First Reprocessing of Southern Hemisphere ADDitional OZonesondes Profile Records: 3. Uncertainty in Ozone Profile and Total Column

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Abstract Reprocessed ozoneonde data from eight SHADOZ (Southern Hemisphere ADDitional OZonesondes) sites have been used to derive the first analysis of uncertainty estimates for both profile and total column ozone (TCO). The ozone uncertainty is a composite of the uncertainties of the individual terms in the ozone partial pressure ($P_{O3}$) equation, those being the ozone sensor current, background current, internal pump temperature, pump efficiency factors, conversion efficiency, and flow rate. Overall, $P_{O3}$ uncertainties ($\Delta P_{O3}$) are within 15% and peak around the tropopause (15 ± 3 km) where ozone is a minimum and $\Delta P_{O3}$ approaches the measured signal. The uncertainty in the background and sensor currents dominates the overall $\Delta P_{O3}$ in the troposphere including the tropopause region, while the uncertainties in the conversion efficiency and flow rate dominate in the stratosphere. Seasonally, $\Delta P_{O3}$ is generally a maximum in the March–May, with the exception of SHADOZ sites in Asia, for which the highest $\Delta P_{O3}$ occurs in September–February. As a first approach, we calculate sonde TCO uncertainty ($\Delta$TCO) by integrating the profile $\Delta P_{O3}$ and adding the ozone residual uncertainty, derived from the McPeters and Labow (2012, doi:10.1029/2011JD017006) TCO on the order of 10 DU that represents ~5–6% of the TCO. Total Ozone Mapping Spectrometer and Ozone Monitoring Instrument (TOMS and OMI) satellite overpasses are generally within the sonde $\Delta$TCO. However, there is a discontinuity between TOMS v8.6 (1998 to September 2004) and OMI (October 2004–2016) TCO on the order of 10 DU that accounts for the significant 16 DU overall difference observed between sonde and TOMS. By comparison, the sonde-OMI absolute difference for the eight stations is only ~4 DU.

Plain Language Summary Electrochemical concentration cell ozonesondes are balloon-borne instruments that measure profiles of ozone from launch up to 35 km. The high vertical resolution allows researchers to capture features in measurement-deficient regions of the atmosphere: the boundary layer, tropopause region that marks the boundary between the troposphere and stratosphere, and the protective ozone shield layer around 20–25 km. The Southern Hemisphere ADDitional OZonesondes (SHADOZ) project has been archiving ozonesonde data from up to 17 stations since 1998 that are available publicly at https://tropo.gsfc.nasa.gov/shadoz. As with any instrument there are uncertainties in the measurements. For ozonesondes the uncertainty in the ozone measurement is associated with the mechanics of the electrochemical concentration cell sensor and the preparation procedures. For the first time we calculate the ozone profile uncertainties measured by the ozonesonde using the SHADOZ 1998–2016 database. The advantage of doing a detailed uncertainty analysis is that it reveals areas of the measurements where we can refine operational procedures to reduce the uncertainty and where additional research is needed to improve the basics of this measurement.

1. Introduction
1.1. Influence of ECC Ozonesonde Measurements

The electrochemical concentration cell (ECC) ozonesonde was developed by Walter Komhyr (Komhyr, 1969) and has been flown at ~80 stations worldwide since the late 1960s (Hassler et al., 2008; Logan, 1985; Oltmans et al., 2006; Stauffer et al., 2016; Tarasick et al., 2005; Tiao et al., 1986). The ECC instrument consists of a...
gas-sampling pump connected to an ozone sensor and an electronic interface that connects the ozone sensor to a radiosonde for data telemetry (see Figure 1 in Komhyr et al., 1995). Measured parameters transmitted to the ground receiving station are ozone current, the ozonesonde’s pump temperature, motor voltage and current, and ambient pressure, temperature, and relative humidity (RH) (P-T-U). In recent decades, winds and Global Positioning System-enabled measurements became available. In flight, the instrument is encased in a weatherproof box that is tethered to a balloon, capable of measuring ozone up to an altitude of ~35 km. The balloon ascent rate, typically around 5 m/s, and data transmission rate lead to a vertical resolution within 150 m.

Light-weight, compact, and relatively easy to prepare and launch, ozonesondes (also referred to here as sondes) fulfill an important role in providing high vertical resolution ozone (O₃) profiles from the surface to the middle stratosphere, capable of making measurements during polar night and in cloudy and rainy conditions. They are readily deployed from remote locations, such as over Antarctica, and high-latitude Europe, United States, and Canada. For example, during the Match campaigns over the Arctic (Rex et al., 1998, 2006; von der Gathen et al., 1995), trajectory pathways of ozone-depleted air parcels measured from one location can be forecast and sondes launched from other sites can intercept the low-ozone filaments. The Intercontinental Chemical Transport Experiment Ozonesonde Network Study (IONS) series of North American campaigns collected hundreds of soundings with daily launches from 8 to 20 sites over 3 to 6 week periods to augment aircraft in situ and lidar profiles (Thompson, Stone, et al., 2007; Thompson et al., 2008, 2011). Studies using tropical ozonesonde measurements have examined the tropical wave-one feature (Sauvage et al., 2006; Thompson et al., 2003, 2017), quasi-biennial oscillations and El Niño–Southern Oscillation features (Lee et al., 2010; Logan et al., 2003; Randel & Thompson, 2011; Thompson et al., 2001; Witte et al., 2008), and the tropical transition layer (Corti et al., 2006; Folkins et al., 1999; Fu et al., 2007; Gettelman & Forster, 2002; Randel et al., 2007; Thompson et al., 2012).

Ozonesonde data have become highly valued over the past 20 years as a large community is focused on O₃ trends in the upper troposphere and lower stratosphere (UT and LS), a region where satellite data do not provide the vertical resolution and sampling frequency that sondes typically do (Bodeker et al., 1998; Gebhardt et al., 2014; Kivi et al., 2007; Rao et al., 2003).

1.2. Reprocessing of ECC Ozonesonde Data

As popular as the sounding data have become, it is clear when long-term sonde-based O₃ records are examined in detail that changes in the ozonesonde instrument, calibration, and preparation techniques, and data processing methods lead to discontinuities and possibly artifact trends at individual sites (Witte et al., 2017). In addition, there are station-to-station variations in satellite O₃ biases versus sondes, biases among stations, and biases within the data record of an individual station that must be corrected for if sondes are used to assess measurement uncertainties and the reliability of O₃ profile trends (Thompson, Witte, et al., 2007; Thompson et al., 2003, 2014).

Accordingly, the ozonesonde community has worked for many years to establish quality assessment standards for ozonesondes. The first important step in this effort was the establishment in the mid-1990s of the World Calibration Center for Ozone Sondes (WCCOS) (Smit & Kley, 1998; Smit & Straeter, 2004a, 2004b). The periodic intercomparison experiments conducted in WCCOS, called Jülich Ozonesonde Intercomparison Experiments (JOSIE), operate with a standard O₃ reference ultraviolet photometer in a chamber. In the test chamber ozone is introduced under changing temperature and pressure conditions at a rate that simulates profiles that correspond to standard high-latitude, midlatitude, subtropical, and tropical conditions. The first JOSIE (JOSIE-1996; Smit & Kley, 1998) included non-ECC sondes that have largely been replaced at operational stations (De Backer et al., 1998; Fujimoto et al., 2004; Stübi et al., 2008). From subsequent JOSIE campaigns (1998 and 2000) the focus of the WCCOS tests has been on ECC sondes manufactured by Science Pump Corporation (SPC) and Environmental Science (ENSCI) and characterizing how different SST (sensing solution type) perform under the various simulations (Smit et al., 2007). These campaigns revealed that differences in O₃ as measured among different ECC sensors, are largely due to differences in preparation procedures and SST used by participating researchers. The outcome was that two combinations of instrument type and SST were recommended as standard operating procedures.
Smit et al., 2007; Smit & ASOPOS (Panel for the Assessment of Standard Operating Procedures for Ozone sondes), 2014). The same combination emerged as the WMO (World Meteorological Organization) preferred standard during the BESOS (Balloon Experiment on Standards for Ozonesondes) campaign in 2004 that evaluated the ozone response of commonly used ECC/SST pairings following JOSIE standard operating procedures guidelines under ambient conditions (Deshler et al., 2008).

After 2010, several Ozonesonde Expert meetings and the SPARC/IO3C-IGACO-NDACC (Stratospheric Processes and their Relation to Climate, International Ozone Commission, International Gases and Aerosols Composition, Network for Detection of Atmospheric Chemical Composition Change) SI2N activities considered how to homogenize long-term data sets for trends because a number of stations had more than 30 years of ECC records, albeit with both ozonesonde and radiosonde changes. These activities and the results of JOSIE, BESOS, and further dual balloon soundings led to the creation of the O3S-DQA (Ozone Sonde Data Quality Assessment) panel report (Smit & O3S-DQA, 2012, hereafter referred to as Smit12) the goals of which are to (1) establish guidelines for reprocessing ozonesonde data records to remove inhomogeneities due to instrumental or procedural artifacts and (2) determine the contributions of the individual uncertainties of the different instrumental parameters to the O3 measurement. The WMO/GAW (Global Atmospheric Watch) Report #201, referenced as Smit and ASOPOS (Panel for the Assessment of Standard Operating Procedures for Ozonesondes) (2014, hereafter referred to as the WMO/GAW Report), is a comprehensive summary of the Smit12 findings. The O3S-DQA panel report has also formalized the concept of transfer functions to compensate for instrument-SST changes. Deshler et al. (2017) have recently published the set of transfer functions based on the JOSIE and BESOS experiments and on unpublished field comparisons that incorporate a total of 197 tests with the SPC and ENSCI ECC sensors.

2. SHADOZ and Data Reprocessing

Since early 2016 we have been reprocessing the Southern Hemisphere ADDitional OZonesondes (SHADOZ) record (Witte et al., 2017; Thompson et al., 2017, hereafter referred to, respectively, as Witte17 and Thompson17) according to the O3S-DQA guidelines using customized software based on Skysonde (developed by Allen Jordan at National Oceanic and Atmospheric Administration (NOAA)/Earth Systems Research Laboratory/Global Monitoring Division (NOAA/ESRL/GMD)).

Figure 1 displays the map of the stations for which data are analyzed in detail in this study. Details of the first reprocessing of SHADOZ data from seven sites appear in Witte17. When added to data from six other SHADOZ stations, including four sets from stations reprocessed by NOAA/ESRL/GMD, 14 stations with continuous data of at least one decade have been evaluated in Thompson17. Those reprocessed SHADOZ data were compared to three backscatter ultraviolet-type satellite total column ozone (TCO) amounts spanning 1998–2016 and to colocated ground-based instruments at nine SHADOZ stations. Thompson17 showed that, compared to earlier evaluations (Thompson, Witte, et al., 2007; Thompson et al., 2003, 2012), offsets between ozonesonde and satellite TCO are reduced due to the homogeneity of the newly reprocessed ozonesonde data records. Most stations ended up with sonde TCO, satellite, and, where applicable, ground-based instruments, within 2% of one another.
In this paper we reprocess data for Réunion a second time and present the first reprocessed data for Costa Rica (various locations around San José) and Nairobi (refer to locations in Figure 1). However, the principal goal here is to report an uncertainty analysis of the ozonesonde measurement system, term by term, for the eight stations we have reprocessed at National Aeronautics and Space Administration/Goddard Space Flight Center (NASA/GSFC), as well as uncertainties in TCO amounts. In the latter case we compare the columns to Earth Probe/TOMS (Total Ozone Mapping Spectrometer) and OMI (Ozone Monitoring Instrument) satellite overpasses.

Following Witte17, this study continues the O3S-DQA goal of determining uncertainties in the ozonesonde measurement system. The treatment of uncertainty in this study closely follows the definitions described in Smit12. Section 3 describes details of the ozone measurement and the reprocessing of SHADOZ data to date. Section 4 analyzes the uncertainty relationships term by term. The profile uncertainties appear in section 5 and column uncertainties in section 6, followed by a summary (section 7).

3. Details of the Ozoneonde Measurement and Reprocessed SHADOZ Ozonesonde Data

3.1. The Ozonesonde Measurement

The ECC sensor measures O3 using iodine/iodide electrode reactions. Two platinum electrodes are immersed in separate cathode and anode chambers of differing concentrations of potassium iodide (KI) solution. The anode cell contains a solution saturated with KI. Both cells contain an equal concentration of potassium bromide (KBr) and a phosphate buffer to maintain a neutral pH. An ion bridge connecting the two chambers allows ions to flow between the two cells but prevents mixing, thereby preserving their respective concentrations. Ambient air containing O3 is pumped into the cathode cell and reacts with iodide (I⁻) in solution to form iodine (I₂). To maintain electrochemical equilibrium, I₂ is converted back to I⁻ on the platinum electrode resulting in the release of two electrons. Thus, each O3 molecule entering the sensor causes two electrons to flow through the ECC’s external circuit, which it measures as a current. The resulting electrical current is proportional to the amount of O3 in the sampled air. The electrochemical technique assumes no secondary reactions take place and a 1:1 stoichiometric relationship of the O3:I2 is maintained. The relationship between O3 and the electrical current is defined by the following equation:

\[ P_{O3} = 4.307 \times 10^{12} \frac{(I_M - I_B)T_P}{\Psi_P \Phi_P \eta_C}, \]

where

- \( P_{O3} \) ozone partial pressure, mPa;
- \( I_M \) cell current, \( \mu A \);
- \( I_B \) cell background current, \( \mu A \);
- \( T_P \) ozonesonde pump temperature, K;
- \( \Phi_P \) pump flow rate, ml/s;
- \( \Psi_P \) pump flow efficiency, unitless; and
- \( \eta_C \) conversion efficiency, which is generally assumed to be 1.

The constant, \( 4.307 \times 10^{-12} \), is the half ratio of the ideal gas constant (8.314 J K⁻¹ mole⁻¹) to Faraday’s constant (9.6487 × 10⁴ C mole⁻¹). Equation (1) is similar to what is written in the WMO/GAW report.

3.2. SHADOZ Reprocessed Data

SHADOZ is the premier archive of tropical and subtropical ECC ozonesonde data. Since this National Aeronautics and Space Administration program started in 1998, SHADOZ has archived ozonesonde profiles from up to 17 tropical sites with support from NOAA/ESRL/GMD and international partners. Data are publicly available at https://tropo.gsfc.nasa.gov/shadoz. Information on the eight SHADOZ sites described in this study (Figure 1) appears in Table 1; each site’s location is summarized. Launches are two to four times per month. We use 1998–2016 data from the six sites that have been reprocessed by Witte17. Costa Rica and Nairobi were later reprocessed based on Witte17 methods that closely follow Smit12 guidelines. Evaluation of these two data sets can be found in Thompson17.
A transfer function based on Deshler et al. (2017) is applied to the Nairobi 1998 to October 2010 data to convert O3 measured with a nonstandard ENSCI ECC/1% full buffer SST to the WMO and manufacturer recommended ENSCI/0.5% half buffer equivalent. A similar transfer function is used to homogenize August 2007–2016 Réunion data from an ENSCI/0.5% full buffer SST to the standard ENSCI/0.5% half buffer. Both applications reduce O3 measurements by about 4%. Witte17 applied a transfer function to 6% of the profiles in the beginning of the Réunion record where SPC/0.5% half buffer SST was adjusted to the WMO recommended ENSCI/0.5% half buffer. An overview of transfer functions applied by Witte17 and in this study to the eight SHADOZ sites is found in Table 2. Transfer functions have been applied to over half the profiles at Réunion and Nairobi and 48% at Hanoi. Transfer functions applied at Ascension and Natal account for 10% and 17% of the data sets, respectively.

Witte17 concluded that O3 trend assessments could not be made using original and initially reprocessed Réunion data due to the solution change after August 2007, for which transfer functions had not yet been applied. We examine the effect of applying this additional transfer function to the reprocessed Réunion data set by comparing time series of TCO. In this study, sonde TCO is calculated by integrating O3 partial pressure up to 10 hPa and adding an O3 climatology from balloon burst to the top of the atmosphere (TOA), taken from the McPeters and Labow (2012) look-up table (reported in Dobson units (DU)). From Figure 2a the reprocessed data used in Witte17 show a significant difference in mean TCO of 16.4 DU between the 1998–2006 and 2007–2016 time periods (black dashed lines). However, this difference is reduced to 6.5 DU (blue) after the additional transfer function has been applied. Thus, as of this study, the significant discontinuity found by Witte17 has almost disappeared, allowing for meaningful trend assessments. Later, we show the impact of the uncertainty of the transfer function to the total ozone uncertainty budget. Further evaluation of this newly homogenized data set has been carried out by Thompson17.

### Table 1

Southern Hemisphere ADditional OZonesondes (SHADOZ) Sites Used in This Study

<table>
<thead>
<tr>
<th>Site</th>
<th>Latitude, Longitude</th>
<th>Time period</th>
<th>Profile total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascension Is., UK</td>
<td>7.98°S, 14.42°W</td>
<td>1998 to August 2010 and 2016^a</td>
<td>632</td>
</tr>
<tr>
<td>Hanoi, Vietnam</td>
<td>21.02°N, 105.80°E</td>
<td>September 2004–2016</td>
<td>245</td>
</tr>
<tr>
<td>La Réunion, France</td>
<td>21.10°S, 55.48°E</td>
<td>1998–2016</td>
<td>618</td>
</tr>
<tr>
<td>Nairobi, Kenya</td>
<td>1.27°S, 36.80°E</td>
<td>1998–2016</td>
<td>827</td>
</tr>
<tr>
<td>Natal, Brazil</td>
<td>5.42°S, 35.38°W</td>
<td>May 1998–2011 and September 2014–2016^a</td>
<td>595</td>
</tr>
</tbody>
</table>

^aNote that there are data gaps. ^bPrevious sites, Alajuela and Heredia, are within 0.5° of San Pedro (current site).

### Table 2

Summary of Transfer Functions Applied for Each SHADOZ Site

<table>
<thead>
<tr>
<th>Site</th>
<th>Transfer function</th>
<th>Dates applied</th>
<th>Conversion applied</th>
<th>Profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascension</td>
<td>Yes</td>
<td>1998–2001</td>
<td>ENSCI/1% to SPC/1%</td>
<td>10%</td>
</tr>
<tr>
<td>Costa Rica</td>
<td>No</td>
<td>—</td>
<td>—</td>
<td>48%</td>
</tr>
<tr>
<td>Hanoi</td>
<td>Yes</td>
<td>2004 to May 2009</td>
<td>ENSCI/2% unbuffered to ENSCI/0.5%</td>
<td>48%</td>
</tr>
<tr>
<td>Irene</td>
<td>No</td>
<td>—</td>
<td>—</td>
<td>48%</td>
</tr>
<tr>
<td>Kuala Lumpur</td>
<td>No</td>
<td>—</td>
<td>—</td>
<td>48%</td>
</tr>
<tr>
<td>La Réunion</td>
<td>Yes</td>
<td>1998 to July 2000</td>
<td>SPC/0.5% to ENSCI/0.5%</td>
<td>7%</td>
</tr>
<tr>
<td>Natal</td>
<td>Yes</td>
<td>March 1999 to July 2002</td>
<td>ENSCI/1% to SPC/1%</td>
<td>17%</td>
</tr>
<tr>
<td>Nairobi</td>
<td>Yes</td>
<td>1998 to June 2010</td>
<td>ENSCI/1% to ENSCI/0.5%</td>
<td>64%</td>
</tr>
</tbody>
</table>

Note. Conversions applied are to World Meteorological Organization recommended electrochemical concentration cell sensor/sensing solution type pairs: ENSCI/0.5% (half buffer) and Science Pump Corporation (SPC)/1% (full buffer).
Results of applying a transfer function to the early part of the Nairobi data set are shown in Figure 2b. As with Réunion, Nairobi retains a significant discrepancy of 9 DU prior to reprocessing between the periods 1998 to October 2010 and November 2010–2016 (black dashed lines). The offset disappears after a transfer function is applied (blue dashed line).

We examine more closely the impact of applying transfer functions to the Réunion and Nairobi data sets by comparing TCO values with OMI (Version 3) TCO overpass data (Levelt et al., 2006) as a reference. Results are shown in Figure 3 as histograms of the percentage difference with respect to sondes. Biases with respect to OMI at Réunion are significantly reduced after transfer functions have been applied (blue hashes, Figure 3a), where the Gaussian peak shifts from 4.3% to 0.7%. Most of the agreement falls within ±5%. The homogenized Nairobi data, in Figure 3b, show a different impact. The Gaussian peak shifts from +2.2% to −1.5%, and the sonde bias with respect to OMI changes from a mostly positive (high-bias) regime to a negative (low-bias) regime. This low-bias relationship between the Nairobi sondes and satellite data is consistent with most of the SHADOZ network data sets (Hubert et al., 2016; Thompson17). Like Réunion, the agreement is ±5% making both these sites a stable reference for trends analysis and satellite validation.

4. The Ozone Uncertainty Equation

To improve the ozonesonde measurement system, Smit12 introduced the first instrumental uncertainty equation of the ECC-type ozonesonde based on the current best knowledge of the ECC performance under lab conditions. After reprocessing to remove all known inhomogeneities, the overall uncertainty in \( P_{O3r} \), shown in equation (2), is the square root of the sum of the squares of the uncertainty in each term of the ozone partial pressure equation (equation (1)). The uncertainties are assumed to be random and Gaussian and therefore follow the Gaussian propagation of uncertainty. In equation (2), the assumption is that the uncertainties are not only random but also uncorrelated.
where

\[ \frac{\Delta P_{O3}}{P_{O3}} = \sqrt{\left(\frac{\Delta I_M}{I_M - I_B}\right)^2 + \left(\frac{\Delta I_B}{I_B}\right)^2 + \left(\frac{\Delta \eta_C}{\eta_C}\right)^2 + \left(\frac{\Delta \Phi_P}{\Phi_P}\right)^2 + \left(\frac{\Delta \Psi_P}{\Psi_P}\right)^2 + \left(\frac{\Delta T_P}{T_P}\right)^2} \] (2)

The individual uncertainties are defined as a relative error \((\Delta x)/x\) and can be expressed as a percentage. The value of \(P_{O3}\) and its error, or uncertainty in this case, can then be expressed as the interval \(P_{O3} \pm \Delta P_{O3}\).

The first application of equation (2) was done for the McMurdo, Antarctic station data set (reference analysis can be downloaded at http://wwwdas.uwyo.edu/~deshler/NDACC_O3S sondes/O3s_DQA/O3s_DQAGuideline_Summary_OzUncertainty_td.pdf). Van Malderen et al. (2016) also applied Smit12 uncertainties to the ECC ozonesonde measurements at Uccle (Belgium). Sterling et al. (2017) applied the formula to two SHADOZ stations (Hilo, Hawaii, and Pago Pago, American Samoa), Boulder, CO, and the South Pole, and Tarasick et al. (2016) applied their own uncertainty estimates to the Canadian ozonesonde records, taking into account the uncertainty terms in equation (2). We take advantage of these studies to compare with our methods and results.

Where applicable, based on Deshler et al. (2017) calculations, the overall uncertainty of the transfer function, \(\Delta T_F\), is 5%. We apply the Smit12 approach and add this uncertainty to the uncertainty in the conversion efficiency term.

Whereas in the report the \(\Delta \Phi_P/\Phi_P\) term includes \(\Delta \Psi_P/\Psi_P\), we separate the two terms for clarity. The rest of the instrumental uncertainty terms are defined in subsequent subsections.

Note that this study focuses only on the uncertainties of the ozonesonde instrument and does not take into account uncertainties due to radiosonde pressure offsets (offsets that lead to errors in the height registry of the computed ozone). Tarasick et al. (2016) do not correct for radiosonde errors but include a pressure offset uncertainty for the VIZ (±1 hPa) and Vaisala RS-80 (±0.5 hPa) manufacturers based on previous studies.
Conversely, Sterling et al. (2017) correct for pressure offsets but do not include the radiosonde pressure uncertainties in their ozone uncertainty calculations. The challenge of determining radiosonde errors, particularly in the non-Global Positioning System era, is still an ongoing debate.

The uncertainty in the ozone current, $\Delta I_A$, is $\pm 0.01 \mu A$ for currents less than 1.0 $\mu A$ and 1% elsewhere. This is taken as the overall resolution of the digital interface board (Smit12). V2 and V7 interface boards have similar piecewise uncertainties (Sterling et al., 2017). The Vaisala OIF11 and current generation OIF92 interface boards have an accuracy of 0.01 $\mu A$ and 0.001 $\mu A$, respectively (taken from the Vaisala manufacturer brochure). Uncertainty analysis done for the McMurdo station data set used $\Delta I_M = 0.1 \mu A$ while this uncertainty was not taken into account by Tarasick et al. (2016). Sterling et al. (2017) used similar $\Delta I_M$ during the digital era of the measurements that started in the 1990s.

SHADOZ sites encompass a wide range of radiosonde/ozone sonde systems that use a variety of interface boards with varying resolutions. For example, the Modem radiosonde used at Réunion, Lockhead-Martin-Sippican used at Ascension and Natal, and Vaisala employed at a number of SHADOZ sites use their own interfaces, which have different analog-to-digital converters and possibly different thermistors. This may impact the uncertainty estimate for the cell current and pump temperature measurement; however, further investigation is needed to determine the effect, if any. In this study, we simplify $\Delta I_M$ to $\pm 0.01 \mu A$ for currents less than 1.0 $\mu A$ and 1% elsewhere, as recommended by Smit12.

Van Malderen et al. (2016) noted that equation (2) does not take into account the uncertainty due to the time lag of the response of the $I_M$, $T_p$, and $I_B$ measurements. Tarasick et al. (2016) incorporated an e-folding response time to the ozone gradient to take into account slow ECC responses to changes in ozone due to variable ascent rates.

### 4.1. Background Current Uncertainty, $\Delta I_B$

The background current ($I_B$) is the residual current measured by the sonde when sampling ozone-free air. Conventional processing of the sonde telemetry assumes that the background current remains constant during flight. There is no statistically robust method for estimating the uncertainty of the background current, $\Delta I_B$. JOSIE studies used small sample sizes, fewer than 14 ECC sensors, to conduct the background current experiments published in Smit et al. (2007) and recommended in the WMO/GAW Report. During JOSIE-1996, significantly high backgrounds were recorded, in part, to the slow decay in the ozone response and not allowing enough time for the background to drop lower (Johnson et al., 2002).

Laboratory experiments by Vömel and Diaz (2010) tracked the decay of the cell current after exposure to ozone and showed that a much longer period of time (hours) can be required to approach initial values. There is also a dependence on the SST where experiments have shown a relationship between buffered KI SST and high ozone measurements due to a hysteresis effect (additional side reactions) that offset the ideal 1:1 stoichiometric ratio expected from the O3 to I2 reaction (Barnes et al., 1985; Johnson et al., 2002).

To further confound the issue, SHADOZ sites measure $I_B$ in a number of different ways: some are based on an average value, the minimum value recorded during the conditioning process, prior to launch either in the lab or at the launch site, or set to an upper limit threshold for $I_B$ values that exceed it. The many ways in which $I_B$ is recorded are compounded by the quality of the ozone destruction filters used that does not guarantee uniformity and introduces a source of random uncertainty that cannot be easily quantified (Reid et al., 1996). This is particularly true for ozonesonde flown in the tropics where high humidity affects the ozone removal efficiency of the filter (Newton et al., 2016). Specific to our study that uses tropical-based sonde data, we use the $1\sigma$ uncertainty of $\pm 0.03 \mu A$ for sites that use the ENSCI ECC sensors and $\pm 0.02 \mu A$ for SPC sensors based on Witte calculations. The $\Delta I_B$ value is doubled, where $I_B$ is missing or exceeds the threshold value of 0.05 $\mu A$ (based on Witte17 reprocessing criteria). Sterling et al. (2017) adopted the same strategy using $\Delta I_B = \pm 0.02 \mu A$ for ENSCI ECCs. For the McMurdo measurements, $\Delta I_B$ was higher for SPC ($\pm 0.05 \mu A$), whereas Tarasick et al. (2016) took a different approach applying a pressure dependent correction. Table 3 summarizes the $\Delta I_B$ applied for the eight reprocessed sites based on the ECC sensor used. In general, one ECC type dominates a single site’s data set. Included is the percent of profiles for which $I_B$ is missing or exceeds the 0.05 $\mu A$ threshold. The large spread of these percentages illustrates the difficulty in establishing low backgrounds in tropical environments as well as the variation in technique. For example, Costa Rica applies a constant...
0.02 μA to all profiles, and Natal recharges the cells with new solutions to determine the final background prior to launch.

In equation (2) \(I_b\) is subtracted from \(I_m\) in the denominator, and thus, its value has a significant impact on that term, particularly in the troposphere where \(I_m\) in the tropical troposphere is typically less than 1 μA and \(I_b\) can be as high as 0.05 μA. Notably, the tropopause is a region of very low ozone, usually \(< 1\) mPa in the tropics. Where \(P_{O_3}\) measures less than 1 mPa, \(I_m\) can approach \(I_b\), thus increasing the dominance of the \((\Delta I_m)^2 + (\Delta I_b)^2 / (I_m - I_b)^2\) term (abbreviated to \(\Delta I_b / \Delta I_m\) hereafter) in equation (2).

### 4.2. Conversion Efficiency Uncertainty, \(\Delta \eta_C / \eta_C\)

The conversion efficiency, \(\eta_C\), comprises two parts: (1) the absorption efficiency (\(\alpha_{O_3}\)) from the gas to liquid phase in the sensing solution and (2) the stoichiometry of the O₃:I₂ relationship (\(S_{O_3}:I_2\)) which is assumed to be 1:1. Interferences with this one-to-one relationship can arise from the buffering of the solution (Johnson et al., 2002; Vömel & Diaz, 2010). Setting the \(\alpha_{O_3}\) equal to 1 applies to cases where the volume of the cathode solution is 3.0 cm³. For SHADOZ sites, such as Ascension, Natal, Irene, and Réunion, that use a 2.5 cm³ cathode volume, we use the following equations in Smit12 to calculate \(\alpha_{O_3}\), as a function of pressure, \(P\):

\[
\alpha_{O_3}(P) = \begin{cases} 
1.0044/C_0 (4.4 \times 10^{-5}) \times P & \text{for } 100 \text{ hPa} < P < 1,050 \text{ hPa}, \\
1.0 & \text{for } P \leq 100 \text{ hPa}.
\end{cases}
\]

In the ozone partial pressure equation (equation (1)), the conversion efficiency is assumed to be unity and is typically excluded from the ozone equation. However, the uncertainty of this unity assumption does contribute to the overall ozone uncertainty. These are constant unitless values for a cathode solution volume of 3.0 cm³. Thus, \(\Delta \eta_C / \eta_C\) can be expressed as follows:

\[
\frac{\Delta \eta_C}{\eta_C} = \sqrt{\left(\frac{\Delta \alpha_{O_3}}{\alpha_{O_3}}\right)^2 + \left(\frac{\Delta S_{O_3}:I_2}{S_{O_3}:I_2}\right)^2}, \tag{3}
\]

where \(\alpha_{O_3} = 1.0, \Delta \alpha_{O_3} = \pm 0.01, S_{O_3}:I_2 = 1.0, \) and \(\Delta S_{O_3}:I_2 = \pm 0.03\). The \(\alpha_{O_3}\) value is ±0.01 for both cathode volumes (Gaussian 1σ value taken from Davies et al., 2003). This is a simplistic approach because \(S_{O_3}:I_2\) will increase over the course of the sonde flight due to slow side reactions involving the phosphate pH buffers (Davies et al., 2000; Johnson et al., 2002). However, at present changes in \(S_{O_3}:I_2\), while recognized, are poorly understood and require further research. Where a transfer function is applied, 0.05 is added to the \(\Delta S_{O_3}:I_2\) term (Smit12).

### 4.3. Pump Flow Rate Uncertainty at the Ground, \(\Delta \Phi_P / \Phi_P\)

A common procedure in the ECC conditioning is the use of a soap bubble flow meter method to measure the volumetric flow rate of the pump, \(\Phi_P\) (mL/s). However, calculating \(\Delta \Phi_P / \Phi_P\) is not straightforward because not

---

**Table 3**

<table>
<thead>
<tr>
<th>Site</th>
<th>ECC</th>
<th>(\Delta I_b) (μA) (fraction of missing or &gt;0.05 μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascension Is., UK</td>
<td>SPC</td>
<td>0.02 (7.2%)</td>
</tr>
<tr>
<td></td>
<td>ENSCI (92 records)</td>
<td>0.03 (7.4%)</td>
</tr>
<tr>
<td>Costa Rica</td>
<td>ENSCI</td>
<td>0.03 (0.0%)</td>
</tr>
<tr>
<td>Hanoi, Vietnam</td>
<td>ENSCI</td>
<td>0.03 (16.0%)</td>
</tr>
<tr>
<td></td>
<td>SPC (15 records)</td>
<td>0.02 (1.6%)</td>
</tr>
<tr>
<td>Irene, S. Africa</td>
<td>SPC</td>
<td>0.02 (44.7%)</td>
</tr>
<tr>
<td>Kuala Lumpur, Malaysia</td>
<td>SPC (1998 to November 2014)</td>
<td>0.02 (86.2%)</td>
</tr>
<tr>
<td></td>
<td>ENSCI (December 2014–2016)</td>
<td>0.03 (14.0%)</td>
</tr>
<tr>
<td>La Réunion, France</td>
<td>ENSCI</td>
<td>0.03 (7.4%)</td>
</tr>
<tr>
<td></td>
<td>SPC (40 records)</td>
<td>0.02 (0.0%)</td>
</tr>
<tr>
<td>Nairobi, Kenya</td>
<td>ENSCI</td>
<td>0.03 (74.2%)</td>
</tr>
<tr>
<td>Natal, Brazil</td>
<td>SPC</td>
<td>0.02 (0.5%)</td>
</tr>
<tr>
<td></td>
<td>ENSCI (104 records)</td>
<td>0.03 (0.2%)</td>
</tr>
</tbody>
</table>

Note. ECC = electrochemical concentration cell; SHADOZ = Southern Hemisphere ADDitional OZonesondes; SPC = Science Pump Corporation.
all quantities are known. Witte17 applied correction formulae found in section 8.4 of Smit12 that compensate for the evaporation of the soap bubble solution and rely on the saturated water vapor pressure under ambient P-T-U conditions (C_{PH}). There is a second correction that takes into account the temperature difference between the internal pump base temperature and the ambient room temperature, C_{PL} = (T_{pump} - T_{lab})/T_{lab}. Our calculations reveal ΔC_{PH} values < 1, and thus, we exclude this term that has a negligible impact on the correction of Φ_P and its uncertainty. The final equation to calculate ΔΦ_P/Φ_P can then be expressed as follows:

\[
\frac{ΔΦ_P}{Φ_P} = \sqrt{\left(\frac{ΔΦ_{\text{reprocessed}}}{Φ_{\text{reprocessed}}}\right)^2 + (ΔC_{PH})^2},
\]

where ΔΦ_{reprocessed}/Φ_{reprocessed} = ±0.02 and ΔC_{PH} is based on the minimum and maximum C_{PH} values in each site’s data set, that is, ±(C_{PH,High} - C_{PH,Low})/2 (Smit12). Here we assume that the uncertainties in the reprocessed flow rates are within the uncertainty of the original measured quantities. Table 4 summarizes the ΔC_{PH} and ΔΦ_{reprocessed}/Φ_{reprocessed} computed for the eight sites. At Irene and Kuala Lumpur, for which lab P-T-U are not documented, we double the ΔΦ_{reprocessed}/Φ_{reprocessed} term to ±0.04 and calculate ΔC_{PH} using the Witte17 tropical climatology of T_{lab} = 25 ± 5°C, RH_{lab} = 50 ± 25%, and P_{sfc} = mean pressure surface at launch. In the case of Costa Rica, Hanoi, and Nairobi for which a fraction of their data sets are missing lab P-T-U, we use the mean C_{PH} for flights with known lab conditions. ΔC_{PH} remains the same since the mean does not affect the min/max range of C_{PH} values and ΔΦ_{reprocessed}/Φ_{reprocessed} = ±0.04.

### 4.4. Pump Flow Efficiency Uncertainty, ΔΨ_P/Ψ_P

The pump flow rate, Φ_P, measured during the conditioning procedures is approximately constant up to 100 hPa and decreases steadily to the top of the atmosphere due to instrumental degradation at low pressures (Komhyr, 1986; Komhyr et al., 1995). From equation (1), the pump flow efficiency, Ψ_P, is based on empirically derived pump correction factors (PCF) that take into account the efficiency loss in Φ_P as a function of pressure. This study follows the WMO/GAW report recommendations and applies the Komhyr (1986) PCF for sondes launched with an SPC sensor and Komhyr et al. (1995) PCF for ENSCI sensors. These PCF compensate for the effect of the buffer that creates side reactions in the solution (Johnson et al., 2002). The exception is at Hanoi for which almost half the data set uses a NOAA sensing solution recipe of 2% unbuffered KI. The unique formula requires its own PCF due to the lack of the buffer in solution (Johnson et al., 2002). These three pump flow efficiencies and their ±1σ uncertainties (±ΔΨ_P) are listed in Table 5. We can interpret the effect of the buffer at low pressures as the difference in Ψ_P between the Johnson et al. (2002) and both Komhyr look-up tables: the difference ranges from 3% at 100 hPa to 15% at 5 hPa. The Deshler et al. (2017) transfer function that corrects for solution changes between the 0.5% half buffer and 1.0% full buffer solution intrinsically takes into account the effect of the buffer, and therefore, its overall uncertainty of ±5% carries within it the uncertainty in the buffering.

The O3S-DQA panel has recommended a revised table of PCF ± ΔΨ_P based on the average of combined laboratory calibration experiments conducted by NOAA/ESRL/GMD, University of Wyoming, and Japan Meteorological Agency. This study uses the revised ±ΔΨ_P values included in Table 5. Note that these
uncertainties are similar to those of Johnson et al. (2002) for a 2% unbuffered SST; thus, we expect \( \Delta \psi_p \) values to be similar across the eight study sites. The revised \( \Delta \psi_p \) values are considered to be a more realistic representation of the PCF uncertainties and are better quantified, being based on hundreds of profiles (refer to Table 2 in Johnson et al., 2002). Refer to Table 3 for a summary of ECC sensor used at each site.

### 4.5. Pump Temperature Uncertainty, \( \Delta T_p/T_p \)

All SHADOZ sites use either an ENSCI-Z or SPC-6A model that measures the pump temperature internally. These measurements are considered to be a close approximation to the “true” pump temperature that is measured in the vicinity of the moving piston, \( T_{piston} \) (Smit12). Witte17 reprocessing includes a correction that accounts for the temperature difference between \( T_{piston} \) and the internal pump temperature. For SHADOZ data sets, the \( \Delta T_p/T_p \) equation is expanded to

\[
\frac{\Delta T_p}{T_p} = \sqrt{\left(\frac{\Delta T_{reprocessed}}{T_{reprocessed}}\right)^2 + \left(\frac{\Delta T_{piston}}{T_{piston}}\right)^2}, \tag{5}
\]

where both \( \Delta T_{reprocessed} \) and \( \Delta T_{piston} \) are \( \pm 0.5 \)°K (Smit12). As with the reprocessed flow rates, we assume that the uncertainties in the reprocessed pump temperatures are within the uncertainties of the original measured values. Witte17 replaced missing pump temperature profile data at Kuala Lumpur (1998–2005) and Irene (1998–2006) with climatological values. For these data sets the 1σ values of the climatology (range between 3° and 4°C) are used to compute \( \Delta T_{reprocessed} \) (see Figure A1 in Witte17).

### 5. Ozone Uncertainty Estimates in SHADOZ Profiles, \( \Delta P_{O3} \)

For the eight reprocessed SHADOZ sites, we compute \( \Delta P_{O3} \) and the individual uncertainty terms defined in equation (2) for each profile. The overall profile average of the uncertainty terms for each site is also shown in Figure 4. The vertical resolution is 50 m. We show the impact of applying a 5% transfer function uncertainty to the Ascension, Natal, Nairobi, Réunion, and Hanoi data sets (Figures 4a–4e, right panels, dashed black line). Note that the overall mean \( \Delta P_{O3} \) profile will lie between the solid black line, which is the data set for which no transfer function is applied, and the dashed line. From Figure 4 (right panels) we observe the following:

1. All sites show a peak in \( \Delta P_{O3} \) around the tropopause region (15 ± 3 km) due to \( I_B \), as nicely illustrated in Figure 1 in Vömel and Diaz (2010).
2. The uncertainty in the background and \( O_3 \) current term (\( \Delta I_B/\Delta I_{O3} \), red) dominates the overall uncertainty of \( P_{O3} \) in the troposphere. Where transfer functions have been applied (Figures 4a–4e), the conversion efficiency term (orange) becomes a significant contributor to the uncertainty.
3. The uncertainties in the conversion efficiency (orange) and flow rate (blue) terms dominate the overall uncertainty of \( P_{O3} \) in the stratosphere.

<table>
<thead>
<tr>
<th>Pressure (hPa)</th>
<th>Komhyr (1986) ( \psi_p ) ± ( \Delta \psi_p )</th>
<th>Komhyr et al. (1995) ( \psi_p ) ± ( \Delta \psi_p )</th>
<th>Johnson et al. (2002) ( a ) ( \psi_p ) ± ( \Delta \psi_p )</th>
<th>O3S-DQA panel ( \psi_p ) ± ( \Delta \psi_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sfc-100</td>
<td>1.000</td>
<td>1.000</td>
<td>1.1.000</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.993 ± 0.005</td>
<td>0.993 ± 0.005</td>
<td>0.967 ± 0.011</td>
<td>±0.010</td>
</tr>
<tr>
<td>50</td>
<td>0.982 ± 0.006</td>
<td>0.982 ± 0.005</td>
<td>0.950 ± 0.012</td>
<td>±0.012</td>
</tr>
<tr>
<td>30</td>
<td>0.978 ± 0.008</td>
<td>0.972 ± 0.008</td>
<td>0.935 ± 0.012</td>
<td>±0.014</td>
</tr>
<tr>
<td>20</td>
<td>0.969 ± 0.009</td>
<td>0.961 ± 0.012</td>
<td>0.919 ± 0.014</td>
<td>±0.017</td>
</tr>
<tr>
<td>10</td>
<td>0.948 ± 0.010</td>
<td>0.938 ± 0.023</td>
<td>0.876 ± 0.020</td>
<td>±0.022</td>
</tr>
<tr>
<td>7</td>
<td>0.935 ± 0.012</td>
<td>0.920 ± 0.024</td>
<td>0.842 ± 0.025</td>
<td>±0.028</td>
</tr>
<tr>
<td>5</td>
<td>0.916 ± 0.014</td>
<td>0.890 ± 0.025</td>
<td>0.803 ± 0.032</td>
<td>±0.037</td>
</tr>
</tbody>
</table>

Note. \( \psi_p \) are taken from the World Meteorological Organization/Global Atmospheric Watch Report. Ozone Sonde Data Quality Assessment panel revised \( \pm \Delta \psi_p \) values are computed to replace Komhyr (1986) and Komhyr et al. (1995) \( \pm \Delta \psi_p \).

\( a \)Average of ENSCI-Z model pump efficiency calibrations.
**Figure 4.** Left panels show the average profile of O$_3$ partial pressure ($P_{O3}$) in mPa (black) and ±uncertainty estimates (cyan) for the eight SHADOZ sites. Right panels are the individual uncertainty contributions to the total O$_3$ uncertainty ($\Delta P_{O3}$) (black) in percent. Solid black lines in the right-hand side panels for (a)–(d) are $\Delta P_{O3}$ average profiles for which no transfer function was applied. Concurrently, dashed black lines are the average $\Delta P_{O3}$ of profiles where a transfer function is applied. The $\Delta g/\Delta M$ term is an abbreviation of the $(\Delta g)^2 + (\Delta g)^2/|M| - g^2$ term in equation (2). Refer to Table 1 for each site’s time period and total number of profiles used to calculate the averages. TF = transfer function
Figure 4. (continued)
4. The application of transfer functions (Figures 4a–4e, purple) has a significant impact on the overall uncertainty of \( P_{O_3} \) throughout the profile.
5. The contribution of the pump temperature uncertainty term (\( \Delta T_p/T_p \) profiles in green) is minimal, accounting for only a few percent.
6. Overall uncertainties are within 15%. Notable exceptions are at Hanoi (Figure 4e, dashed line) and Kuala Lumpur (Figure 4f) around the tropopause region.
7. Costa Rica (Figure 4g) displays a unique maximum in \( \Delta P_{O_3} \) and \( \Delta I_p/\Delta I_m \) between 2 and 7 km.
8. Irene results show the smallest \( P_{O_3} \) uncertainties (less than 7%), relative to the other sites (Figure 5h), while Kuala Lumpur shows the largest values of \( \Delta P_{O_3} \).

In the vicinity of the tropopause (15 ± 3 km), \( P_{O_3} \) is a minimum (Figure 4, left panels). This is particularly true for Hanoi and Kuala Lumpur data sets that show the lowest mean \( P_{O_3} \) relative to the other sites. As the sensor current (\( I_p \)) approaches the measured background current value (\( I_b \)), the significant increase and dominance in the \( \Delta I_p/\Delta I_m \) term indicates that the sensor measurement is approaching its detection limit. Here we define the detection limit where the total uncertainty is equal to the measured signal (~0.02–0.05 \( \mu \)A range). This is particularly true at Nairobi where the \( \Delta I_p/\Delta I_m \) uncertainty term matches the transfer function uncertainty between 10 and 18 km (Figure 4c, right panel). Further investigation reveals a prevalence of \( I_p > 0.05 \mu \)A in the Nairobi metadata, which contributes to a doubling of its uncertainty. In contrast, Irene (Figure 4h) shows the highest measurements of \( P_{O_3} \) in the same region concurrent with the lowest values in the \( I_p/\Delta I_m \) and \( \Delta P_{O_3} \). Irene is located in the very edge of the subtropics and can exhibit midlatitude behavior (i.e., stratospheric fold events) as well as Southern Hemisphere pollution transport (Thompson et al., 2014). Hanoi and Kuala Lumpur are the only Asian tropical sites in the SHADOZ network and due to their geographic proximity to one another likely exhibit similar dynamics and transport features in the UT/LS region (Ogino et al., 2013). Thompson et al. (2012) show that Hanoi and Kuala Lumpur have a similar annual cycle with almost double the \( O_3 \) amount at the Hanoi site throughout the troposphere. In fact, values of \( O_3 \) at Kuala Lumpur and Hanoi are among the lowest relative to other SHADOZ sites, corroborating the Thompson et al. (2012) result. Both sites show a higher gradient in \( \Delta P_{O_3} \) and a larger peak >15%, relative to the other sites.

As noted above, there is a second peak in \( \Delta P_{O_3} \) in the lower troposphere in the Costa Rican data set (Figure 4g). There is a notch in \( P_{O_3} \) between 2 and 7 km (left panel) that is due to sulfur dioxide (SO2) interference from the nearby active Turrialba volcano (Diaz et al., 2012; Morris et al., 2010). Profiles that record near-zero \( I_p \) due to volcanic SO2 plumes are not uncommon in a given year (Diaz et al., 2012). This is seen in the right panel of Figure 4g where the uncertainty in the \( I_p/\Delta I_m \) term (red) increases significantly as \( I_p \) approaches \( I_b \) and thus the detection limit of the sensor. The data set reveals that roughly 10% of all profiles have SO2 interference, with years 2010–2012 being particularly volcanically active. This uncertainty peak is really due to the reduction in the conversion efficiency (\( \eta_c \)), whereby SO2 interference reduces \( \eta_c \) to 0. This is not captured in the uncertainty discussion because chemical interference is not assumed in equations (1) and (2). The near-zero cell current measurements amplify the \( \Delta P_{O_3} \) and \( \Delta I_p/\Delta I_m \) terms generating values that are much larger than they should be.

Van Malderen et al. (2016) applied corrections to the Uccle data set for high-SO2 interference in the Brewer-Mast ozonesondes using in situ SO2 measurements from a nearby site. No corrections were necessary during the ECC sonde era (1996 to present) because SO2 concentrations had diminished to levels that would not impact the ECC measurements. By filtering the obvious SO2 layers in the Costa Rican data set, the peak would still be present but not as large or as dominant (Thompson et al., 2010).

Figure 5 presents the uncertainty terms arranged by season. \( P_{O_3} \) is shown in the background in silver. Similarly, we find that \( \Delta P_{O_3} \) is a maximum around the tropopause and is dominated by the \( \Delta I_p/\Delta I_m \) term. In particular, in the vicinity of the tropopause region we observe in Figure 5 the following:

1. The overall uncertainty of \( P_{O_3} \) is the highest in December–February (DJF) and March–May (MAM) (with or without transfer functions) for sites in the Atlantic and Africa: Ascension, Natal, Nairobi, Réunion, and Irene.
2. The overall uncertainty of \( P_{O_3} \) is highest in DJF and September–November (SON) at the two northern tropical Asian sites, Hanoi (Figure 5e) and Kuala Lumpur (Figure 5f), where \( \Delta P_{O_3} \) peaks are over 20%. \( \Delta P_{O_3} \) gradients are highest for these two sites.
Figure 5. Similar to the right panels in Figure 4 but by season: DJF = December-January-February; MAM = March-April-May; JJA = June-July-August; SON = September-October-November. Average seasonal \( P_{O3} \) is shown in silver in mPa units. Dashed black lines in (a)–(e) are the average \( \Delta P_{O3} \) profiles for which a transfer function was applied. The solid black line denotes the average \( \Delta P_{O3} \) for profiles that did not apply a transfer function. TF = transfer function.
Figure 5. (continued)
3. High $\Delta P_{O3}$ in the Costa Rican data set (Figure 5g) due to volcanic SO2 interference between 2 and 7 km occurs throughout the year.

4. Relative to other sites, the overall uncertainty of $P_{O3}$ is smallest at Irene for all seasons (Figure 5h). SON is a minimum ($\Delta P_{O3}$ is less than 8%).

Overall, the $\Delta I/\Delta M$ term dominates $\Delta P_{O3}$ in the troposphere. The exception is where $P_{O3}$ measurements are high in the lowermost troposphere (silver profile), such as during the biomass burning season in SON over the Atlantic sites: Ascension (Figure 5a), Natal (Figure 5b) as well as Réunion (Figure 5d), and Irene (Figure 5h) and where the boundary layer is polluted such as at Hanoi (Figure 5e). $P_{O3}$ is elevated below 5 km for all seasons in the Irene data set (Figure 5h), accounting for the relative minima in $\Delta I/\Delta M$ (red). For all seasons, Kuala Lumpur (Figure 5f) stands out as having the highest $\Delta P_{O3}$ in the tropopause region, particularly in DJF and
SON, where uncertainties peak sharply at around 30%, coincident with high $\Delta P_{O_3}$ (red). Interestingly, the Nairobi data set also shows a relative $\Delta P_{O_3}$ maximum in DJF (Figure 5c). Logan et al. (2003) found that ozone concentrations at Nairobi are lowest from December to April from the tropopause to 50 hPa (~20 km). This corroborates the uncertainty results in Figure 5c that show relatively higher $\Delta P_{O_3}$ during DJF and MAM where the $\Delta \rho/\Delta \rho$ uncertainty term peaks at 15 ± 3 km.

Examples of applying uncertainties to profile comparisons with satellite can be found in Figure 6. We use Microwave Limb Sounder (MLS) v4.2 overpass profiles (Waters et al., 2006) at pressure levels between 261 and 10 hPa matched to the sonde location (within 200 km and 18 h). The four profile examples represent a cross section of reprocessing techniques. Transfer functions were applied to Nairobi and Réunion profiles (Figures 6a and 6b), Kuala Lumpur profiles incorporated a pump temperature climatology (Witte17) (Figure 6c), and Costa Rica is a site that required very little reprocessing and therefore had a minor impacts to the overall data set, relative to the original v5 data set (Thompson17). One notes patterns of agreement/disagreement on a profile-by-profile basis. Applying sonde uncertainties will provide a robust metric of evaluating the accuracy of current and future generations of satellite O$_3$ profilers, particularly in the climate sensitive UT/LS region.

How do our uncertainty estimates compare with previous studies? The WCCOS simulation by Smit and ASOPOS (2014) of a tropical profile estimate a similar range of $\Delta P_{O_3}$ values that also maximize around the tropopause (up to ~17%) due to the dominance of the $\Delta \rho/\Delta \rho$ term. The main difference is that this term dominates $\Delta P_{O_3}$ values throughout the profile, whereas in our study, the flow rate and conversion efficiency uncertainty dominate in the stratosphere. Sterling et al. (2017) present $\Delta P_{O_3}$ mean profiles for April and October at Hilo, Hawaii, and American Samoa (two SHADOZ sites), which we interpret as similar to the seasonal plots shown in Figure 5. Here we observe that their range of $\Delta P_{O_3}$ values is similar to ours, that is, maxima at the tropopause (>10%) and minima elsewhere in the profile (~5%). Sterling et al. (2017) show a relative minimum (maximum) in MAM (SON), similar to that shown for Hanoi and Kuala Lumpur (Figures 5e and 5f). In comparison, midlatitude and high-latitude ozonesonde profiles from previous studies show that (1) the overall uncertainty is smaller, that is, less than ~10% throughout the profile, (2) the conversion efficiency uncertainty term is a significant contributor to $\Delta P_{O_3}$ throughout the profile, and for some sites like Uccle is the dominant uncertainty term, and (3) the impact of the $\Delta \rho/\Delta \rho$ term remains an important contributor to $\Delta P_{O_3}$ around the tropopause (McMurdo uncertainty analysis; T. Deshler, 2017).
Figure 7. Time series of total column ozone (TCO) of every sonde launch (red) matched to a satellite overpass (Total Ozone Mapping Spectrometer (TOMS) and Ozone Monitoring Instrument (OMI), black). Red shading denotes the sonde TCO ± uncertainties ($\Delta$TCO). Satellite data sets are filtered for clouds >60% and distance from the sites location >200 km, then compared to the date of each sonde launch at the given site. The transition from TOMS to OMI overpasses occur in October 2004 and are marked by the black triangle on the $x$ axis. Results are plotted in sequence, accounting for the uneven spacing of the years on the $x$ axis.
Figure 7. (continued)
personal communication, 2015; Smit & ASOPOS, 2014; Sterling et al., 2017; Tarasick et al., 2016; Van Malderen et al., 2016).

6. Ozone Uncertainty Estimates in SHADOZ TCO

6.1. Calculating Total Column O₃ Uncertainty, ΔTCO

Profiles of O₃ partial pressure are integrated up to 10 hPa to generate integrated column amounts of O₃ in DU. To capture the O₃ maximum, we exclude profiles that burst at pressures less than 15 hPa. We limit our column integration to 10 hPa based on the Witte17 recommendation. They found that the accuracy of O₃ profile measurements below 10 hPa with respect to MLS did not improve even after reprocessing and remains highly variable and suspect. To compute the sonde TCO values, the McPeters and Labow (2012) O₃ climatology is used to extract the O₃ amount from the sonde’s balloon burst to the TOA. This is termed the “O₃ residual” in this paper ($P_{O₃\text{residual}}$). McPeters and Labow (2012) derived an O₃ climatology based on combining MLS (2004–2010) and ozonesonde (1988–2010) data sets. The climatology is a look-up table of monthly averaged ozone profiles from the surface to the TOA for 10° latitude zones. Previous studies have used the same sonde TCO formulation when analyzing SHADOZ data (Witte17; Thompson17, and references therein).

### Table 6

<table>
<thead>
<tr>
<th>Satellite period</th>
<th>Sample No.</th>
<th>$TCO_{sonde}$ ± $\Delta TCO_{sonde}$</th>
<th>Satellite ± $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Costa Rica (data since 2005)</td>
<td>277</td>
<td>255.3 ± 12.6</td>
<td>255.4 ± 14.3</td>
</tr>
<tr>
<td>Hanoi (data since September 2004)</td>
<td>147</td>
<td>261.7 ± 14.7</td>
<td>264.5 ± 17.6</td>
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<tr>
<td>Ascension</td>
<td>445</td>
<td>260.4 ± 13.1</td>
<td>271.6 ± 12.3</td>
</tr>
<tr>
<td>TOMS</td>
<td>220</td>
<td>259.1 ± 13.4</td>
<td>277.7 ± 10.9</td>
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<tr>
<td>OMI</td>
<td>225</td>
<td>261.6 ± 12.8</td>
<td>265.7 ± 10.6</td>
</tr>
<tr>
<td>Irene</td>
<td>250</td>
<td>272.4 ± 15.0</td>
<td>269.6 ± 16.4</td>
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<tr>
<td>TOMS</td>
<td>122</td>
<td>274.2 ± 15.4</td>
<td>274.7 ± 16.2</td>
</tr>
<tr>
<td>OMI</td>
<td>128</td>
<td>270.7 ± 14.7</td>
<td>265.8 ± 15.2</td>
</tr>
<tr>
<td>Kuala Lumpur</td>
<td>215</td>
<td>247.3 ± 14.9</td>
<td>260.6 ± 14.1</td>
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<tr>
<td>TOMS</td>
<td>86</td>
<td>249.7 ± 14.9</td>
<td>267.4 ± 14.5</td>
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<tr>
<td>OMI</td>
<td>129</td>
<td>245.8 ± 14.9</td>
<td>256.1 ± 11.9</td>
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<td>La Réunion</td>
<td>454</td>
<td>264.9 ± 15.8</td>
<td>268.5 ± 15.7</td>
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<tr>
<td>TOMS</td>
<td>129</td>
<td>255.8 ± 13.1</td>
<td>272.4 ± 16.0</td>
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<tr>
<td>OMI</td>
<td>325</td>
<td>268.6 ± 16.8</td>
<td>266.9 ± 15.2</td>
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<tr>
<td>Nairobi</td>
<td>570</td>
<td>255.8 ± 15.9</td>
<td>262.1 ± 13.3</td>
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<tr>
<td>TOMS</td>
<td>199</td>
<td>257.7 ± 17.3</td>
<td>270.2 ± 12.9</td>
</tr>
<tr>
<td>OMI</td>
<td>371</td>
<td>254.7 ± 15.1</td>
<td>257.7 ± 11.3</td>
</tr>
<tr>
<td>Natal</td>
<td>436</td>
<td>261.1 ± 13.4</td>
<td>269.2 ± 12.7</td>
</tr>
<tr>
<td>TOMS</td>
<td>188</td>
<td>258.9 ± 14.4</td>
<td>275.3 ± 11.2</td>
</tr>
<tr>
<td>OMI</td>
<td>248</td>
<td>262.8 ± 12.7</td>
<td>264.5 ± 11.9</td>
</tr>
</tbody>
</table>

Note. Units are in Dobson units. $\Delta TCO_{sonde}$ is the mean uncertainty. The ± $\sigma$ standard deviations are computed for the TOMS and OMI periods separately and the combined TOMS/OMI period. Note that matched satellite overpasses are filtered for clouds >60% and distance from the site location >200 km. OMI overpasses start in October 2004. TCO = total column ozone; OMI = Ozone Monitoring Instrument; TOMS = Total Ozone Mapping Spectrometer.
As a first approach, we compute sonde TCO uncertainties ($\Delta\text{TCO}$) by integrating the $\text{O}_3$ partial pressure uncertainties ($\Delta P_{\text{O}_3}$) generated from equation (2) and adding the uncertainty in the $\text{O}_3$ residual amount ($\Delta P_{\text{O}_3\text{residual}}$); that is, $\Delta\text{TCO} = \Delta P_{\text{O}_3} + \Delta P_{\text{O}_3\text{residual}}$. For example, if $\text{TCO} = \int_{\text{sfc}}^{\text{TOA}} P_{\text{O}_3}(z) \, dz + P_{\text{O}_3\text{residual}}$, then $\Delta\text{TCO} = \int_{\text{sfc}}^{\text{TOA}} \Delta P_{\text{O}_3}(z) \, dz + \int_{\text{sfc}}^{\text{TOA}} \Delta P_{\text{O}_3\text{residual}}(z) \, dz$. To generate an equivalent look-up table of $\Delta P_{\text{O}_3\text{residual}}$ uncertainties, we use the table of monthly averaged $1\sigma$ mixing ratios taken from McPeters and Labow (2012) and convert to DU following Ziemke et al. (2001) formulation (refer to equation (1) in that study). Thus, we can extract the $\Delta P_{\text{O}_3\text{residual}}$ at the sonde’s lower limit altitude (15–10 hPa) in the same way. Look-up tables of $\Delta P_{\text{O}_3\text{residual}}$ for the tropical latitude zones between 15 and 8 hPa are found in Table S1 in the supporting information. For example, for a 10 hPa pressure burst the $P_{\text{O}_3\text{residual}} = \Delta P_{\text{O}_3\text{residual}}$ range is (48–58 DU) ± (1.5–3 DU). We recognize that this approach may be an oversimplified calculation and hope that this study motivates future evaluation and refinement of this method.

6.2. Comparisons With TOMS and OMI Overpasses

As a reference, sonde TCO ± $\Delta\text{TCO}$ are compared with satellite overpass TCO from Earth Probe TOMS (V8.6 provided by the TOMS/OMI science team, McPeters et al., 1998) and the OMI V3, (Leveilt et al., 2006). TOMS and OMI have a local equator crossing time of 11:16 and 13:30, respectively. Sonde launch times (local) vary provided by the TOMS/OMI science team, McPeters et al., 1998) and the OMI V3, (Levelt et al., 2006). TOMS measures 11 DU higher TCO than OMI (TOMS = 267.3 ± 14.5 DU versus OMI = 256.1 ± 11.9 DU from Table 6). The Kuala Lumpur sonde data set does not show a similarly large discontinuity in its TCO time series between the TOMS and OMI periods (249.7 ± 14.9 DU during the TOMS period versus 245.8 ± 14.9 DU during the OMI period). Interestingly, the agreement between Irene sonde TCO and TOMS is excellent; however, the agreement between TOMS and OMI is offset by 9 DU (Table 6, right column). From Table 6, excluding Irene, the average difference between sonde and TOMS is 16 DU and is significantly higher than the 4 DU difference computed for the difference between sonde and OMI. This discontinuity is likely due to a change in the TOMS processing algorithm and is currently being investigated by the TOMS/OMI science team. This TOMS to OMI TCO discontinuity is not apparent in Witte17 and Thompson17 that used an older version 8 TOMS overpass data set taken from the Aura Validation Data Center (https://avdc.gsfc.nasa.gov).

The sonde low bias at Costa Rica (Figure 7g) observed at the end of 2015 points to a change in the ENSci instrument. Other SHADOZ sites (Samoa, Fiji, and Hilo) that use ENSci during that period also exhibit a low bias relative to satellite overpasses (Thompson17). The MLS/sonde profile comparison in Figure 6d highlights the significant underestimate in the sonde (red) observed after 2015 in Figure 7g and in
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Thompson17. The sonde underestimate appears above 50 hPa and is typical of sonde/MLS profile comparisons after 2015.

7. Summary
For the first time, uncertainty estimates in profile and total column O3 are computed using reprocessed data from eight SHADOZ sites. As a first approach, we also create a look-up table of monthly averaged O3 residual uncertainties to compute the uncertainty in sonde TCO. Variations in reprocessing procedures at each site require a tailored approach when calculating uncertainties. For example, missing metadata such as background current and flow rate measurements require climatological values specific to each site and thus a doubling of the uncertainty; not all sites require a transfer function.

A significant fraction of the Réunion and Nairobi data sets have been homogenized with the use of transfer functions, 63% and 64%, respectively. We demonstrate the efficacy and success of applying the Deshler et al. (2017) formulae to generate consistent and stable reference data sets for trends analysis and satellite validation. Biases are reduced (Réunion = 0.7% and Nairobi = −1.5%) and preliminary agreement with OMI is within 5%.

Overall, O3 profile uncertainties are less than 15% with a persistent maximum in the vicinity of the tropopause where O3 values are low and approach the detection limits of the ECC sensor. Here the background and sensor current uncertainties dominate, as well as in the troposphere. Stations for which transfer functions have been applied show a significant contribution from the conversion efficiency uncertainty. In the stratosphere, the conversion efficiency and flow rate uncertainty terms dominate. We observe a unique second peak in the free troposphere in the Costa Rican data set due to SO2 interference from volcanic plumes. Seasonally, uncertainties are a maximum in MAM when O3 values are the lowest. Exceptions are at Hanoi and Kuala Lumpur, the only two northern tropical Asian sites in the SHADOZ network. Both display the highest uncertainties in DJF and SON, indicating unique meteorology relative to the other sites. The Irene data set displays the lowest O3 uncertainties, among the eight sites.

Overall, TCO uncertainties are less than 15 DU and represent −5–6% of the TCO, consistent with the stated uncertainties in Thomson17. TOMS/OMI overpass comparisons are within the sonde TCO uncertainties with the exception of Kuala Lumpur for which the sondes are low biased by about 5%. The persistent offset mimics that found in the Réunion and Nairobi data sets for which an error in the sensing solution formulae was found. However, due to the current lack of verification in the metadata, we can only speculate on the offset.

In addition, there is a discontinuity between the latest TOMS v8.6 and OMI TCO overpasses at almost all sites. TOMS measures higher TCO than OMI on the order of 10 DU that is not readily apparent in the older version 8 overpasses used in Witte17 and Thompson17 studies.

The advantage of doing a detailed uncertainty analysis is that it reveals areas of the measurements where we can refine operational procedures to reduce the uncertainty and where additional research is needed to improve the basics of this measurement. (1) To improve O3 measurements in the UT/LS in SHADOZ, we need to improve our understanding of the background current. This means that the actual measurement as done at present needs to be better quality controlled, that is, using a high-quality zero air ozone filter, lapsed time of measurement after reconditioning, and consistency of procedures. For example, the large spread of SHADOZ Ig observed in Witte17 (range is 0.01 μA–0.12 μA) is a result of varying procedures and not a property of the sonde instrument. It also means that the definition of the background current needs to be better agreed upon. (2) To reduce the uncertainty of the middle stratospheric measurements, that is, region of high O3, we need to better characterize the pump efficiency and conversion efficiency at low pressures. This is also the reason that transfer functions become pressure dependent at lower pressures. (3) Careful and complete metadata collection of lab P-T-U during preparation will reduce the uncertainty of the RH correction (ΔCPH), and careful metadata collection of the O3 destruct filter methods being used during the background measurements will help in estimating the quality of that measurement.

References


