunion for La Réunion. FZ-Jülich JOSIE participant test method used at Irene, Paramaribo.

^bPCF key: N, NOAA/CMDL [Johnson *et al.*, 2002]; K, Komhyr [1986] and Komhyr *et al.* [1995]; W, Wallops laboratory test [Torres, 1981].

^cMixture of solution strengths, instruments used; see details given by Thompson *et al.* [2003a].

^dCampaign data in SHADOZ archive, January–March 1999. 23 sondes from Aerosols99 cruise [Thompson *et al.*, 2000] and 54 sondes from Kaashidhoo [Thompson *et al.*, 2003b, Figure 11b].

paradox” [Thompson *et al.*, 2000], referring to a higher tropospheric ozone column over the Southern Hemisphere than over the Northern Hemisphere during the northern tropical biomass fire season. The paradox has led to a number of interpretive studies [Edwards *et al.*, 2003; Jenkins *et al.*, 2003; Chatfield *et al.*, 2004; Sauvage *et al.*, 2006].

1.2. Ozonesonde Precision, Accuracy, and Technical Variations in the SHADOZ Record

[4] In the work by Thompson *et al.* [2003a], SHADOZ soundings from 1998 to 2000 were used to make a preliminary evaluation of instrumental characteristics and potential impact on the sonde data record. We found the following:

[5] 1. The precision of total ozone measured by a sonde instrument is 5%, an improvement over published evaluations [e.g., WMO, 1998]. This owes partly to SHADOZ data being taken in a fairly uniform meteorological regime.

[6] 2. Agreement between ground-based instruments at five SHADOZ stations and integrated total ozone from the sondes ranged from 2 to 7%.

[7] 3. Comparison with total ozone from the TOMS satellite (version 7) indicated variability among stations, with the satellite measurement 2–11% higher than sonde total ozone. A known TOMS overestimate of tropospheric ozone [Thompson *et al.*, 2003b, Figure 8] is a factor in the disagreement between TOMS and the sondes at four Pacific SHADOZ sites.

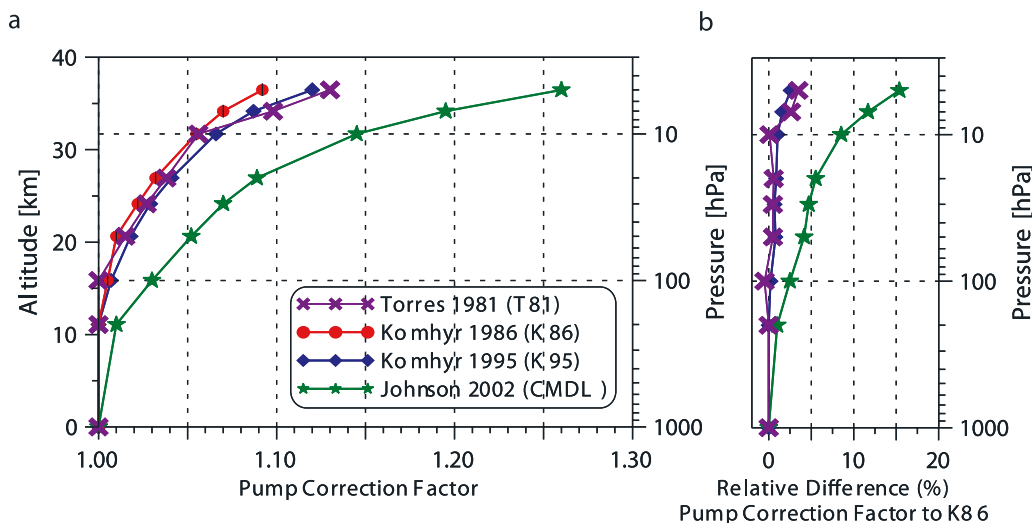


Figure 1. (a) Different sets of pump flow (PCF) correction factors as a function of altitude and pressure, for EEC-ozonesondes as reported by Torres [1981], Komhyr [1986], Komhyr *et al.* [1995], and Johnson *et al.* [2002]. (b) Relative differences of PCFs compared to Komhyr [1986].

Table 2. JOSIE-2000 Tests Simulating SHADOZ Conditions

Test Date	Simulation	Condition	SHADOZ Participant
7 Sep 2000	91	tropical	NOAA/CMDL
8 Sep 2000	92	tropical	NOAA/CMDL
12 Sep 2000	94	subtropical	NOAA/CMDL
13 Sep 2000	95	subtropical	NOAA/CMDL
21 Sep 2000	98	tropical	NASA/WFF, Meteoswiss, Univ. Réunion
22 Sep 2000	99	tropical	NASA/WFF, Meteoswiss, Univ. Réunion
25 Sep 2000	100	subtropical	NASA/WFF, Meteoswiss, Univ. Réunion
27 Sep 2000	102	subtropical	NASA/WFF, Meteoswiss, Univ. Réunion

[8] 4. Preliminary reports from a series of chamber tests of ozonesonde performance suggested that the sonde instrument type (manufacturer) could be a factor in station variability. However, manufacturer bias was hard to ascertain in data from four SHADOZ stations where a mixture of instrument type was employed in 1998–2000. Two stations showed no variation; the other two showed bias.

[9] Geophysical variability in ozone readings at SHADOZ sites was also considered by *Thompson et al.* [2003a]. There was no statistically significant difference among the stratospheric ozone column determined from SHADOZ stations between 0 and 22°S, except at Nairobi, which is 10–15 DU higher than the other stations. Examination of SHADOZ upper stratospheric variability shows the Nairobi disagreement is greatest at the ozone maximum and above, not where true physical differences are expected. Ozone column amounts in the lower stratosphere, below 20 km (70 hPa) are the same at all SHADOZ sites when allowance is made for different meteorological regimes at Kaashidhoo in the Northern Hemisphere and Irene, which has considerable midlatitude character [*Thompson et al.*, 2003a, Figure 12].

[10] Thus, except for Irene, where geophysical deviations from the other Southern Hemisphere SHADOZ stratospheric readings are expected, variability among stations may be due to instrumental effects. It is the purpose of this paper to examine that possibility because, although all SHADOZ stations use electrochemical concentration cell (ECC) technology, the network was initiated with minor variations in instrument type, software, and sonde preparation (Table 1). For example, there are two ECC sonde manufacturers; this

may affect the ozone measurement [*Johnson et al.*, 2002; *Smit and Sträter*, 2004a, 2004b].

1.3. Updates and Outline of Present Study

[11] New data are available for evaluation of ozone variability in the SHADOZ data set. (1) The Jülich Ozone-sonde Intercomparison Experiment (JOSIE) conducted under World Meteorological Organization (WMO) sponsorship in 2000 tested the techniques used in the SHADOZ network through intercomparison with a standard reference instrument (H. G. J. Smit et al., Assessment of the performance of ECC-sondes under quasi-flight conditions in the environmental chamber: Insights from the Jülich Ozone Sonde Intercomparison Experiment (JOSIE), submitted to *Journal of Geophysical Research*, hereinafter referred to as Smit et al., submitted manuscript, 2006); (2) the number of sonde measurements in the SHADOZ database has more than doubled since the analysis by *Thompson et al.* [2003a, 2003b]; and (3) TOMS total ozone was reprocessed, version 8 release, at <http://toms.gsfc.nasa.gov>.

[12] 1. The present paper uses a SHADOZ climatological “tropical ozone profile” to examine variations in profiles at individual sites. The latter results, that take advantage of the large statistics offered by the SHADOZ data, are compared to JOSIE chamber profiles (section 3). In the work by *Thompson et al.* [2003a] only column ozone amounts were compared.

[13] 2. This paper also evaluates stratospheric column ozone to see where biases might occur (section 3).

[14] 3. This paper compares total ozone column amounts from SHADOZ sondes to TOMS version 8 (v 8) ozone

Table 3. JOSIE 2000: Summary of Mean Relative Bias of the Ozone Measurement, in 5-km Altitude Bins, to the UV Ozone-Photometer (OPM) of ENSCI-Z and SPC-6A Sondes for Various Sensing Solutions (SST)^a

Altitude Range, km	ENSCI-Z Sonde Bias, %			SPC-6A Sonde Bias, %		
	1.0% KI, Full Buffer (SST-1), PCF:K86	0.5% KI, Half Buffer (SST-2), PCF:K86	2.0% KI, No Buffer (SST-3), PCF:CMDL	1.0% KI, Full Buffer (SST-1), PCF:K86	0.5% KI, Half Buffer (SST-2), PCF:K86	2.0% KI, No Buffer (SST-3), PCF:CMDL
30–35	10	4	5	–2	–11	–6
25–30	10	5	4	3	–4	–2
20–25	7	3	1	0	–3	–4
15–20	3	1	–2	–2	–3	–4
10–15	9	3	–3	3	–7	–6
5–10	15	6	–3	5	0	–9
0–5	9	2	–5	1	0	–10
Total column	6	4	0	0	–3	–5

^aData processing was made according to *Komhyr* [1986]. Pump correction factor (PCF) for sondes operated with SST-1 and SST-2 is from the K86. For SST-3 the CMDL PCF was applied [*Johnson et al.*, 2002]. Last row based on integrals over the vertical O₃ column between the surface and 8–10 hPa pressure.

Table 4. Ozone Summary From 1998–2004 SHADOZ Data^a

Site	Sample/Total Profiles	Integrated O ₃ , 1σ	Tropospheric O ₃ , 1σ	Integrated O ₃ -Tropospheric O ₃ , 1σ	CMR Add-On, 1σ	SBUV Add-On, 1σ	Total Sonde O ₃ + CMR, 1σ	Total Sonde O ₃ + SBUV, 1σ	(CMR-SBUV), 1σ
Ascension	178/318	196.5, 18.0	37.1, 8.2	159.5, 12.4	77.7, 9.4	56.0, 1.7	274.2, 24.3	252.6, 17.7	21.6, 9.4
Fiji	165/232	185.2, 14.3	23.8, 7.5	161.3, 17.4	70.2, 7.6	55.6, 1.8	255.4, 16.4	240.7, 14.0	14.6, 6.9
Irene	113/169	210.5, 18.5	33.2, 5.9	177.4, 16.3	65.7, 7.6	53.9, 1.4	276.2, 21.8	264.4, 18.6	11.8, 6.9
Watokusek	85/236	187.5, 12.3	23.5, 5.8	164.1, 9.9	78.2, 10.5	55.8, 1.2	265.7, 19.0	243.3, 12.4	22.4, 10.3
Malindi	35/82	203.6, 13.1	32.1, 6.0	171.5, 9.8	80.7, 6.6	56.3, 1.7	284.3, 14.6	259.9, 12.2	24.5, 6.4
Nairobi	216/317	202.3, 12.1	28.8, 5.2	173.5, 9.4	81.4, 5.6	56.0, 1.6	283.7, 13.5	258.3, 11.5	25.4, 5.7
Natal	185/267	200.3, 15.5	33.1, 8.1	167.1, 10.9	79.2, 7.5	56.2, 1.6	279.5, 20.1	256.5, 15.4	23.0, 7.4
Paramaribo	146/243	215.9, 14.6	31.6, 5.7	184.2, 13.0	87.4, 7.1	56.0, 0.9	303.2, 17.8	271.8, 14.6	31.4, 7.2
Reunion	87/203	197.8, 14.2	32.9, 6.7	165.0, 9.8	68.4, 8.9	53.8, 1.5	266.3, 17.7	251.6, 14.2	14.6, 8.1
Samoa	191/263	180.2, 11.3	19.7, 5.6	160.5, 7.9	74.9, 6.9	55.7, 1.8	255.1, 14.4	235.9, 11.2	19.2, 6.2
San Cristóbal	218/278	179.8, 13.2	23.3, 4.5	156.5, 10.8	72.1, 7.9	56.2, 1.5	252.0, 17.6	236.0, 12.6	15.9, 8.1
Kuala Lumpur	68/170	180.7, 13.3	22.6, 4.3	158.1, 12.7	69.4, 8.5	55.9, 0.9	250.1, 18.0	236.6, 12.9	13.5, 8.6

^aTotal sample number given along with the number of profiles to 10 hPa, on which statistics are based. Total samples used in statistical analyses (first column): 2778. The SHADOZ project archives data in a uniform format, with initial analysis and calibration performed by the station coinvestigator, who may reprocess at any time. Updates (with most recent processing date) are given on the Website. Some sites report data every 10 s during a flight, whereas other profiles are archived with 1-s frequency. Data from SHADOZ stations maintained at other archives may differ from SHADOZ in format, O₃ integration, and extrapolation.

and to colocated total ozone instruments where possible (section 4).

[15] The ozonesonde measurement and relevant JOSIE-2000 results are first described (section 2).

2. Ozonesonde Measurement: JOSIE-2000 and SHADOZ

2.1. Ozonesonde Measurement

[16] The ECC sensor measures O₃ using a potential difference that is set up between two cells of different KI (potassium iodide) solution strength [Komhyr, 1969]. The O₃ partial pressure, P_{ozone} in mPa, is recorded with a 1–2 s sampling interval during the ascent:

$$P_{\text{ozone}} = 4.307 \times 10^{-2} \times (I - I_{\text{bg}}) \times T(\text{pump}) \times \text{PCF}(1/F) \quad (1)$$

The current, I in μA , that develops because of ozone's electrochemical reactions is referenced to a “no-ozone” background value, I_{bg} , measured in the laboratory prior to the balloon flight. The first term on the right side is a units conversion that incorporates the gas constant and the Faraday constant and T (K) is the temperature inside the sampling pump, operating with flow rate, F in $\text{cm}^3 \text{ s}^{-1}$ [Smit and Sträter, 2004a]. T is recorded during flight; F is determined in the laboratory prior to launch. As the balloon rises, a pump correction factor (PCF) adjusts for a decrease in the pump's efficiency. The PCF is most critical above 25 km [Johnson et al., 2002].

[17] Several tests conducted in the Jülich ozonesonde chamber in 1996 and 1998 [Smit and Kley, 1998; Smit and Sträter, 2004a] showed that differences in data processing, as well as in sonde manufacturer and instrument preparation, can contribute to systematic variations among O₃ measurements. Johnson et al. [2002], Thompson et al. [2003a] and Smit and Sträter [2004a, 2004b] describe four factors that may affect the measurement: (1) the background current, (2) the concentration of KI in the cell cathode, (3) strength of any buffer used, and (4) the PCF used to correct for variation in pump efficiency. From JOSIE tests of ECC ozonesondes in 1996 and 1998 [Smit and Kley, 1998; Smit and Sträter, 2004a, 2004b; Smit et al., submitted

manuscript, 2006] it can be inferred that factor 1 should be a relatively minor issue in SHADOZ because of sonde improvements in the past decade but the other factors may have a detrimental effect on instrument performance in the network.

[18] Table 1 presents technique, latitude and longitude of SHADOZ stations. SHADOZ stations include the use of three different sensing solutions: 1% KI with full buffer, 0.5% KI with half-buffer; 2% KI with no buffer. SHADOZ stations also use two instrument types and at least four altitude-dependent sets of PCF. For example, a uniform technique with 2% KI solution type, no buffer, is used at the four Pacific stations (Fiji, Samoa, San Cristóbal, Tahiti) in SHADOZ, normally with the Science Pump Corporation (SPC) instrument. The processing at those stations includes the PCF determined by NOAA/CMDL [Johnson et al., 2002]. The procedures at Natal and Ascension, with 1% KI, full buffer, also normally use the SPC instrument, but with a PCF determined by Wallops Flight Facility [Torres, 1981]. All other stations use 1% KI full buffer or 0.5% KI with half buffer, and apply a PCF for SPC instruments after Komhyr [1986] and for ENSCI instruments after Komhyr et al. [1995]. Figure 1 illustrates the four PCF (Figure 1a). At pressures below 200 hPa only the NOAA/CMDL values [Johnson et al., 2002] are significantly (5–10%) greater than the other three curves [Torres, 1981; Komhyr, 1986; Komhyr et al., 1995] which are within 1–2% down to 10 hPa (Figure 1b).

[19] The use of different sensing solutions can also introduce systematic deviations [Boyd et al., 1998; Johnson et al., 2002] in the upper part of the O₃ profile where an increase of sensitivity due to evaporation over the course of the soundings is observed. Johnson et al. [2002] showed that sondes with buffers are most affected by this height-dependent artifact in the profile measurements.

2.2. JOSIE-2000

[20] The JOSIE-2000 campaign was conducted at the Forschungszentrum-Jülich World Calibration Centre for Ozonesondes (WCCOS [Smit et al., 2000], <http://www.fz-juelich.de/icg/icg-ii/esf>) to test SHADOZ methods [Smit and Sträter, 2004b; Smit et al., submitted manuscript, 2006]

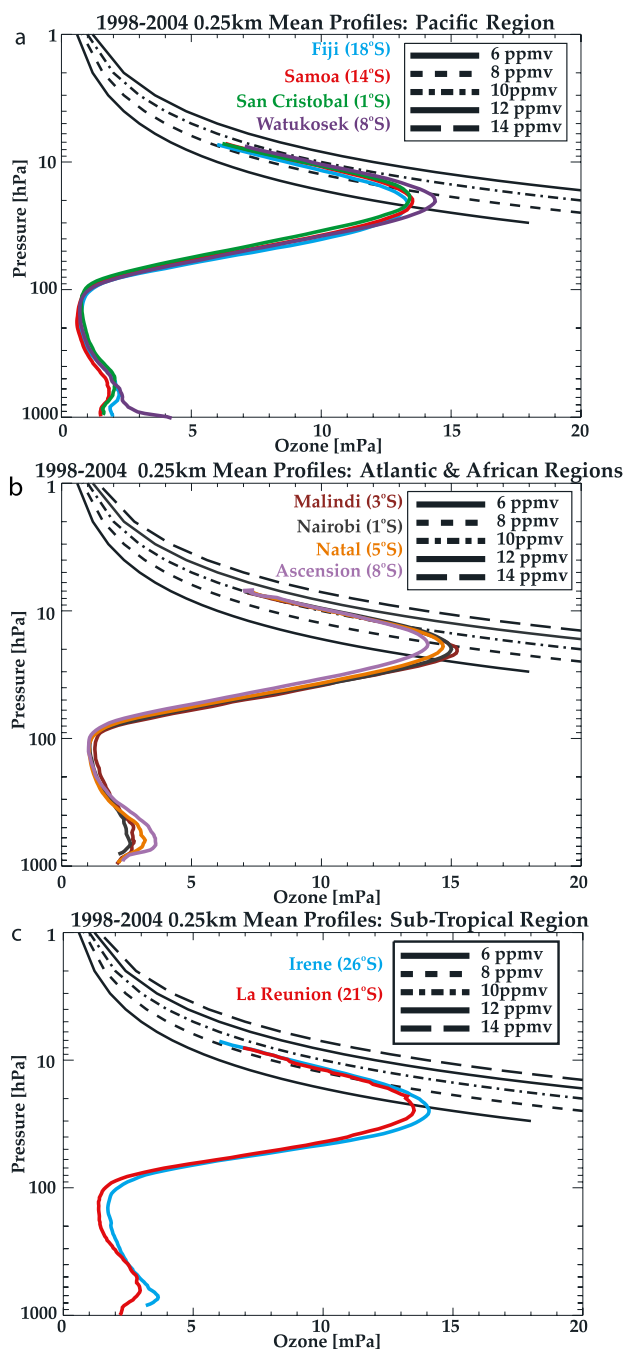


Figure 2. Mean O_3 profiles (from 1998 to 2004) from Southern Hemisphere SHADOZ soundings that reached 7.0 hPa pressure based on 0.25 km averages. (a) Pacific and eastern Indian Ocean stations, Fiji, American Samoa, San Cristóbal, and Watukosek; (b) Atlantic and Kenyan sites, Natal (Brazil), Ascension, Nairobi, and Malindi; and (c) two subtropical stations, Réunion and Irene. Our CMR definition uses the uppermost measured points before 10 hPa, then adds a column amount up to 1 hPa. The corresponding mean CMR is given in Table 4.

with a special emphasis on the three different sensing solutions and two instrument types described above. The simulation chamber holds four instruments plus the ozone photometer (OPM) as a reference, operated by the WCCOS

calibration team. The instrument type and sensing solution were varied in the chamber tests as shown in Appendix A and Tables 1 and 2. Two sequences of four investigator teams (institutions listed in Table 2) participated, with each group preparing sondes for six chamber simulations from 1000 to 10 hPa. An overview of major results appears in Appendix A.

[21] Simulation tests typical of SHADOZ conditions are listed in Table 2. A summary of results of JOSIE-2000 relevant to SHADOZ is given in Table 3. The best results relative to the OPM are obtained for the SPC-6A sonde operated with 1% KI and full buffer (Sensing Solution Type (SST)-1) or the ENSCI-Z sonde with 0.5% KI and half buffer (SST-2), assuming the PCF after Komhyr [1986, hereinafter referred to as K86] (Figure 1 and Table 3). JOSIE-2000 [see also Johnson *et al.*, 2002] showed that the ENSCI-Z sonde with 2% KI and no buffer (SST-3) and NOAA/CMDL processing (column 4 in Table 3) is not uniform with respect to the OPM. However, the column integral agrees well with the reference and SPC-SST-1 and ENSCI-SST-2 combinations (Table 3). In SHADOZ all sondes operated with the unbuffered 2% KI sensing solution use the PCF table provided by NOAA/CMDL so that the observed tendency of lower O_3 readings for unbuffered solutions is largely compensated by the 5–10% larger PCF compared to the PCFs of Torres [1981], Komhyr [1986], or Komhyr *et al.* [1995] (Figure 1). The latter PCFs are normally applied by SHADOZ stations operating sondes with SST-1 or SST-2 (Table 1).

[22] WCCOS processed each set of raw O_3 data with PCF functions (Tables 1 and 3) provided by the participants [Smit and Sträter, 2004a, 2004b]. The results are summarized in Appendix A. In applying JOSIE-2000 results in the present study, note that the SHADOZ archive receives data already processed. Although PCFs were supplied by SHADOZ participants to WCCOS, actual processing of data delivered to SHADOZ may include some proprietary steps. Thus PCF cannot be separated in analysis of instrumental effects on SHADOZ profiles (section 4).

2.3. SHADOZ, TOMS, and Ground-Based Ozone Data

[23] SHADOZ data are archived as O_3 partial pressure, O_3 mixing ratio, pressure, pressure altitude, and temperature at the SHADOZ website: <http://croc.gsfc.nasa.gov/shadoz>. The corresponding TOMS v 8 overpass total O_3 column and, where applicable, total O_3 column from a colocated Dobson or Brewer spectrophotometer, are given with each record. Most stations launch ozonesondes between 0700 and 1000 local time, so the TOMS satellite overpass (~1130 local) and sonde measurements match well. Section 4 compares SHADOZ and v 8 TOMS total O_3 .

[24] In the present analysis, profiles for 1998–2004 (Table 4) are used except in comparisons with TOMS where 1998–2001 data are employed. After 2001 the Earth-Probe (EP)/TOMS instrument diverged too much from the Dobson network to be reliable for our purposes (R. McPeters, personal communication, 2004). To obtain a total column O_3 value from SHADOZ profiles, an extrapolation is made because typically 15–30% of the O_3 column is above the balloon burst. Analyses here are based on O_3 profiles from balloons that reached at least 10 hPa. Extrapolation to the top of the atmosphere is made with an add-on column from

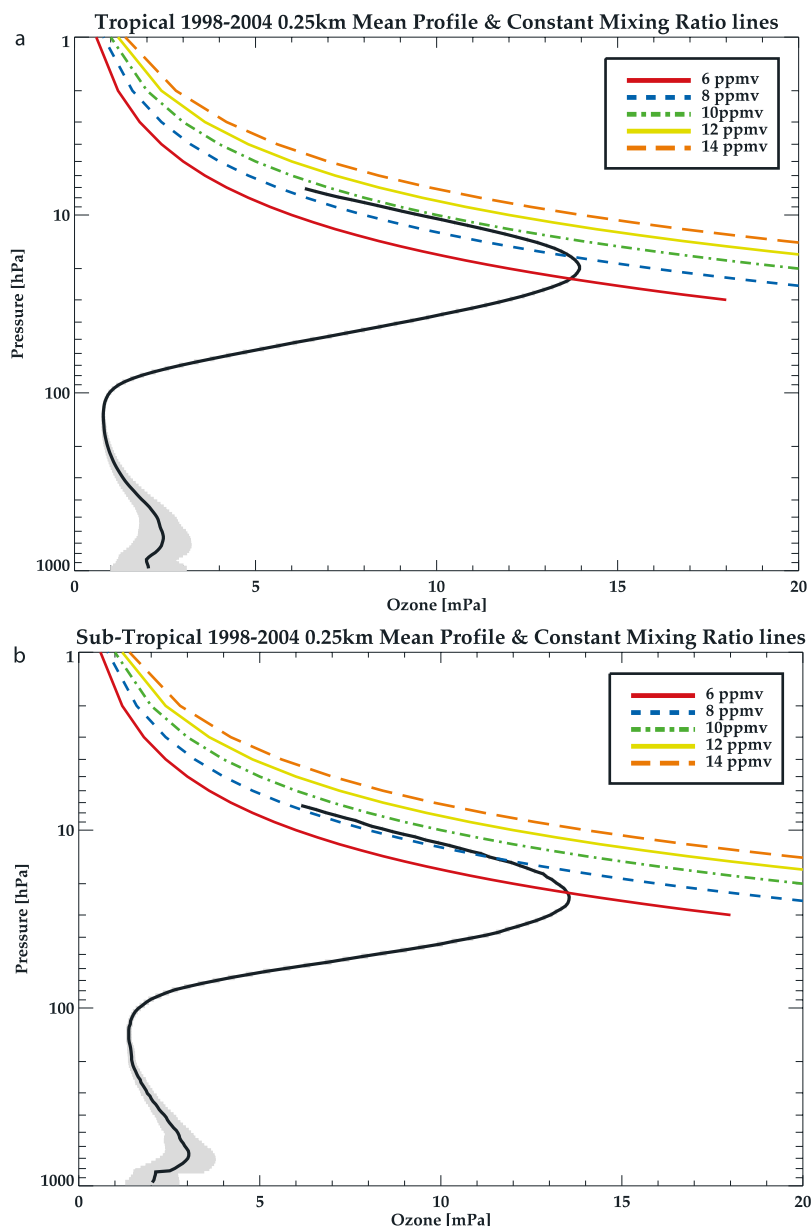


Figure 3. (a) Climatological mean “tropical ozone” profile based on 1998–2004 SHADOZ data with mean and 1- σ standard deviation (shaded). The mean is based on all Southern Hemisphere SHADOZ stations except Réunion and Irene. Constant mixing ratio isolines shown. (b) Subtropical profile average of Réunion and Irene profiles.

the SBUV satellite climatology of *McPeters et al.* [1997]. Extrapolation by assuming a constant mixing ratio (CMR) for O_3 above balloon burst is used for diagnostic purposes; however, total O_3 computed with CMR overestimates total O_3 [*McPeters et al.*, 1997].

3. SHADOZ Ozone Profile Analysis

[25] Although there are relatively small differences in stratospheric O_3 column among SHADOZ stations, it is important to evaluate variability arising from the O_3 measurement in various parts of the profile. This is done in two steps. First, mean SHADOZ O_3 profiles from each station are compared to an overall mean SHADOZ profile (sections 3.1 and 3.2). Second, biases in the stratospheric O_3

segments at SHADOZ stations are compared to corresponding technique as tested in JOSIE-2000 (section 3.3).

3.1. Characteristics of Mean SHADOZ Profiles

[26] Figure 2 shows mean profiles from Southern Hemisphere SHADOZ stations. The CMR isolines are drawn to show tendencies for upper stratospheric variability among the SHADOZ stations. What is observed? For the three Pacific stations and Watukosek (Figure 2a) O_3 profiles are nearly identical in the lower stratosphere but there is divergence at the stratospheric maximum. For Watukosek the maximum occurs at ~ 15 hPa and the corresponding partial pressure is 14.5 mPa. For Fiji the maximum partial pressure is ~ 13.5 mPa. Extrapolations above 7 hPa (the minimum pressure plotted) fall between the 8 and 10 ppmv

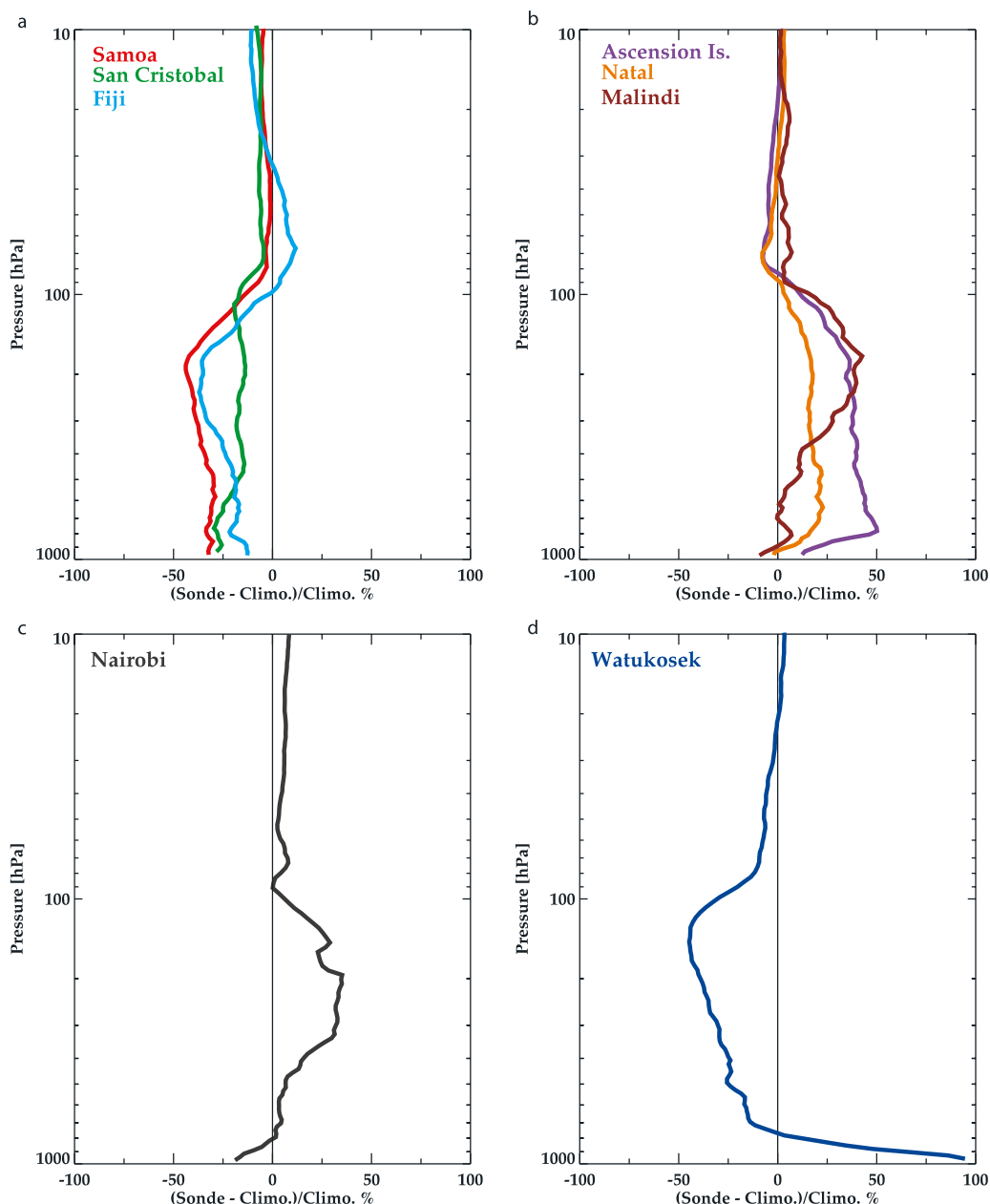


Figure 4. Mean SHADOZ station profiles (1998–2004) shown in Figure 2 normalized to the climatological tropical mean profile in Figure 3a. (a) Samoa, San Cristóbal, and Fiji; (b) Ascension, Natal, and Malindi; (c) Nairobi; and (d) Watukosek.

isolines. The tropospheric profiles of the three Pacific stations are generally similar in shape (Figure 2a). At the surface, O_3 is <2 mPa (14.5 ppbv), declining to the top of the mixed layer. Ozone then increases to ~ 500 hPa where a second decline begins that continues to the tropopause. The lower tropospheric layer of maximum O_3 is due to imported pollution. Watukosek, among Southern Hemisphere SHADOZ sites, displays the greatest amount of surface O_3 pollution.

[27] Figure 2b shows that the two Atlantic and two Kenyan stations are similar in the stratosphere (~ 15 mPa at maximum) except for Ascension where the maximum is ~ 14 mPa. In the troposphere, Natal and Ascension have peak O_3 partial pressure at 700 hPa, a consequence of long-

range pollution transport. Back trajectories initialized at 700 hPa from Natal and Ascension on days of ozonesonde launch (images available at the SHADOZ website) typically show African origins for the highest O_3 episodes [cf. Logan and Kirchhoff, 1986]. The two subtropical SHADOZ stations (Figure 2c) have peak O_3 partial pressure lower, ~ 30 hPa instead of 20 mPa (Figures 2a and 2b).

[28] For purposes of examining relative features of individual station profiles, it is useful to define “mean tropical” and “mean subtropical” O_3 profiles from SHADOZ data. These can be viewed as analogous to the JOSIE-2000 OPM “standard” tropical and subtropical profiles (Appendix A). A SHADOZ “mean tropical” O_3 profile, with 1- σ standard deviation (Figure 3a), is based on the eight stations illus-

1998-2004 SHADOZ/JOSIE profile comparisons

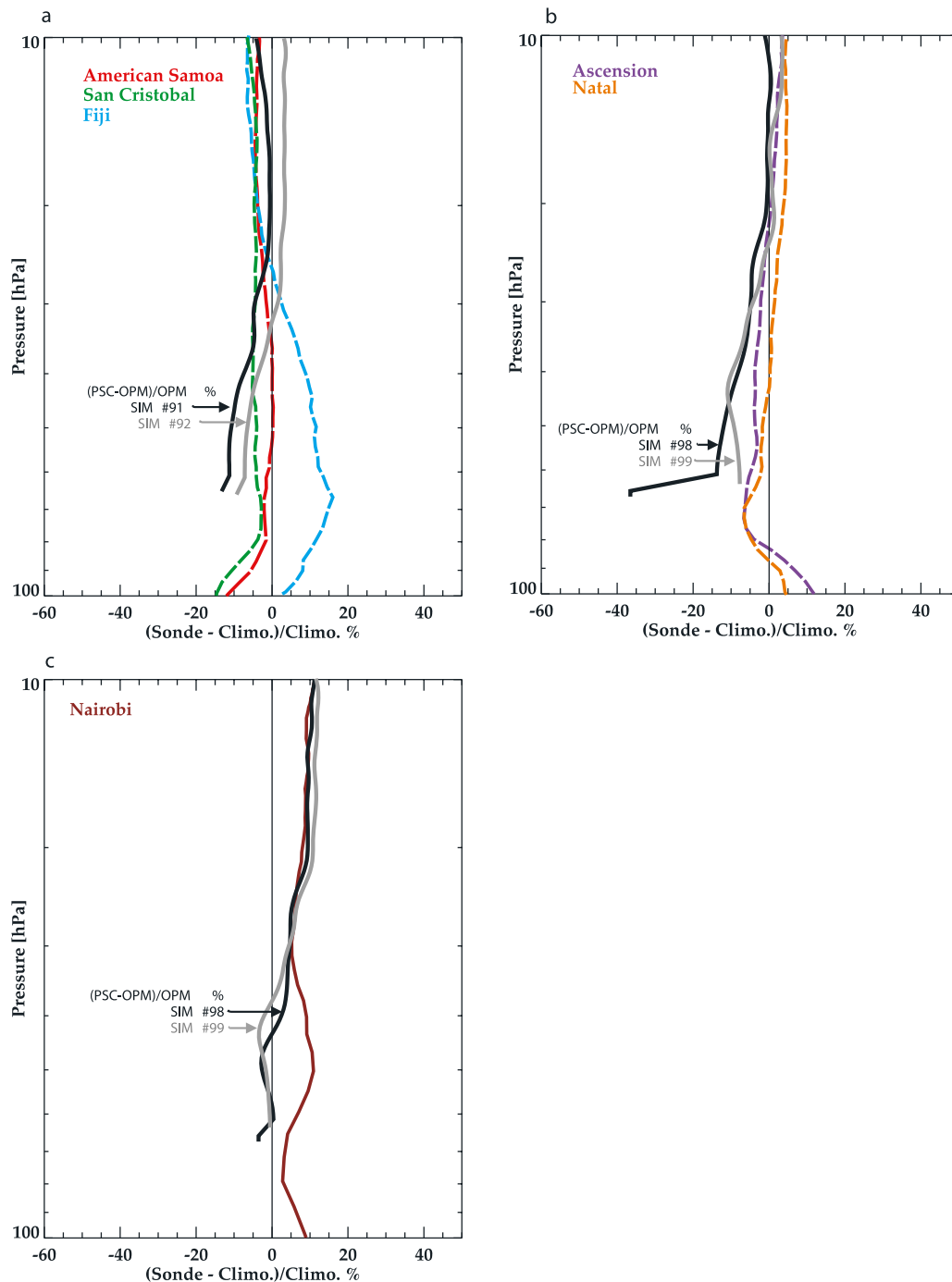


Figure 5. Similar deviations as in Figure 4 except stratospheric portion of sonde illustrated from 100 to 10 hPa. Stations are clustered according to technique used. Also shown are deviations from OPM standard in JOSIE-2000. (a) NOAA/CMDL JOSIE (SST-3A) with deviations from SHADOZ tropical mean profile for Samoa, Fiji, and San Cristóbal; (b) NASA/WFF JOSIE (SST-1) deviations with SHADOZ deviations based on Natal and Ascension data; and (c) Meteoswiss JOSIE (SST-1) deviations with Nairobi deviation from SHADOZ tropical mean.

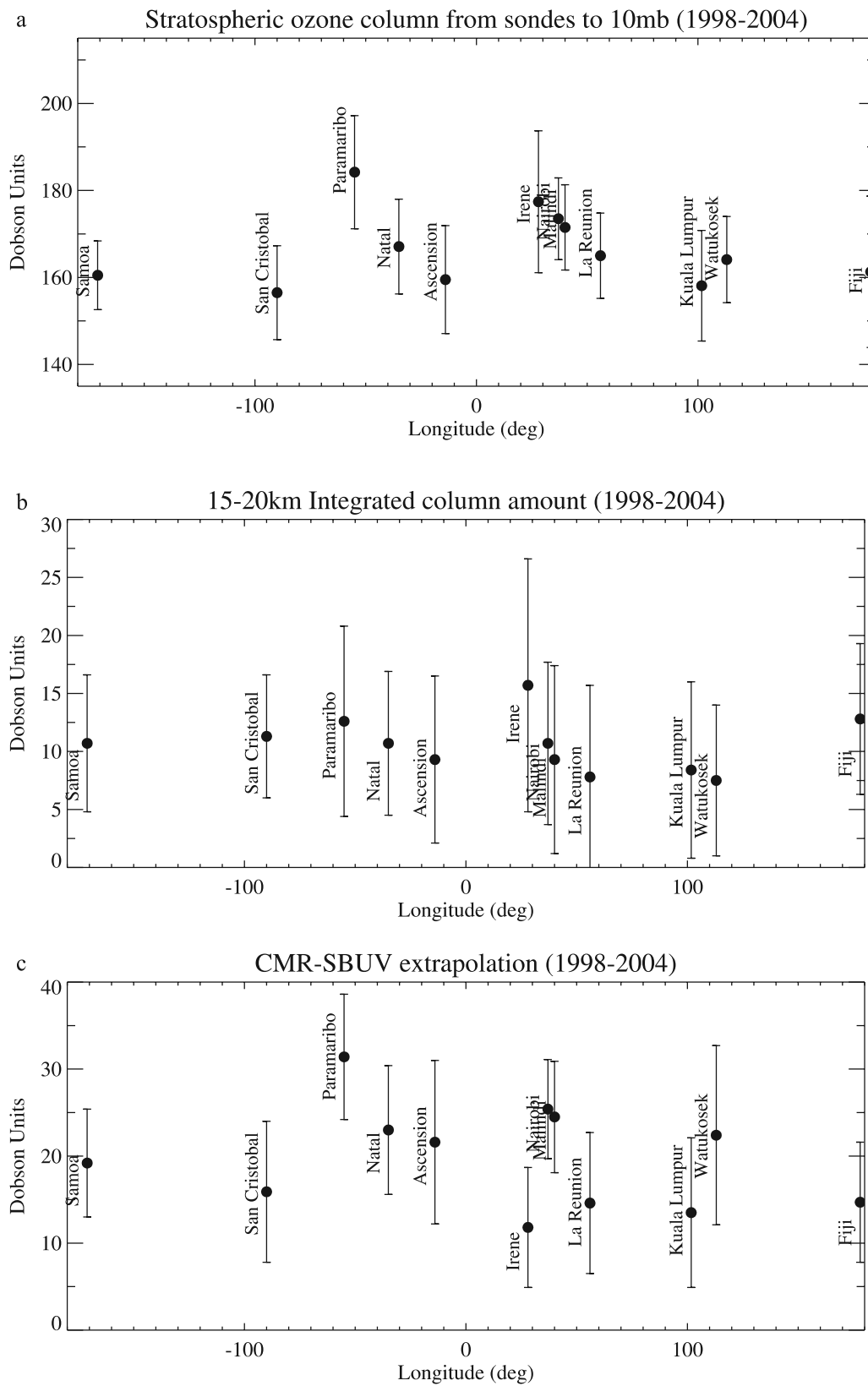


Figure 6

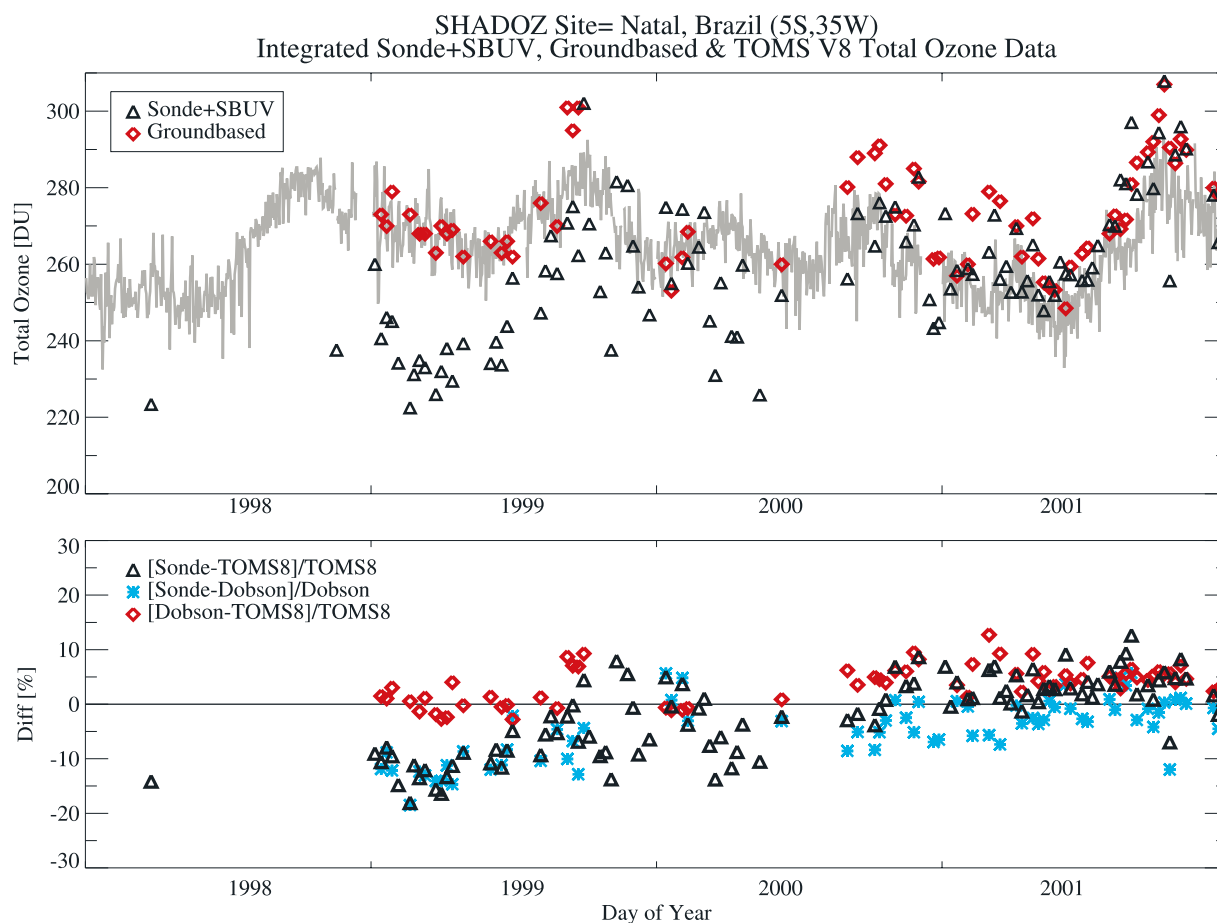


Figure 7a. (top) A comparison of integrated total O_3 from sondes, TOMS satellite (level 2, version 8 (v 8)) overpasses and Dobson or Brewer instruments at the Natal SHADOZ stations. (bottom) Percent deviation relative to the sonde or the ground-based instrument (TOMS v 8). Sonde-ground-based instrument differences are indicated by asterisks. Integrated O_3 from sondes based on data to 10 hPa with extrapolation above 10 hPa from *McPeters et al.* [1997] is shown. In the work by *Thompson et al.* [2003a], comparisons are with TOMS v 7 total O_3 and sondes reaching 7 hPa before balloon burst.

trated in Figures 2a and 2b plus 1998–1999 statistics from Tahiti [*Thompson et al.*, 2003a, Table 3]. For Watukosek, only data after July 1999, when soundings with ECC instruments were initiated, appear in the average. The Réunion (21°S) and Irene (26°S) O_3 data define a SHADOZ “mean subtropical” O_3 profile (Figure 3b). Integrated O_3 column amounts show a tropical-subtropical difference of ~ 15 DU:

Integrated O_3 , surface – 10 hPa : 189.4 DU, tropical
206.1 DU, subtropical

3.2. SHADOZ Ozone Profile Climatologies Relative to Means

[29] In Figures 4a–4d individual station O_3 profiles, normalized to the SHADOZ tropical mean, are depicted. Positive deviations signify a higher bias at the same pressure at a SHADOZ station relative to the climatological O_3 value. Tropospheric absolute deviations may exceed 40%. In the stratosphere (taken as above 100 hPa for convenience), the deviations rarely exceed 10%. Fiji is distinctive among the stations illustrated in Figure 4a in having the largest positive deviation in the stratosphere between 40 and 95 hPa. Ascension and Natal (Figure 4b)

Figure 6. (a) Zonal view of stratospheric column O_3 determined from integrated stratospheric O_3 of soundings plus SBUV extrapolation. Bars indicate 1σ standard deviation. For Irene, column may be higher because midlatitude stratospheric conditions often prevail. The lack of distinct zonal variation in the stratospheric column signifies the absence of a zonal wave-one in the stratosphere. (b) Zonal view of integrated column O_3 (DU) between 15 and 20 km (115–42 hPa), with 1σ standard deviation, and (c) zonal view of the difference between average CMR (constant-mixing-ratio) extrapolations and SBUV for SHADOZ stations. Comparison of Figure 6b with *Thompson et al.* [2003a, Figure 12] shows systematic differences greater than expected from the added observations. It is concluded that the earlier calculations were in error.

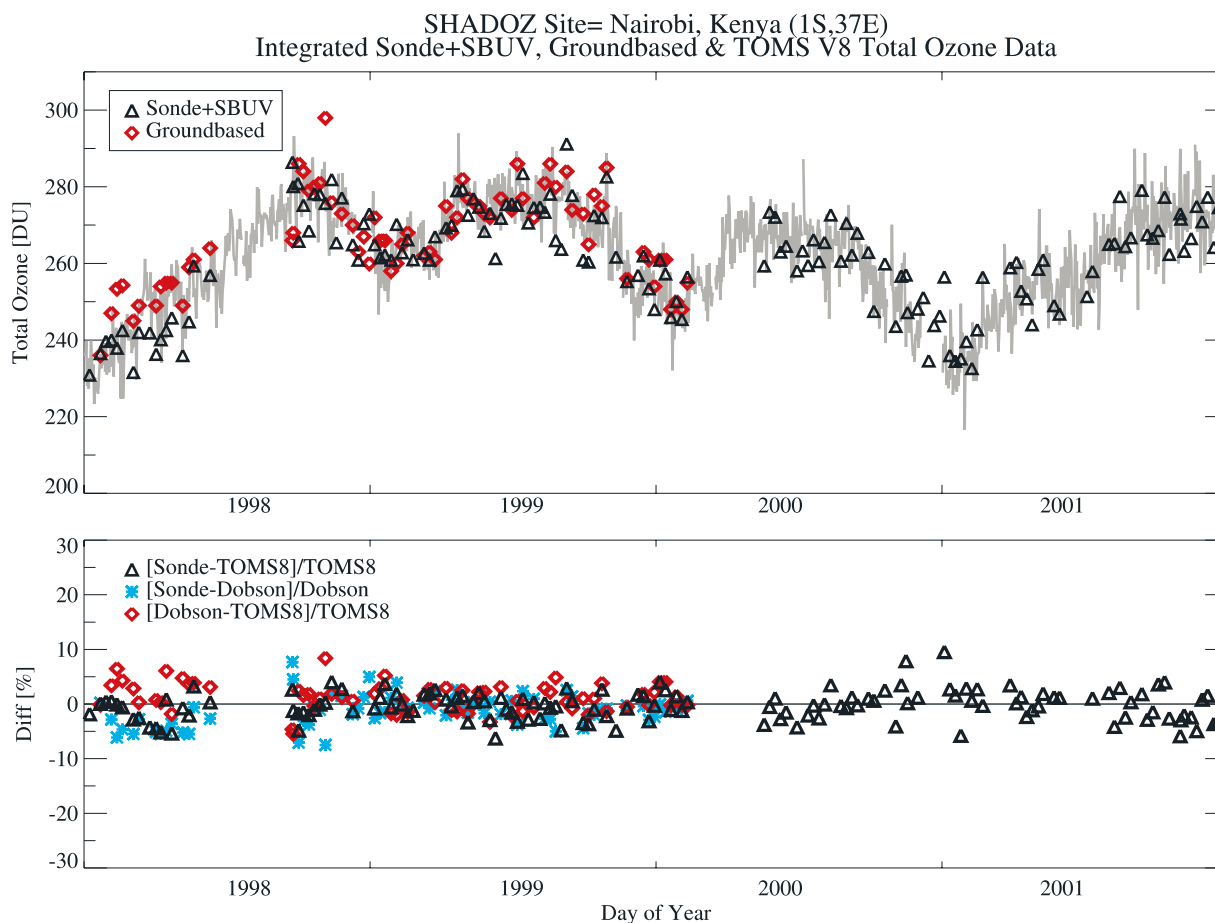


Figure 7b. Same as Figure 7a except for Nairobi, where Dobson measurements were interrupted in 2000 until 2005.

parallel one another in the stratosphere. There is a monotonic change in the deviation, starting from a bias in which the stations are low relative to climatology. At 10 hPa, Ascension and Natal are within 3% of the mean O_3 value and greater than Samoa, San Cristobal and Fiji at 10 hPa. There is similarity in shape among Malindi, Natal and Ascension (Figure 4b) with all three coming close to the mean above 30 hPa. At Nairobi (Figure 4c), in the 80–60 hPa range, the sondes are greater than climatology by $\sim 7\%$ whereas Natal and Ascension (Figure 4b) are low by 5–10%. Watukosek (Figure 4d) has a relatively high deviation from the climatology at 100 hPa but above 60 hPa is always within 5%.

3.3. SHADOZ Profile Biases and JOSIE-2000 Results

[30] How do the deviations at individual SHADOZ stations, relative to the tropical climatology, compare to profile deviations for the given technique as recorded in the JOSIE-2000 tests with a reference O_3 standard? Figure 5 illustrates the stratospheric offsets from the SHADOZ climatology (as in Figure 4) along with deviations between the corresponding chamber instrument and the JOSIE OPM (see Appendix A). The latter deviations are based on the individual investigators' PCF.

[31] Comparisons in Figure 5 are given for three instrument types: NOAA/CMDL method (Samoa, Fiji, San Cristóbal,

Figure 5a); NASA/WFF method with Natal and Ascension (Figure 5b); the Meteoswiss method with Nairobi (Figure 5c). In each panel of Figure 5 two JOSIE-2000 simulations are displayed as deviations of the sonde from the OPM standard. For Figure 5a, simulations of two different instrument types with the NOAA/CMDL method are shown. They are low (up to 50%) compared to the OPM at 100 hPa; however, at pressures < 60 hPa, agreement improves to within 20% of the standard. For the NASA/WFF (Figure 5b) and Meteoswiss (Figure 5c) methods, JOSIE-2000 shows an underestimate of O_3 relative to the OPM in the 100–60 hPa range, though of less magnitude (10–20% deviation) than the NOAA/CMDL method. Deviations of NASA/WFF JOSIE and SHADOZ Natal sondes are 5% or less above 40 hPa (Figure 5b).

[32] In Figure 5 the low- O_3 bias in all cases in the 100–60 hPa region in the JOSIE-2000 tests partially reflects the very low absolute O_3 amount at 100 hPa in the simulated profile. The sonde responses, determined in preexperiment tests (or prelaunch, in the field), are typically 22–35 s, whereas the photometer senses an O_3 change within a second. In the chamber simulation, the O_3 partial pressure was nearly zero from 180 to 100 hPa. Above 100 hPa, O_3 increases but the sondes do not respond as quickly as the photometer. As O_3 further increases with declining pressure, the percentage lag is less; agreement with OPM improves.

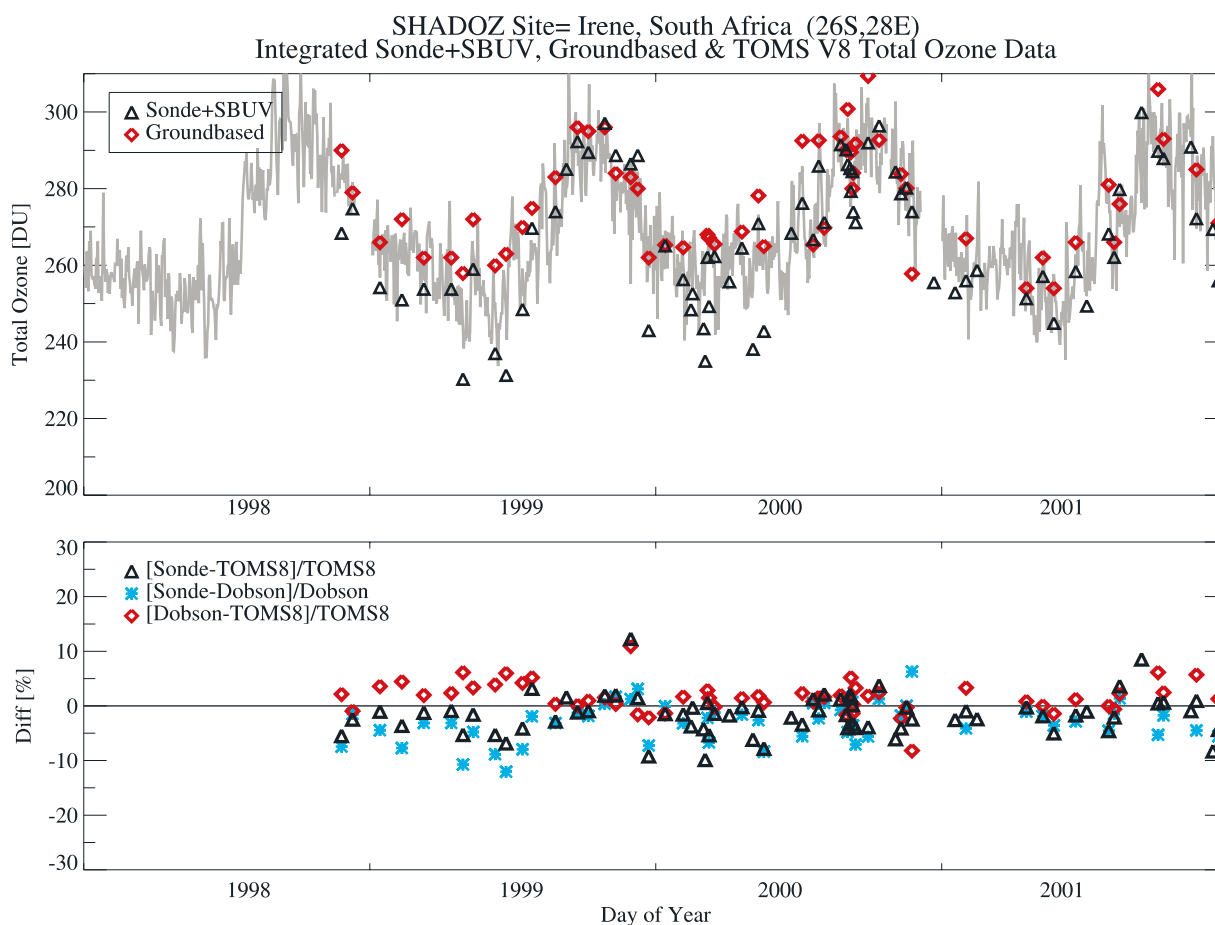


Figure 7c. Same as Figure 7a except for Irene, South Africa.

[33] The impact of buffering may be significant in the upper stratospheric portion of the O_3 profile (40–10 hPa in Figure 5) where the O_3 maximum occurs (Figure A1). However, this influence is more difficult to gauge because PCFs are included in both the JOSIE-2000 and SHADOZ data. In the case of the NOAA/CMDL method (Figure 5a) one JOSIE-2000 test shows a slight positive bias above 20 hPa but the SHADOZ data are slightly low compared to the tropical climatology. Fiji, Samoa, San Cristóbal O_3 deviations (Figure 5a) average $\sim 20\%$ lower than O_3 at Nairobi above 20 hPa (Figure 5c) and 5–10% lower than Natal (Figure 5b). This can be explained largely by the combination of instrument type and sensing solution used in the Pacific sondes (Table 3).

[34] The Meteoswiss JOSIE-2000 results and SHADOZ Nairobi sonde deviations (Figure 5c) generally follow one another. The Nairobi sondes are higher than the SHADOZ climatology throughout the stratosphere. The JOSIE-2000 tests showed a mostly positive bias for the Meteoswiss method above 65 hPa (Figure A1, top left). The Meteoswiss and NASA/WFF results appear to illustrate a difference in instrument type. The JOSIE readings shown in Figures 5b and 5c were taken during the same chamber simulations (Nos. 98 and 99) with identically prepared sensing solution. Relative to the OPM, the raw signal recorded with the Meteoswiss ENSCI-Z instruments measured 5–10% more O_3 throughout the simulated stratosphere than NASA/WFF

with SPC (Table 3). This is equivalent to an integrated O_3 difference of ~ 20 DU, similar to the high bias depicted for Nairobi in Figure 5c. These contrasts resemble those of the Nairobi sondes relative to the SHADOZ tropical climatology and to the Natal and Ascension offsets above ~ 85 hPa (compare Figures 5b and 5c). The tendency for the ENSCI-Z instrument to record 5–7% more total O_3 from 100 to 10 hPa than the SPC when the same solution composition and processing are employed, was a major finding of JOSIE-1998 and JOSIE-2000 (Table 3 and Figure A1) [Smit and Sträter, 2004a, 2004b; Smit et al., submitted manuscript, 2006]. The same behavior is observed when ENSCI-Z and SPC instruments prepared identically are launched on one balloon [Johnson et al., 2002; F. J. Schmidlin, personal communication, 2003]. The high ENSCI-Z bias may explain why Watukosek is higher in the upper stratosphere than similarly prepared sondes at the three Pacific stations where the SPC instrument is used (Figure 2a).

4. Column Ozone Comparisons: Total Ozone, Stratospheric Ozone, and Station Variability

[35] Thompson et al. [2003a] compared column-integrated O_3 amounts. First, stratospheric column amounts from 1998–2000 data were evaluated to see whether or not there were significant differences as a function of longitude.

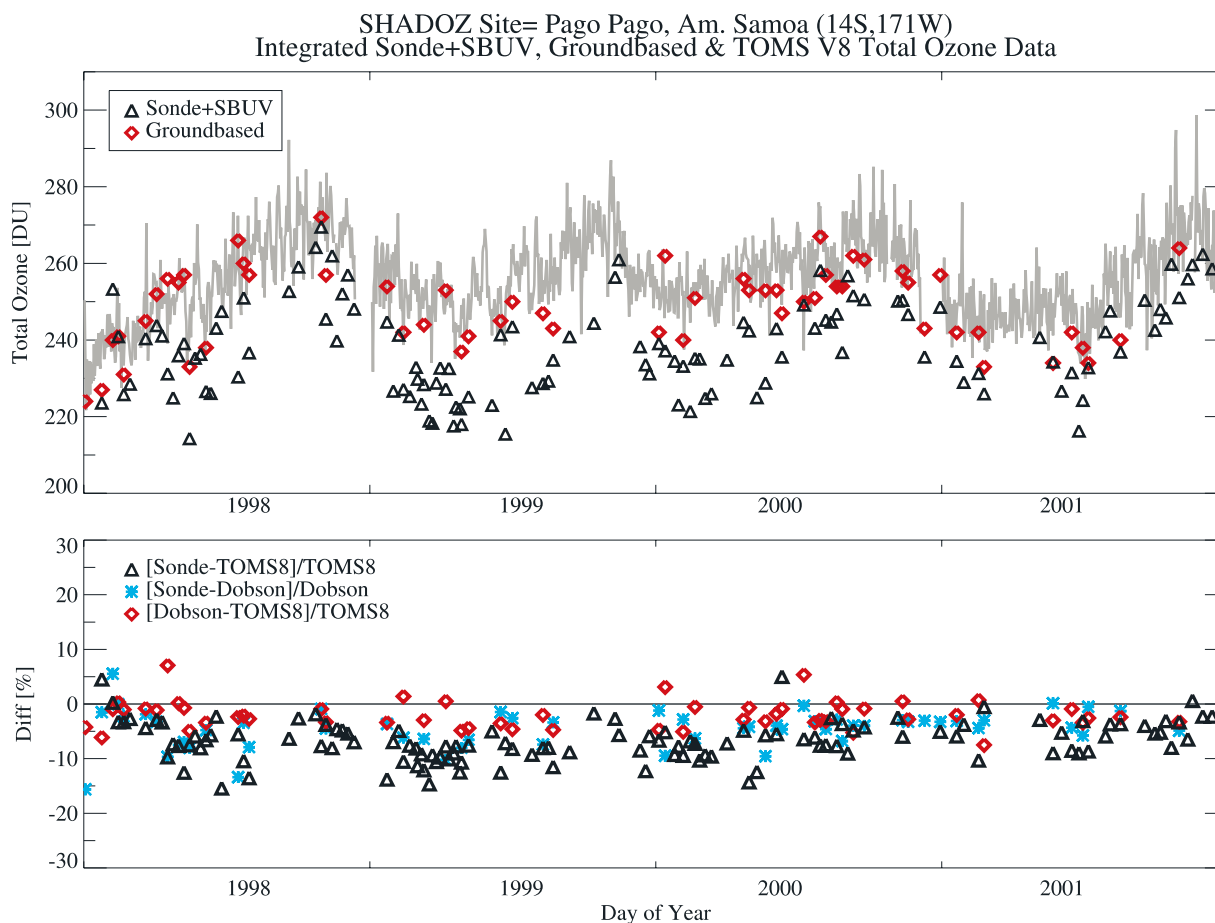


Figure 7d. Same as Figure 7a except for American Samoa.

Thompson *et al.* [2003a, Figures 10–12] are updated in section 4.1. Second, comparisons among ground-based total O_3 instrumentation, integrated O_3 from the sondes and satellite overpasses are made for a check on accuracy (section 4.2).

4.1. Stratospheric Ozone Comparisons From SHADOZ Sondes

[36] We also examined the integrated stratospheric O_3 column to see whether some of the SHADOZ station variability is due to stratospheric O_3 variability. These analyses are performed with the 1998–2004 sondes in three ways, as illustrated in Figures 6a–6c. The total integrated stratospheric O_3 column in Figure 6a includes the measured O_3 column to 10 hPa (column 5 in Table 4). Figure 6a, which presents the total integrated stratospheric O_3 column ($\pm 1\sigma$), shows all the stations overlapping except for divergence of Samoa and San Cristóbal (small σ) from Paramaribo (highest at 184 DU). All other SHADOZ stations are within the range 156–177 DU. Thompson *et al.* [2003a] concluded that the SHADOZ record does not show a statistically significant stratospheric wave-one pattern. Additional data in the present analysis compared to Thompson *et al.* [2003a] leads to the same conclusion.

[37] Two diagnostics are used to look more closely at stratospheric variability: the 15–20 km integral (~ 110 –60 hPa) and the CMR extrapolation. Figure 6b, depicting

the lower stratospheric integrated O_3 column, shows no statistically significant variation among the SHADOZ stations (similar to Thompson *et al.* [2003a]). At Irene, the standard deviation is relatively high; roughly half the record comes from midlatitude conditions. Not counting Irene, the mean 15–20 km O_3 column are within a 5 DU range. The 15–20 km O_3 column uniformity is further evidence for the lack of a stratospheric wave because zonal variation is expected in the lower stratosphere [Shiotani and Hasebe, 1994; Newchurch *et al.*, 2001].

[38] The CMR is used to diagnose the relative behavior of the upper stratosphere which is not expected to vary among the Southern Hemisphere SHADOZ sites. In Figure 6c, raw CMR values are not displayed but rather their deviation from the SBUV add-on (last column in Table 4). Variations in the CMR-SBUV parameter may reflect the effect of the sensing solution, the instrument used or data processing (primarily the PCF employed by each station coinvestigator). Here, in contrast to the lower stratosphere bias (Figure 6b), the range across the SHADOZ stations exceeds 10 DU. The Atlantic stations (Paramaribo–Natal–Ascension) are relatively high whereas for total stratospheric O_3 , Ascension is relatively low (Figure 6a). Irene is lowest in normalized CMR. Can the precision of the stratospheric quantities be estimated using the CMR normalized statistics? The Natal–Ascension pair and Fiji–Samoa–San Cristóbal (similar method) are only 6–7 DU apart. Nairobi

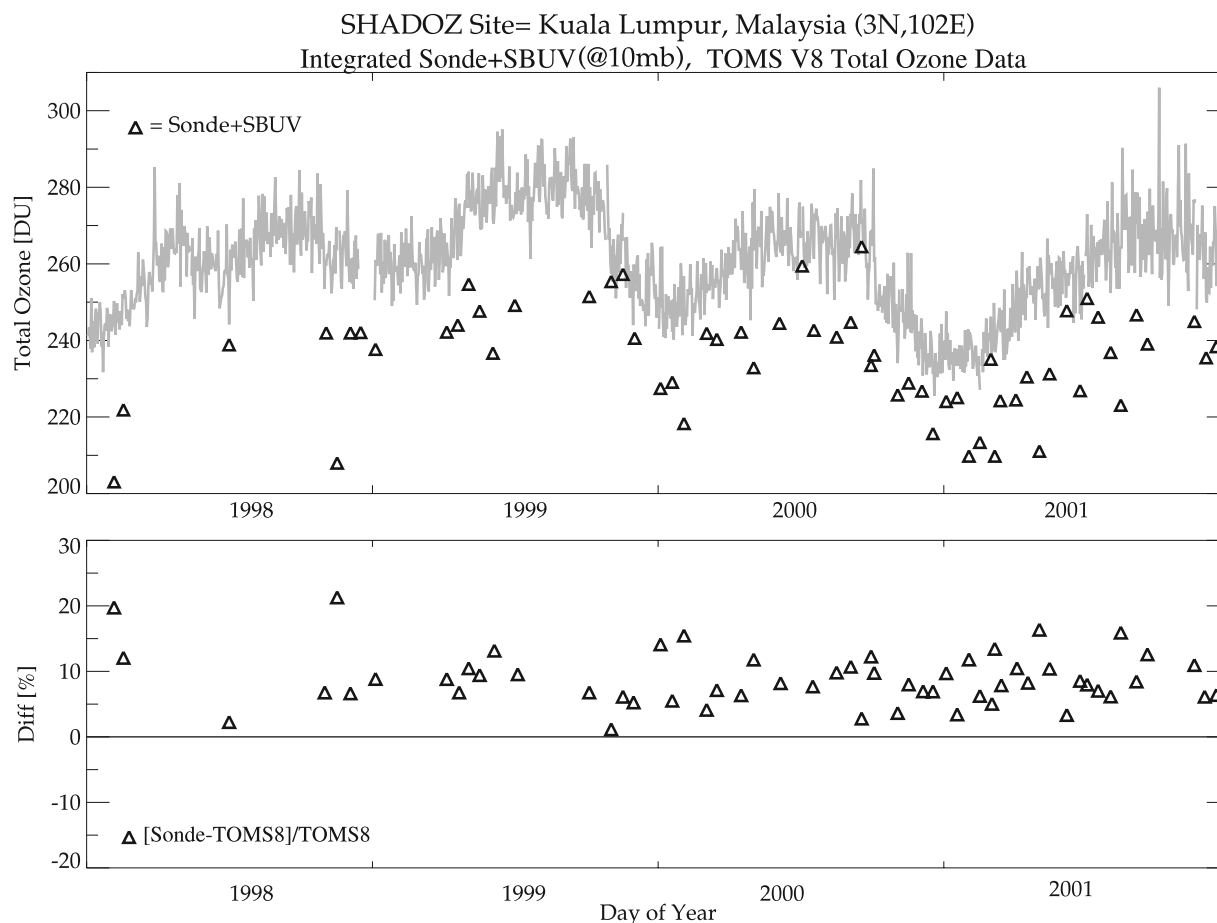


Figure 7e. Same as Figure 7a except for Kuala Lumpur, Malaysia.

and Malindi, stations ~ 400 km apart, are within 2 DU of one another in all three stratospheric analyses shown in Figure 6.

4.2. Total Ozone Comparisons With TOMS Version 8

[39] Figures 7a, 7b, 7c, 7d, and 7e shows daily TOMS overpass data (v 8 processing, 2004 release) for 1998 through 2001 for five stations, together with total O_3 integrated from the sonde (as described in section 2). Comparison of TOMS, sonde-integrated O_3 and a ground-based Dobson instrument is shown for four sites where the spectrophotometers are regularly calibrated. In Figures 7a–7e (bottom), offsets among sonde, TOMS, and the ground-based instrument are shown. Total O_3 comparisons similar to those in Figures 7a–7e were depicted by *Thompson et al.* [2003a] using TOMS v 7 O_3 .

[40] The O_3 column measurement from the sondes in Figure 7a (Natal) is $>5\%$ lower in 1998–1999 compared to 2000 onward. From 1997 to 1999 a change in the solution composition recommended by the ENSCI-Z manufacturer (0.5% KI compared to 1%) was employed even when the SPC sonde was flown. This is consistent with results of the JOSIE tests. During JOSIE-2000 it was shown that when the same instrument type and data processing are used, the 0.5% KI solution gives an averaged 5% lower O_3 throughout the profile than does the 1% KI solution (Smit et al., submitted manuscript, 2006). In addition to known changes in the sonde technique at Natal, there is evidence in both the

colocated Dobson and Brewer instruments (latter not shown) that TOMS O_3 declined and became more variable in 2001 compared to the prior four years. Similar behavior among Brewer, Dobson and TOMS O_3 was noted at Cachoeira Paulista, Brazil (23S, 38W (V. W. J. H. Kirchhoff and N. Paes Leme, unpublished manuscript, 2004)).

[41] The African stations are those with the closest agreement between TOMS and the sonde total O_3 column (Figures 7b and 7c). This holds throughout the SHADOZ record, although the Dobson at Irene seems noisier in 1998 than later on. Both the Nairobi and Irene Dobson instruments were calibrated with the traveling world standard Dobson in April 2000. Data from the Nairobi Dobson were not available from that time until operations resumed in 2005. In *Thompson et al.* [2003a] it was noted that Irene and Nairobi are the two SHADOZ stations with elevation >1 km. This possibly implied better agreement at sites with less tropospheric air mass because TOMS is not very sensitive below 500 hPa [*Hudson et al.*, 1995]. However, *Thompson et al.* [2003a, Figures 10–12] also found that much of the disagreement between TOMS total O_3 and the sonde integral originates in the stratospheric profile. With Figure 8 showing similar TOMS-sonde offsets at Malindi (sea level) and Nairobi (1.3 km altitude, 400 km from Malindi), there is further evidence that tropospheric discrepancies do not dominate sonde-satellite differences.

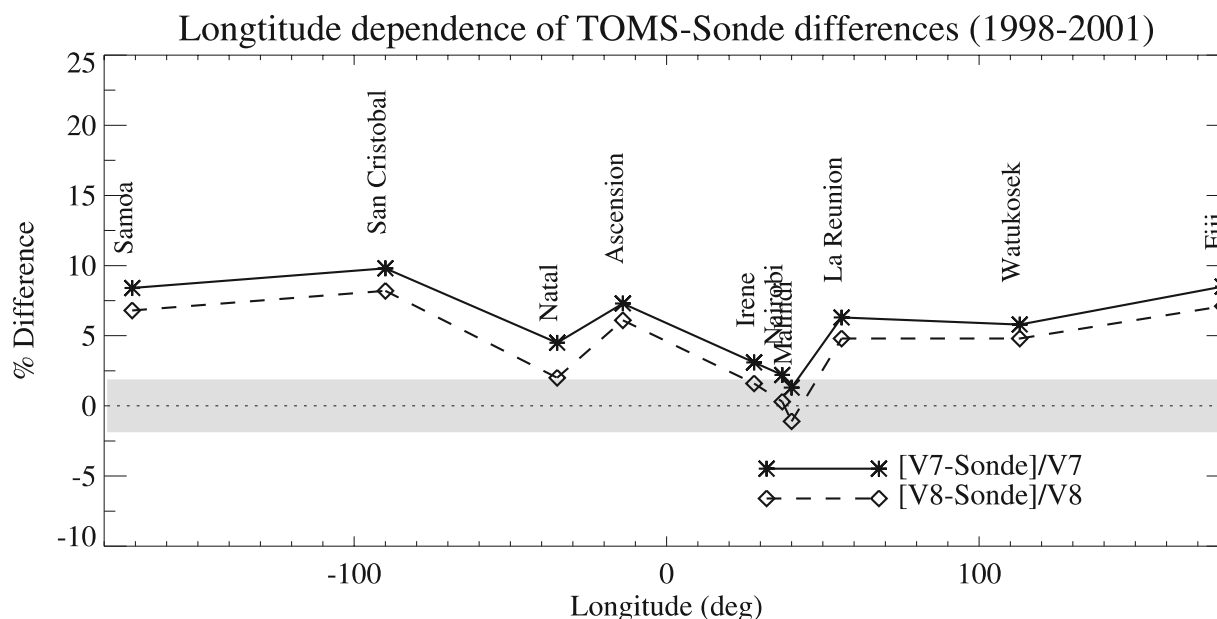


Figure 8. Summary of averaged differences between total O_3 from SHADOZ sondes and from TOMS (v 7 [cf. Thompson *et al.*, 2003a, Figure 9]) and sondes and TOMS v 8. Data to 10 hPa (Table 4) with SBUV extrapolation are used for sonde total ozone. Shaded region corresponds to “best total ozone” based on Dobsons and most recent TOMS calibration.

[42] At Samoa (Figure 7d) TOMS total O_3 appears to be declining relative to the sonde measurement, although the early 1998 sonde data are too noisy to be definitive in this respect. There is less drift in TOMS compared to the Dobson. The tendency for the TOMS O_3 column to exceed that of the Dobson by overestimating tropospheric O_3 in the satellite algorithm [Thompson *et al.*, 2003b, Figure 4c], appears unchanged in the transition from v 7 to v 8. At Kuala Lumpur (Figure 7e) sonde total O_3 is less than the TOMS v 8 measurement, similar to the Pacific stations and Watukosek.

[43] In Figure 8, where the TOMS-sonde total O_3 differences are displayed for v 7 and v 8 TOMS, there is a tendency for the Pacific SHADOZ stations and Watukosek to be biased lower relative to TOMS than the Atlantic and African stations. One reason for this is that the TOMS algorithm (both versions 7 and 8) assumes a greater tropospheric O_3 column depth (29.8 DU [Thompson *et al.*, 2003b, Table 4]) than actually measured at the Pacific stations (mean tropospheric column depth, ~ 19 DU). There is only a 1–2 percentage point change to the TOMS-normalized data at the SHADOZ stations (Table 4) using v 8 compared to v 7. However, agreement between the Southern Hemisphere Dobson stations and TOMS v 8, spanned within the shading in Figure 8, improved over v 7 (compare offsets given by Bodeker *et al.* [2001]).

[44] Instrument effects, as revealed in JOSIE-2000 (Appendix A), are also a factor that may suppress total O_3 readings at the Pacific stations relative to other O_3 measurements. For example, Table 3 shows that the combination of the SPC sonde with 2% KI (SST-3) with NOAA PCF leads to a column O_3 integral $\sim 5\%$ lower than the O_3 reference in JOSIE-2000. A parallel can be made between the JOSIE instrument performance relative to the OPM and the

corresponding SHADOZ O_3 column relative to the “best” O_3 range (shading in Figure 8). This would imply that the values for the three Pacific stations are $\sim 5\%$ too low and that a more appropriate comparison would relocate the stars (for v 7) and diamonds (for v 8) closer to the shaded best. Likewise, the JOSIE-2000 evaluation for the technique used at Nairobi (ENSCI-Z with SST-1, K86 PCF) may register several percent too high in column O_3 .

5. Summary

[45] Issues about SHADOZ ozonesonde accuracy and precision raised in our previous study [Thompson *et al.*, 2003a] have been addressed with the results of chamber tests, additional sonde data, and a new release of TOMS total O_3 (v 8). Ozone profiles are examined to see where variations from a tropical mean are large (presumed to be geophysical) and small (possibly instrumental). Tropospheric variations are real, exceeding 50% relative to the mean at Pacific stations and Watukosek. However, within the stratosphere, deviations are usually $<10\%$ for all SHADOZ sites. JOSIE-2000 chamber tests are used in considering whether stratospheric biases might be explained by sonde instrument and technique. We conclude the following:

[46] 1. The high- O_3 bias at Nairobi results from a combination of the instrument type and sensing solution employed by the Meteoswiss-Kenya Meteorological Department experimental team. Above the 20-km mark in the JOSIE chamber, the Meteoswiss (ENSCI) instrument read 5–10% higher than the NASA/WFF instrument (SPC) that used the same solution type. Similar contrasts occur in normalized Nairobi and Ascension/Natal O_3 profiles.

[47] 2. The impact of sensing solution composition on SHADOZ station variability is harder to assess because PCF

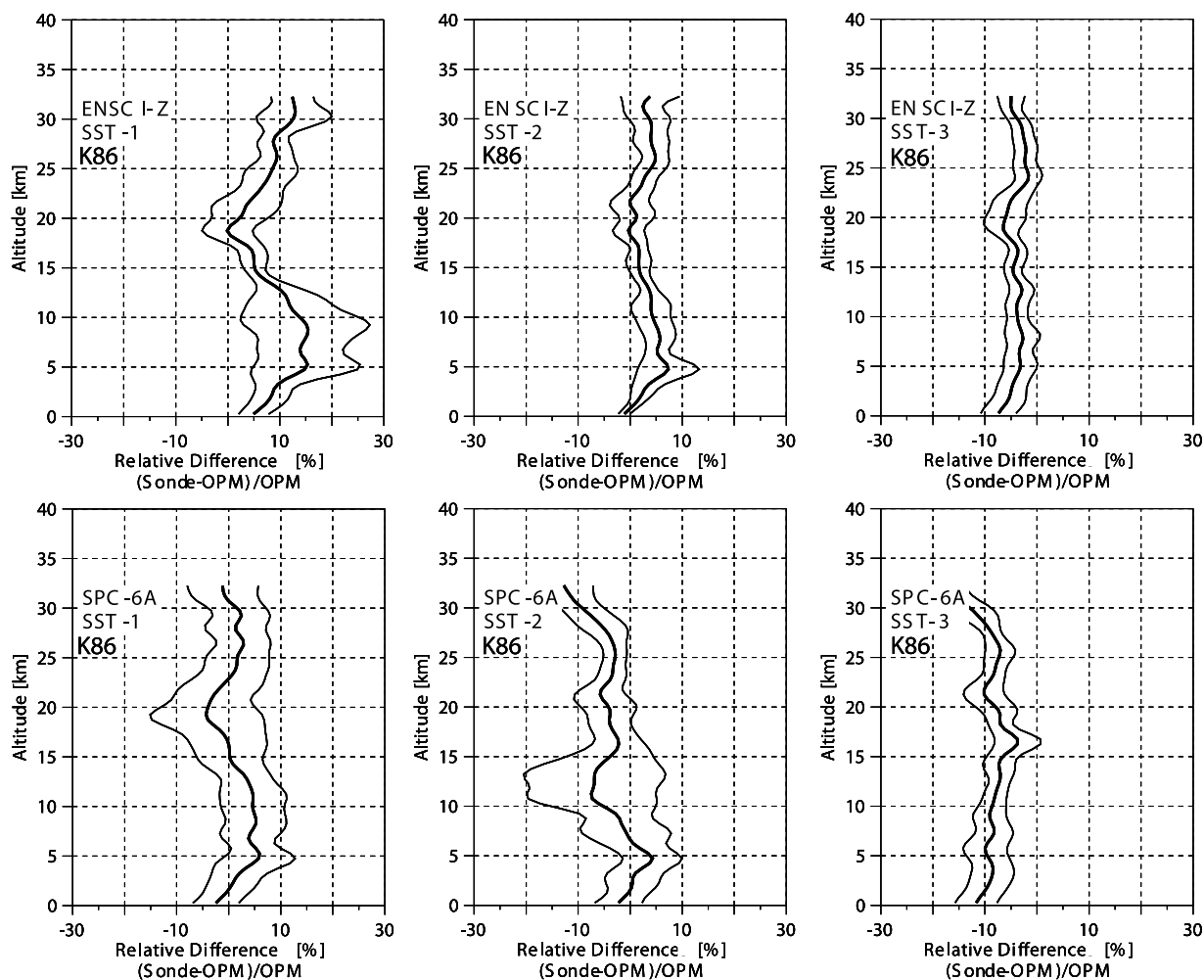


Figure A1. JOSIE 2000 comparison of (top) ENSCI-Z and (bottom) SPC-6A versus UV-photometer for sensing solution type SST-1, SST-2 and SST-3, respectively. Averages ($\pm 1\sigma$) of the relative deviations of the individual sonde data from the UV-photometer for each ensemble of sonde type and sensing solution type are shown. All data are processed using the PCF of Komhyr [1986].

are included in the archived data. JOSIE-2000 results show artifacts associated with buffered solutions (SST-1 and SST-2 here), especially in the lowest O_3 segments (~ 100 hPa). At Fiji, Samoa and San Cristóbal, where unbuffered solutions are used, upper stratospheric O_3 profiles are lower than the SHADOZ-defined climatology. At five SHADOZ sites, comparisons are made among O_3 from the sondes, TOMS and ground-based instruments that measure total O_3 . The results are summarized:

[48] 3. Comparison of total O_3 from the SHADOZ sondes and v 8 TOMS shows that, on average, the satellite records greater O_3 column amount than the sondes. These results are similar to sonde and v 7 TOMS comparisons [Thompson *et al.*, 2003a] except for a 1–2% improvement in agreement between sonde O_3 and v 8 due to recalibration of TOMS.

[49] 4. As with v 7, the poorest agreement between TOMS v 8 and the sondes occurs at Pacific stations with the lowest tropospheric column O_3 . Higher TOMS than Dobson at Samoa implicates a TOMS algorithm overestimate of total O_3 under these conditions. TOMS v 8 does not account for longitudinal variability in equatorial O_3 (see the Algorithm Basis Document at <http://toms.gsfc.nasa.gov>).

[50] 5. Agreement of sonde total O_3 for selected SHADOZ stations with the “best O_3 ” deduced from TOMS and ground-based instruments can be interpreted in analogy with the JOSIE performance of the station method relative to the JOSIE standard. The three Pacific stations would be in $\sim 5\%$ better agreement with the satellite if the instrument type and technique were taken into account. Nairobi disagreement would increase a few percent.

[51] Using the 1998–2004 sonde data, we reexamined stratospheric column amounts. Omitting Irene (too midlatitude), Kuala Lumpur and Paramaribo (north of the Inter-tropical Convergence Zone), the stratospheric O_3 column over all SHADOZ stations shows uniformity (to ± 8 DU) and absence of a longitudinal wave-one. This is similar to Thompson *et al.* [2003a]. The absence of a wave-one is reinforced by noting the uniformity of the lower stratospheric column O_3 amount.

[52] Because WMO uses SHADOZ as a model for new stations in the Global Atmospheric Watch (GAW) program, it is important to understand instrument influences on the O_3 profiles at individual SHADOZ stations. SHADOZ statistics represent hundreds of balloon flights at some stations, taken

under varying atmospheric conditions where factors reflecting technical variations are difficult to unravel. JOSIE represents a limited number of simulations in a controlled environment where aspects of the O₃ measurement can be assessed separately. The two approaches offer a consistent view, with sonde behavior in SHADOZ reproduced fairly well in JOSIE. Ozone sonde instrument performance is being further evaluated with results from an April 2004 balloon intercomparison called BESOS (Balloon Experiment for Standards of Ozonesondes; <http://croc.gsfc.nasa.gov/besos>). As in JOSIE-2000, BESOS featured a standard ozone photometer through which a set of sondes flown on the same gondola are intercompared [cf. Hilsenrath *et al.*, 1986].

Appendix A: JOSIE-2000 Background

[53] The environmental simulation facility operated at Forschungszentrum Jülich (FZJ) is established as the World Calibration Centre for Ozone Sondes [Smit *et al.*, 2000] (<http://www.fz-juelich.de/icg/icg-ii/esf>) as part of the quality assurance plan for ozonesondes deployed in WMO's GAW Program. The facility enables the control of pressure, temperature and O₃ concentration under simulated flight conditions up to an altitude of 35 km. A high-performance UV-photometer serves as a reference system. Within the framework of WMO's quality assurance plan, a series of JOSIE chamber tests was conducted at FZJ in 1996, 1998, and 2000 to assess the performance of ozonesondes (<http://www.fz-juelich.de/icg/icg-ii/josie/>). JOSIE-2000 brought together scientists participating in seven ECC sounding stations within the GAW network. Five of the representatives covered operating methods used at all the SHADOZ stations. In JOSIE-2000, two ECC types were operated: the SPC-6A and ENSCI-Z instruments with three different sensing solution types (SSTs): (1) SST-1, 1% KI, with full buffer; (2) SST-2, 0.5% KI with half buffer; and (3) SST-3, with 2% KI, no buffer. The participating laboratories worked in two groups, as displayed in Table 2. Complete details of JOSIE-2000 are given by Smit and Sträter [2004b] and by Smit *et al.* (submitted manuscript, 2006).

[54] For each combination of ECC-sonde type (SPC-6A and ENSCI-Z) and SST (SST-1, SST-2, and SST-3) a total of six simulation experiments was performed, using different prototype profiles (two each midlatitude, subtropical and tropical). All sonde data were processed according to the guidelines of Komhyr [1986]; thorough discussion appears in the works by Smit and Sträter [2004b] and Smit *et al.* (submitted manuscript, 2006). A summary of the profile results appears in Figure A1. The experiments showed that the characteristics of the two ECC sonde types are not always the same, even when operated under the same conditions. Significant differences occur above 20 km where the ENSCI-Z sonde tends to measure 5–10% more O₃ than the SPC-6A sonde (Table 3). Below 20 km the differences are 5% or less, but earlier JOSIE tests [Smit and Sträter, 2004a] demonstrated that instrument performance can vary from one manufacturer batch to another. There is also significant difference in O₃ readings when sondes of the same type are operated with different SSTs. For each ECC-type the use of 1% KI (SST-1 in Figure A1) gives 5% larger O₃ values compared to the 0.5% KI (SST-2), and up

to 10% larger values compared to 2% KI (SST-3). In practice, this means a change of SST or ECC sonde type can cause a change of $\pm 5\%$ or more in the sounding record of a given station. The offset between instrument types is fairly consistent throughout troposphere and lower/middle stratosphere.

[55] **Acknowledgments.** SHADOZ has been supported by NASA's Atmospheric Chemistry Modeling and Analysis (ACMAP) and Upper Atmosphere Research (UARP) programs and the TOMS, OMI, and Aura projects. Individual SHADOZ sites are supported by in-country agencies and universities: NOAA, JAXA (Japanese Agency for Exploration of the Atmosphere), LAPAN (Lembaga Penerbangan Rangan Dan Antariksa Nasional, the National Institute of Aeronautics and Space Agency of Indonesia), INPE (Instituto Nacional de Pesquisas Espaciais, the National Space Agency of Brazil), the South African Weather Service, KNMI (Royal Netherlands Meteorological Institute), the Meteorological Service of Surinam, the Malaysian Meteorological Department, the Swiss Meteorological Agency, the Kenyan Meteorological Department, the University of the South Pacific (Suva, Fiji), and the University of Réunion (France). We appreciate the opportunity to participate in JOSIE-2000 and WMO workshops on ozone instrumentation sponsored by M. Proffitt.

References

- Bodeker, G. E., J. C. Scott, K. Kreher, and R. L. McKenzie (2001), Global ozone trends in potential vorticity coordinates using TOMS and GOME intercompared against the Dobson network: 1978–1998, *J. Geophys. Res.*, **106**, 23,029–23,042.
- Boyd, I. S., G. E. Bodeker, B. J. Connor, D. P. J. Swart, and E. J. Brinksma (1998), An assessment of ECC ozone sondes operated using 1% and 0.5% KI cathode solutions at Lauder, New Zealand, *Geophys. Res. Lett.*, **25**, 2409–2412.
- Chatfield, R. B., H. Guan, A. M. Thompson, and J. C. Witte (2004), Convective lofting links Indian Ocean air pollution to paradoxical south Atlantic ozone maxima, *Geophys. Res. Lett.*, **31**, L06103, doi:10.1029/2003GL018866.
- Edwards, D. P., *et al.* (2003), Tropospheric ozone over the tropical Atlantic: A satellite perspective, *J. Geophys. Res.*, **108**(D8), 4237, doi:10.1029/2002JD002927.
- Fishman, J., and A. Balok (1999), Calculation of daily tropospheric ozone residuals using TOMS and empirically improved SBUV measurements: Application to an ozone pollution episode over the eastern United States, *J. Geophys. Res.*, **104**, 30,319–30,340.
- Fishman, J., and J. C. Larsen (1987), Distribution of total ozone and stratospheric ozone in the tropics: Implications for the distribution of tropospheric ozone, *J. Geophys. Res.*, **92**, 6627–6634.
- Hilsenrath, E., *et al.* (1986), Results from the Balloon Ozone Intercomparison Campaign (BOIC), *J. Geophys. Res.*, **91**, 13,137–13,152.
- Hudson, R. D., J. Kim, and A. M. Thompson (1995), On the derivation of tropospheric column ozone from radiances measured by the Total Ozone Mapping Spectrometer, *J. Geophys. Res.*, **100**, 11,138–11,145.
- Jenkins, G. S., J.-H. Ryu, A. M. Thompson, and J. C. Witte (2003), Linking horizontal and vertical transports of biomass fire emissions to the Tropical Atlantic Ozone Paradox during the Northern Hemisphere winter season: 1999, *J. Geophys. Res.*, **108**(D23), 4745, doi:10.1029/2002JD003297.
- Johnson, B. J., S. J. Oltmans, H. Vömel, T. Deshler, C. Kroger, and H. G. J. Smit (2002), ECC ozonesonde pump efficiency measurements and sensitivity tests of buffered and unbuffered sensor solutions, *J. Geophys. Res.*, **107**(D19), 4393, doi:10.1029/2001JD000557.
- Komhyr, W. D. (1969), Electrochemical concentration cells for gas analysis, *Ann. Geophys.*, **25**, 203–210.
- Komhyr, W. D. (1986), Operations handbook—Ozone measurements to 40 km altitude with model 4A-ECC-ozone sondes, *NOAA Tech. Memo. ERL-ARL-149*.
- Komhyr, W. D., R. A. Barnes, G. B. Brothers, J. A. Lathrop, and D. P. Opperman (1995), Electrochemical concentration cell ozonesonde performance during STOIC, *J. Geophys. Res.*, **100**, 9231–9244.
- Liu, X., K. Chance, C. E. Sioris, R. J. D. Spurr, T. P. Kurosu, R. V. Martin, and M. J. Newchurch (2005), Ozone profile and tropospheric ozone retrievals from the Global Ozone Monitoring Experiment: Algorithm description and validation, *J. Geophys. Res.*, **110**, D20307, doi:10.1029/2005JD006240.
- Logan, J. A. (1994), Trends in the vertical distribution of ozone: An analysis of ozone sonde data, *J. Geophys. Res.*, **99**, 25,553–25,585.
- Logan, J. A., and V. W. J. H. Kirchhoff (1986), Seasonal variations of tropospheric ozone at Natal, Brazil, *J. Geophys. Res.*, **91**, 7875–7881.

- Logan, J. A., D. B. A. Jones, I. A. Megretskaya, S. J. Oltmans, B. J. Johnson, H. Vömel, W. J. Randel, W. Kimani, and F. J. Schmidlin (2003), Quasi-biennial oscillation in tropical ozone as revealed by ozone-sonde and satellite data, *J. Geophys. Res.*, **108**(D8), 4244, doi:10.1029/2002JD002170.
- 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.
- McPeters, R. D., G. J. Labow, and B. J. Johnson (1997), A satellite-derived ozone climatology for balloonsonde estimation of total column ozone, *J. Geophys. Res.*, **102**, 8875–8885.
- Newchurch, M. J., D. Sun, and J.-J. Kim (2001), Zonal wave-1 structure in TOMS tropical stratospheric ozone, *Geophys. Res. Lett.*, **28**, 3151–3154.
- Sauvage, B., V. Thouret, A. M. Thompson, J. C. Witte, J.-P. Cammas, P. Nédélec, 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.
- Shiotani, M. (1992), Annual, quasi-biennial and El Niño–Southern Oscillation (ENSO) time-scale variations in Equatorial total ozone, *J. Geophys. Res.*, **97**, 7625–7634.
- Shiotani, M., and F. Hasebe (1994), Stratospheric ozone variations in the equatorial region as seen in Stratospheric Aerosol and Gas Experiment data, *J. Geophys. Res.*, **99**, 14,575–14,584.
- Smit, H. G. J., and D. Kley (1998), JOSIE-1998: Jülich Ozone Sonde Intercomparison Experiment (JOSIE), *Global Atmos. Watch Rep. Ser.*, **130**, Tech. Doc. TD926, Global Ozone Res. and Monit. Proj., World Meteorol. Organ., Geneva, Switzerland.
- Smit, H. G. J., and W. Sträter (2004a), JOSIE-1998: Performance of ECC ozone sondes of SPC-6A and ENSCI-A type, *WMO Global Atmos. Watch Report Ser.*, **157**, Tech. Doc. 1218, World Meteorol. Organ., Geneva, Switzerland.
- Smit, H. G. J., and W. Sträter (2004b), JOSIE-2000: The 2000 WMO international intercomparison of operating procedures for ECC-sondes at the environmental simulation facility at Jülich, *Global Atmos. Watch Rep. Ser.*, **158**, Tech. Doc. 1225, World Meteorol. Organ., Geneva, Switzerland.
- Smit, H. G. J., W. Sträter, M. Helten, and D. Kley (2000), Environmental simulation facility to calibrate airborne ozone and humidity sensors, *Jülich Ber.* 3796, Forschungszent. Jülich, Jülich, Germany.
- Thompson, A. M., and R. D. Hudson (1999), Tropical tropospheric ozone (TTO) maps from Nimbus 7 and Earth-Probe TOMS by the modified-residual method: Evaluation with sondes, ENSO signals and trends from Atlantic regional time series, *J. Geophys. Res.*, **104**, 26,961–26,975.
- Thompson, A. M., B. G. Doddridge, J. C. Witte, R. D. Hudson, W. T. Luke, J. E. Johnson, B. J. Johnson, S. J. Oltmans, and R. Weller (2000), A tropical Atlantic ozone paradox: Shipboard and satellite views of a tropospheric ozone maximum and wave-one in January–February 1999, *Geophys. Res. Lett.*, **27**, 3317–3320.
- Thompson, A. M., et al. (2003a), Southern Hemisphere Additional Ozone-sondes (SHADOZ) 1998–2000 tropical ozone climatology: 1. Comparison with 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 ozone variability and the zonal wave-one, *J. Geophys. Res.*, **108**(D2), 8241, doi:10.1029/2002JD002241.
- Torres, A. L. (1981), ECC ozonesonde performance at high altitude: Pump efficiency, *NASA Tech. Memo.* 73290, 10 pp.
- World Meteorological Organization (1998), WMO/SPARC/IOC/GAW assessment of trends in the vertical distribution of ozone, edited by N. Harris, R. Hudson, and C. Phillips, *SPARC Rep. 1, Rep. 43*, Global Ozone Res. and Monitoring. Proj., Geneva, Switzerland.
- Ziemke, J. R., S. Chandra, and P. K. Bhartia (1998), Two new methods for deriving tropospheric column ozone from TOMS measurements: The assimilated UARS MLS/HALOE and convective-cloud differential techniques, *J. Geophys. Res.*, **103**, 22,115–22,128.
- Ziemke, J. R., S. Chandra, and P. K. Bhartia (2003), Upper tropospheric ozone derived from the cloud slicing technique: Implications for large-scale convection, *J. Geophys. Res.*, **108**(D13), 4390, doi:10.1029/2002JD002919.

B. J. Johnson and S. J. Oltmans, Global Monitoring Division, NOAA, 325 Broadway, Boulder, CO 80305, USA. (bryan.johnson@noaa.gov; samuel.j.oltmans@noaa.gov)

V. W. J. H. Kirchhoff, Laboratório De Ozônio/INPE-CP 515, Instituto Nacional de Pesquisas Espaciais, Av. Astronautas 1758, São José dos Campos, São Paulo 12201-970, Brazil. (kir@dge.inpe.br)

F. J. Schmidlin, NASA Wallops Flight Facility, Code 614.6, Wallops Island, VA 23337, USA. (fjs@osb1.wff.gsfc.gov)

H. G. J. Smit, Research Centre Jülich, Institute for Chemistry and Dynamics of the Geosphere: Troposphere, P.O. Box 1913, D-52425 Jülich, Germany. (h.smit@fz-juelich.de)

A. M. Thompson, Department of Meteorology, Pennsylvania State University, 503 Walker Building, University Park, PA 16802-5013, USA. (anne@met.psu.edu)

J. C. Witte, Science Systems and Applications, Inc., Lanham, MD 20706, USA. (witte@gavial.gsfc.nasa.gov)