- 1 An Examination of the Recent Stability of Ozonesonde Global Network Data
- 2 Date Updated: 30 August 2022
- 3 Ryan M. Stauffer¹, Anne M. Thompson^{2,1}, Debra E. Kollonige^{3,1}, David W. Tarasick⁴,
- 4 Roeland Van Malderen⁵, Herman G. J. Smit⁶, Holger Vömel⁷, Gary A. Morris⁸, Bryan J.
- 5 Johnson⁸, Patrick D. Cullis^{9,8}, Rene Stübi¹⁰, Jonathan Davies⁴, and Michael M. Yan^{11,1}
- ⁶ ¹Atmospheric Chemistry and Dynamics Laboratory, NASA/GSFC, Greenbelt, MD, USA
- ⁷ ²Joint Center for Earth Systems Technology, University of Maryland Baltimore County,
- 8 Baltimore, MD, USA
- 9 ³Science Systems and Applications, Inc., Lanham, MD, USA
- ⁴Environment and Climate Change Canada, Downsview, ON, CA
- ⁵Royal Meteorological Institute of Belgium, Uccle (Brussels), Belgium
- ¹²⁶Institute for Energy and Climate Research: Troposphere (IEK8), Jülich Research Centre, Jülich,
- 13 Germany
- ¹⁴ ⁷National Center for Atmospheric Research Earth Observations Laboratory, Boulder, CO, USA
- ¹⁵ ⁸Global Monitoring Laboratory, NOAA Earth System Research Laboratory, Boulder, CO, USA
- ¹⁶ ⁹Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder,
- 17 CO, USA
- ¹⁰Federal Office of Meteorology and Climatology, MeteoSwiss, Aerological Station, Payerne,
- 19 Switzerland
- 20 ¹¹Kellogg Brown & Root, Fulton, MD, USA
- 21
- 22 Corresponding author: Ryan M. Stauffer (<u>ryan.m.stauffer@nasa.gov</u>)

23 Key Points:

- Global ozonesonde total column ozone stability averages ~±2% relative to measurements
 from multiple satellite instruments since 2004
- A sudden ozonesonde low bias affects a subset of stations using one manufacturer, and is
 mostly confined to the tropics
- Continuous evaluation of ozonesonde data against independent measurements will
 facilitate ongoing monitoring of the stability of the data
- 30
- 31 Keywords: Ozonesonde, Data Quality Assurance, Satellite Ozone, Ozone Trends
- 32 Index Terms: 0340, 0394, 0365

33 Abstract

34	The recent Assessment of Standard Operating Procedures for OzoneSondes (ASOPOS
35	2.0; WMO/GAW Report #268) addressed questions of homogeneity and long-term stability in
36	global electrochemical concentration cell (ECC) ozone sounding network time series. Among its
37	recommendations was adoption of a standard for evaluating data quality in ozonesonde time-
38	series. Total column ozone (TCO) derived from the sondes compared to TCO from Aura's
39	Ozone Monitoring Instrument (OMI) is a primary quality indicator. Comparisons of sonde ozone
40	with Aura's Microwave Limb Sounder (MLS) are used to assess the stability of stratospheric
41	ozone. This paper provides a comprehensive examination of global ozonesonde network data
42	stability and accuracy since 2004 in light of the sudden post-2013 TCO "dropoff" of \sim 3-4% that
43	was reported previously at select stations (Stauffer et al., 2020). Comparisons with Aura OMI
44	TCO averaged across the network of 60 stations are stable within about $\pm 2\%$ over the past 18
45	years. Sonde TCO has similar stability compared to three other TCO satellite instruments, and
46	the stratospheric ozone measurements average to within $\pm 5\%$ of MLS from 50 to 10 hPa. Thus,
47	sonde data are reliable for trends, but with a caveat applied for a subset of dropoff stations in the
48	tropics and subtropics. The dropoff is associated with only one of two major ECC instrument
49	types. A detailed examination of ECC serial numbers pinpoints the timing of the dropoff.
50	However, we find that overall, ozonesonde data are stable and accurate compared to independent
51	measurements over the past two decades.

52 Plain Language Summary

53 Ozonesondes provide accurate ozone measurements from the surface to ~30 km altitude 54 and are used as a reference for studies of satellite data, trends, pollution and climate. Updated

guidelines for sonde preparation and adoption of sonde total column ozone (TCO) comparisons 55 with satellite TCO as a "data quality" reference were published in 2021 by the ASOPOS 56 (Assessment of Standard Operating Procedures for OzoneSondes) 2.0 panel in WMO/GAW 57 Report 268. We report the first application of the ASOPOS 2.0 protocol to TCO evaluation from 58 the 60-station global ozonesonde network (42,042 profiles total). With Aura OMI TCO as the 59 satellite reference (Oct. 2004 to mid-2021), we find that TCO readings from the global 60 ozonesonde network are remarkably stable, consistently within $\pm 2\%$ of the satellite. An 61 exception occurs at only a small subset of tropical and subtropical locations that use one type of 62 ozonesonde instrument. The latter result confirms our earlier report that a sudden TCO drop 63 occurs at selected sites after 2013. The timing and magnitude of the dropoff are revisited. The 64 hypothesis that ozonesonde production changes are a contributor remains, with station-specific 65 factors possibly affecting the magnitude of the bias. Overall, global ozonesonde network data are 66 of high quality and stability. 67

68 **1 ECC Ozonesondes and Data Quality Assurance**

69 **1.1 The ECC Ozonesonde and Evaluations of Its Data Quality**

70 The electrochemical concentration cell (ECC) ozonesonde, versions of which have existed since the 1960s (Komhyr, 1969; Komhyr and Harris, 1971; Komhyr 1986), are 71 72 expendable, balloon-borne instruments that serve a vital role in global atmospheric ozone monitoring. Always paired with a meteorological radiosonde, the ECC provides continuous, 73 high-quality, in-situ measurements of ozone with high vertical resolution (100-150 m) from the 74 75 surface to over 30 km altitude, characteristics that no other instrument, remote-sensing or otherwise, can match. The measurement principle of the ECC is based on the wet chemical 76 reaction of ozone in a neutral-buffered potassium iodide (KI) solution, such that approximately 77 two electrons flow in an external circuit in the ECC for each ozone molecule absorbed into the 78 solution (Smit, Thompson, and ASOPOS 2.0, 2021; Tarasick et al., 2021). The magnitude of 79 80 the resulting current is transmitted via the radiosonde to a receiving station and converted into 81 ozone partial pressure. ECC ozonesondes are currently launched at over 50 stations around the globe with regularity (Smit, Thompson, and ASOPOS 2.0, 2021), forming the global 82 83 ozonesonde network. The data are used for satellite and model evaluation (Hubert et al., 2016; Stauffer et al., 2019), developing ozone climatologies (Tilmes et al., 2012; Liu et al., 2013a,b; 84 Hassler et al., 2018; Stauffer et al., 2018), pollution and climate studies (Logan et al., 2003; 85 Witte et al., 2008; Cooper et al., 2010; Moeini et al., 2020), and calculating ozone trends 86 (Logan et al., 1999; WMO, 2018; Petropavlovskikh et al., 2019; Thompson et al., 2021). 87 Ozonesondes produced by one of two ECC manufacturers are operated at nearly all global 88 network stations: Environmental Science (EnSci; currently Z model; Westminster, CO, USA) 89 and Science Pump Corporation (SPC; currently 6A model; Camden, NJ, USA). 90

91	Over the past 25+ years, significant effort has been invested to increase our
92	understanding of ECC measurements and the factors affecting their uncertainty. Instrument
93	performance has been evaluated through laboratory experiments (Smit et al., 2007; Smit and
94	ASOPOS, 2014; Thompson et al., 2019; Smit, Thompson, and ASOPOS 2.0, 2021), field
95	campaigns (Komhyr et al., 1995; Boyd et al., 1998; Deshler et al., 2008), and analysis of
96	historical records (Tarasick et al., 2019). Uncertainties associated with ECC ozonesonde
97	measurements have decreased from >10% in the late 1990s, to near 5% today (Witte et al.,
98	2018; Tarasick et al., 2021; Smit, Thompson, and ASOPOS 2.0, 2021). The satellite
99	instrument community has requested even more stable and reliable data to detect and quantify
100	drift in satellite measurements that span a decade or more (Hubert et al., 2016).
101	Laboratory tests include the series of Jülich OzoneSonde Intercomparison Experiments
102	(JOSIE; Smit and Kley, 1998; Smit and Straeter, 2004; Smit et al., 2007; Thompson et al.,
103	2019), held at the World Calibration Centre for OzoneSondes (WCCOS) in Jülich, Germany. In
104	the JOSIE experiments, ozonesondes are placed in the WCCOS environmental chamber and
105	compared to a reference UV ozone photometer (OPM) during simulated atmospheric soundings
106	(Profitt and McLaughlin, 1983; the OPM was also flown in the field experiment described in
107	Deshler et al., 2008). The JOSIE experiments have examined the varying performance among
108	ECC (and other ozonesonde type) manufacturers, multiple KI sensing solution types (SSTs)
109	employed in the network, and the parameters used in the equation to convert the raw ozonesonde
110	cell current to ozone partial pressure, e.g., pump efficiency (Johnson et al., 2002) and
111	temperature, "background" current (Thornton and Niazy, 1982; Reid et al., 1996; Vömel and
112	Diaz, 2010; Newton et al., 2016), ozone absorption (Davies et al., 2003) and conversion
113	efficiency, and time response of the cell (Johnson et al., 2002; Vömel et al., 2020).

The results from the JOSIE experiments led to the formulation of ozonesonde standard 114 operating and data processing procedures by the Assessment of Standard Operating Procedures 115 116 for OzoneSondes Panel (ASOPOS; Smit and ASOPOS, 2012; Deshler et al., 2017). The data processing techniques devised by ASOPOS led to a common method by which a station's 117 ozonesonde data record can be "homogenized". Homogenization accounts for changes in 118 119 instrumentation, SST, preparation procedures, and other factors, and reduces or eliminates 120 artifacts which may otherwise appear as step changes in the ozonesonde time series. Homogenized ozonesonde data show better agreement with independent ozone measurements 121 compared to the non-homogenized versions (Tarasick et al., 2016; Van Malderen et al., 2016; 122 Witte et al., 2017; Thompson et al., 2017; Sterling et al., 2018; Witte et al., 2019; Ancellet et 123 124 al., 2022). The most recent report on ozonesonde measurement principles and best-practices was published in mid-2021 by the ASOPOS 2.0 Panel (Smit, Thompson, and ASOPOS 2.0, 2021). 125

126 **1.2 Data Quality Indicators for Ozonesonde Measurements**

One of the most significant advances in the ASOPOS 2.0 Report was the adoption of 127 128 stronger recommendations for assessing ozonesonde data quality across the global network. Although co-located ground-based instruments are a logical first choice for evaluating the quality 129 of soundings at individual sites (e.g., Sterling et al., 2018; Witte et al., 2019), not all stations 130 have such an instrument, usually a Dobson, Brewer or SAOZ. Furthermore, ground-based 131 132 instruments must themselves be calibrated with global standards and the frequency of calibration varies from site to site. Thus, with the emergence of high-quality, consistently calibrated, and 133 134 regularly updated satellite ozone measurements over the past two to three decades, providers of ozonesonde data typically compare their integrated total column ozone (TCO) amounts with 135 136 satellite overpass measurements. Improved agreement of reprocessed sonde data with satellite

137 TCO has been a major criterion for evaluating the success of homogenization in the studies cited138 above.

139	Given the longevity and coordinated calibration of the NASA and NOAA UV-based
140	satellite instruments, ASOPOS 2.0 recommends that Aura's Ozone Monitoring Instrument
141	(OMI) be used to assess global data quality in sondes after 2004 (Chapter 5 in Smit, Thompson,
142	and ASOPOS 2.0, 2021). For example, the post-2013 ozonesonde TCO "dropoff", first noted at
143	Costa Rica in reprocessed SHADOZ data (Thompson et al., 2017) and at several NOAA
144	stations (Sterling et al., 2018) was identified with OMI comparisons. Likewise, with Aura's
145	Microwave Limb Sounder (MLS) giving very stable ozone measurements for 18 years, ASOPOS
146	2.0 recommends the use of MLS profiles to track data quality in the stratospheric segment of the
147	sondes. Thus, using a combination of OMI and MLS from 2004-2019, Stauffer et al. (2020;
148	"S20" hereafter) were able to demonstrate that most of the unexpected low ozone at $\sim 1/3$ of 37
149	stations worldwide is due to anomalous apparent losses in the lower and middle stratosphere.
150	Other than at the Hilo and Costa Rica stations, no systematic low bias in tropospheric
151	measurements was found. The anomalously low tropospheric ozone found at those two stations
152	may or may not be related to the TCO drop. Several potential sources of the bias, including the
153	radiosondes paired with the ozonesondes and radiosonde pressure offsets (Steinbrecht et al.,
154	2008; Stauffer et al., 2014; Inai et al., 2015) were ruled out. The TCO drop appeared only at
155	stations launching the EnSci ECC. Manufacturing changes in the EnSci ECC were suspected as a
156	contributor, as an analysis of serial numbers (S/Ns) revealed that the sudden drop and a
157	consistent low ozone bias began approximately with S/N 25000 (~2013-2014, depending on
158	station) when considering all affected stations.

Since the revelation that significant portions of the global network appear to be affected by this problem, ASOPOS 2.0 formed a Task Team to more closely examine the TCO drop and expand the analysis to additional ozonesonde stations. Efforts have been focused on metadata gathering, additional laboratory and field tests, and enhanced data analysis, the last of which is the subject of this paper. Our intentions are: (1) to provide the community with an update on the current state of the stability and quality of ozonesonde data in the global network, and (2) better characterize the TCO drop throughout the global network.

This study is the first application of the ASOPOS 2.0 recommendations for data quality 166 evaluation to data collected from the global ozonesonde network since 2004. Measurements are 167 taken from 60 stations for which data are publicly available. We extend the records of the 37 168 169 stations analyzed in S20 and feature more homogenized data than the earlier study. The paper is organized as follows: Section 2 describes the data sets and methods used to assess the global 170 ozonesonde network data; Section 3 presents the time series of ozonesonde and satellite 171 172 comparisons for the network in various latitude bands, and a detailed analysis of EnSci S/Ns to better pinpoint the timing of the dropoff and quantify the resulting step change in ozone. We also 173 174 discuss the next steps that the ASOPOS Task Team will pursue to solve the TCO drop. Section 4 is a summary, and advocates standard operating procedures to monitor the future stability of 175 176 network data against changes to instrumentation or preparation procedures, and to quantify the effects of ozonesonde data homogenization. 177

178 **2 Data and Methods**

We employ satellite data as our primary reference to evaluate global ozonesonde network
data because independent ground-based TCO data are unavailable at some stations.

181 **2.1 Ozonesonde Data at 60 Global Stations**

A total of 60 global ozonesonde stations are analyzed to assess the recent stability of the 182 large majority of global network data. All but one station, Hohenpeissenberg (Brewer-Mast type; 183 Steinbrecht et al., 1998), currently launch ECC ozonesondes from the two major manufacturers, 184 185 EnSci and SPC. Ozonesonde stations included in this analysis appear on the map in Figure 1, 186 with S20 dropoff stations indicated by the red dots (see Section 2.3 for a brief note on corrected Canadian data; orange dots). Metadata and the data repository accessed for each station are 187 188 contained in Table 1. Of the 60 ozonesonde sites, 37 have had their data homogenized according 189 to ASOPOS/ASOPOS 2.0 standards (Section 1). There are 42,042 ozonesondes analyzed for the 190 60 stations in our study period of August 2004 to present.

All ozonesonde profile data are first placed into 100 m binned averages. To obtain TCO from the ozonesondes, an identical method to S20 is used: The ozonesonde ozone is integrated up to 10 hPa or balloon burst, whichever is lower in altitude, and the **McPeters and Labow** (2012) ozone climatology is added to that value to obtain TCO. Any ozonesonde not reaching 30 hPa is discarded from the TCO data set.

196 **2.2 Satellite and Ground-Based Ozone Data**

Satellite TCO and stratospheric ozone profile data are used as references to evaluate the
quality of the past 18 years (since mid-2004) of global ozonesonde network data. Ground-based
TCO (Dobson, Brewer, SAOZ) measurements from the World Ozone and Ultraviolet Data
Centre (WOUDC) are available at 40 of the 60 stations (**Table 1**). While ground-based TCO
comparisons are typically preferred over satellite data, unfortunately, as discussed in S20, a
number of the affected dropoff stations (e.g., Costa Rica, San Cristóbal, Ascension, Fiji,

Kelowna, Yarmouth) do not have ground-based measurements available. However, the
characteristics of the ozonesonde dropoff and sudden TCO low bias at stations such as Hilo are
identified by both satellite and ground-based Dobson and Brewer data (see Figure S4 in S20).
Level 2 (L2) satellite TCO and stratospheric ozone overpass data from multiple satellites are
available at all 60 stations.

208 All L2 satellite overpass data are collected from NASA/GSFC's Aura Validation Data Center (AVDC; https://avdc.gsfc.nasa.gov/pub/data/satellite/). There are five satellite 209 210 instruments included for analysis. For TCO, we use Aura OMI (McPeters et al., 2008; 2015), 211 the Suomi National Polar-orbiting Partnership Ozone Mapping and Profiler Suite (OMPS; 212 McPeters et al., 2019), the Meteorological Operational satellites A/B Global Ozone Monitoring 213 Experiment-2 (MetOp-A/B GOME-2A/2B; Munro et al., 2016), and for stratospheric ozone Aura MLS (Froidevaux et al., 2008; Livesey et al., 2021). The Aura MLS instrument team 214 215 recently released the v5 ozone data used here (Livesey et al., 2022), which show negligible differences in the stratosphere compared to v4.2 (used in S20; MLS Version 5.0x Level 2 and 3 216 data quality and description document: Livesey et al., 2021). 217

MetOp-A (GOME-2A) was retired in November 2021 and data are unavailable thereafter. In general, GOME-2A/B measure higher TCO amounts than OMI and OMPS (**Figure S1**), a result consistent with that observed in comparisons to the ozonesonde data in Section 3, and in the analysis of GOME-2A/B compared to ground-based Dobson and Brewer TCO by **Hao et al.** (2014). OMI has a continuous, nearly 18-year record and is the primary satellite TCO instrument used in our analysis.

The ozonesonde/satellite overpass coincidence criteria are as follows: For satellite TCO 224 comparisons, the L2 data are restricted to within 12 hours and 100 km of the ozonesonde launch. 225 226 The ± 12 hour coincidence criterion was chosen to ensure that virtually every ozonesonde had a candidate satellite TCO comparison (e.g., to account for days when the station was located 227 between satellite measurement swaths). No filtering for satellite cloud fraction is applied. As 228 discussed in S20, cloud fraction filtering produces no appreciable change to our results. Only one 229 satellite TCO measurement (closest in time and space) from each instrument is matched to each 230 ozonesonde. An addition to this analysis is that satellite/ozonesonde (and ground-based) TCO 231 differences beyond $\pm 20\%$ are discarded as outliers, although this is rare. Just 0.8%, or 246 of all 232 ozonesonde/OMI TCO comparisons exceed $\pm 20\%$. These outliers are mostly confined to mid- to 233 high-latitudes, but no clear pattern emerges to otherwise explain the causes for the cases of poor 234 agreement. For Aura MLS stratospheric ozone, all ozone profiles within 1 day, $\pm 5^{\circ}$ latitude, and 235 $\pm 8^{\circ}$ longitude of the ozonesonde are averaged, and the 100 m-averaged ozonesonde data are 236 237 linearly interpolated to the MLS pressure levels to make comparisons. As with S20, the MLS weighting functions are not applied to the ozonesonde data. 238

239 Comparisons among satellite and ground-based TCO data are included in **Figure S1**. 240 These indicate the relative stability of satellite TCO compared to ground-based measurements 241 during our study period, and that the satellite TCO data are a consistent reference suitable for 242 characterizing the ozonesonde network data quality.

The total number of available ozonesonde comparisons are as follows: 30,751 for OMI (Oct. 2004-present), 19,280 for OMPS (Jan. 2012-present), 22,026 for GOME-2A (Jan. 2007-Nov. 2021), 15,317 for GOME-2B (Jan. 2013-present), and 39,703 for Aura MLS (Aug. 2004present).

2.3 Focus of Analysis: Ozonesonde Network Data Stability and TCO Drop Status

Our primary focus is on expanding the analysis of ozonesonde/satellite TCO and 248 stratospheric ozone comparisons to assess the accuracy and stability of ozonesonde network data 249 over the past two decades. The 14 S20 "dropoff" stations will still be used here as a reference to 250 characterize the effects of the TCO drop, and an analysis of ECC S/Ns is leveraged to investigate 251 252 potential biases at "unaffected" stations including the 23 stations not appearing in S20 (total of 46 "non-S20" stations). To quantify the magnitude of the TCO drop, we determine the timing, 253 254 based on EnSci S/N, of a step change in ozonesonde TCO using the Matlab function ischange, 255 which locates breakpoints in a time series by finding abrupt changes to the mean values for 256 segments of the dataset. Detailed documentation on *ischange* can be found at 257 https://uk.mathworks.com/help/matlab/ref/ischange.html, which is based on work by Killick et al., (2012). The function was applied to the OMI and EnSci ECC TCO percentage differences for 258 259 the EnSci S/Ns at the 14 S20 stations. The *ischange* function iteratively minimizes cost functions to determine how well segments of the dataset are represented by its mean, and we use this 260 method to identify the single largest change in the mean of the OMI and EnSci ECC TCO 261 comparisons. 262

Of the 60 global stations used here, 37 have homogenized their time series (see **Table 1**). It should be noted that step changes in TCO of both signs are found in the data of a select few non-homogenized stations (e.g. Scoresbysund and Idabel for EnSci, Legionowo for SPC). The step changes in non-homogenized time series can be significant as shown in previous studies (e.g., **Witte et al., 2017; Sterling et al., 2018; Ancellet et al., 2022**). However, these are often the result of instrumental, station operational, or data processing changes, and are typically removed with homogenization.

Since the publication of S20, the data from two Canadian "dropoff" stations, Kelowna 270 and Yarmouth, have been properly homogenized by applying a transfer function for use of the 271 272 1% KI, full buffer SST in the EnSci ozonesonde (Deshler et al., 2008). The resulting update to the Canadian data homogenization reduces the pre-2015 EnSci TCO by approximately 4%. The 273 corrected versions of the data are used here, which indicates that Kelowna and Yarmouth are not 274 nearly as affected by the TCO drop as reported in S20, although a small dropoff remains at both 275 stations (Kelowna is shown in Figure S2). The Canadian network has since switched to the SPC 276 ozonesonde, mitigating the ~2-3% TCO drop found in the network's EnSci time series (Figure 277 **S3**). For simplicity, we retain the 14 S20 TCO drop stations in this analysis to describe the 278 effects of the dropoff. As indicated below, data users should refer to Table 2 to gauge the effects 279 of the TCO drop at EnSci stations in this analysis. Because of the corrected Kelowna and 280 Yarmouth data, corrections to the applied stratospheric pump efficiencies at Costa Rica in 2013-281 2015, and the addition of 23 more stations including several with newly homogenized data, the 282 283 results here supersede those presented in S20. The focus of our analysis is as follows: 1) In light of the TCO dropoff, we assess the 284 overall stability of the global ozonesonde network data and examine the ozonesonde time series

from stations grouped into latitudinal bands, commonly used to report ozone trends in the 286

WMO/UNEP Ozone Assessment Reports and related activities (WMO, 2018; 287

285

Petropavlovskikh et al., 2019). 2) We scrutinize the S/Ns of the ECCs to pinpoint step changes 288 in the global network data, and more precisely define which and to what degree stations are 289 affected by the TCO drop. 290

291 **3 Results**

292

3.1 Ozonesonde Comparisons with Five Satellite Instruments since 2004

We begin with an analysis of the past ~18 years of ozonesonde network data compared to 293 satellite measurements to examine the overall stability of the measurements. Since ozonesonde 294 295 ozone trends are typically computed for stations within prescribed latitude (ϕ) bands, we examine ozonesonde/satellite TCO and stratospheric ozone comparisons for various latitudinal 296 regions. In Figure 2 we present the time series of ECC TCO and stratospheric ozone 297 298 comparisons with the five satellite instruments for all 60 stations. The top panel of Figure 2 shows the comparisons with Aura MLS on MLS pressure levels, which gives no indication of 299 any sustained low or high biases in the stratosphere above 50 hPa. The Figure 2 middle panel 300 shows the time series of 500-point centered, moving averages for TCO comparisons in percent 301 302 difference. The moving average comparisons with OMI deviate by no more than $\pm 2\%$ over the 303 18-year record. In general, the ozonesondes measure lower relative to GOME-2A/B, as is also the case for the ground-based TCO data compared to GOME-2A/B (see Figure S1). 304

The bottom panel of **Figure 2** shows the 25th to 75th percentile, and median comparisons with the four TCO satellite instruments for each year from 2005-2021. The middle and bottom panels of **Figure 2** indicate a slight drop in the ozonesonde measurements relative to satellite data in 2016-2018. However, for all four satellite instruments and for each year, the interquartile range of the TCO comparisons always encompasses the 0% line. Considering all available data, the means \pm one standard deviation of ozonesonde TCO comparisons with the four satellite instruments for the 60 global stations are $+0.0 \pm 4.8\%$ ($\mu \pm 1\sigma$; OMI), $-0.8 \pm 4.8\%$ (OMPS), -1.9

312	\pm 4.9% (GOME-2A), and -2.2 \pm 4.8% (GOME-2B). Overall, the global ozonesonde network data
313	are remarkably accurate and stable relative to the satellite data since late 2004.

-	2	1	/

314	Figures 3-5 present the same analysis as Figure 2 for various latitudinal groupings of
315	ozonesonde stations. The ozonesonde measurements at polar stations ($ \phi \ge 60^\circ$; 17 stations)
316	shown in Figure 3 are arguably more stable relative to the satellite TCO than the network as a
317	whole in Figure 2. Again, the ozonesondes measure lower relative to GOME-2A/B compared to
318	OMI and OMPS. This is a common feature across all latitudes. The midlatitude stations (Figure
319	4; $20^{\circ} \le \phi < 60^{\circ}$; 31 stations) display a similar pattern in the time series as the entire global
320	network, which is not surprising since mid-latitudes comprise the densest distribution of stations.
321	A small decrease in the ozonesonde TCO measurements relative to satellites is noted between
322	\sim 2017-2018. However, the deviation of the OMI comparison moving averages in Figure 4 never
323	exceeds $\pm 2\%$, and the interquartile range of the comparisons for each year encompasses the 0%
324	line for all four satellite TCO instruments in both Figures 3 and 4. We note the apparent annual
325	cycle, which is out of phase for OMI/OMPS and GOME-2A/B, in the ozonesonde/satellite
326	comparisons at the mid-latitude stations in Figure 4. This cycle in GOME-2A/B TCO is clearly
327	shown by Hao et al., (2014; their Figure 13), which also indicates that GOME-2A/B measure
328	about 1 to 2% higher than ground-based Dobson and Brewer TCO, and matches our results.

The tropical ozonesonde stations (**Figure 5**; $|\phi| < 20^{\circ}$; 12 stations) measure within approximately 0 to -2% relative to OMI TCO for the entire period from 2005-2014. After 2014, there is a marked decrease in ozonesonde stratospheric ozone mixing ratio and TCO compared to satellites. The maximum low bias occurs in 2016-2017, when the tropical ozonesondes average 4-6% low relative to the satellite TCO. A notable drop in the stratospheric ozone comparisons with Aura MLS also appears during this period, indicated by the increased blue coloring on the

top panel of Figure 5. The overall means and standard deviations of ozonesonde comparisons 335 with the four satellite instruments for the 12 tropical stations are $-2.2 \pm 4.0\%$ (OMI), $-2.9 \pm 3.8\%$ 336 337 (OMPS), $-2.8 \pm 4.1\%$ (GOME-2A), and $-4.0 \pm 3.9\%$ (GOME-2B). Even prior to the low bias period that begins in 2014, the tropical ozonesondes measure consistently low relative to the 338 satellite TCO. The ozone partial pressure peak at tropical latitudes occurs at approximately 20 339 hPa, compared to ~50 hPa at mid- and high-latitudes. Thus, stratospheric pump efficiency 340 corrections have more impact on the calculation of ozone partial pressure and TCO in the tropics, 341 and any under/overestimation of applied ECC pump efficiencies will have a larger effect in the 342 tropics compared to the extratropics. This is a topic for further investigation by the ASOPOS 2.0 343 panel. 344

345 The low biases in the tropical ozonesonde network improved slightly after 2017, with a relative increase in the ozonesonde measurements of about 2% TCO in the past 3-4 years. 346 However, the TCO drop of several percent relative to satellite measurements from 2014-2017 347 may affect calculations of ozone trends using tropical ozonesonde data. Data users are advised to 348 proceed with caution when computing tropical TCO and stratospheric ozonesonde trends over 349 the past ~two decades. While we show that, on average, tropical stations show larger TCO low 350 biases associated with the TCO drop, it is important to note that not all tropical stations are 351 affected by this sudden low bias. More discussion on the dropoff affected stations and 352 magnitudes of the TCO drop are found in Section 3.2. 353

Figure 6 provides a closer examination of the stratospheric ozonesonde measurement comparisons with the Aura MLS instrument since late 2004. The profile comparisons in percent difference (25th, 50th, and 75th percentiles) are presented for the same groups of stations (**Figure 6a-d**) as in **Figures 2-5**. In general, the ozonesonde network agreement with Aura MLS is

excellent, and lies within $\pm 5\%$ from 50 to 10 hPa. Because a number of factors can decrease the 358 reliability of ozonesonde data above 10 hPa (e.g., the effects of boiling or freezing ozonesonde 359 360 solutions, decreasing ozonesonde pump efficiencies/increasing pump efficiency uncertainties), we choose to halt ozonesonde integration at 10 hPa prior to adding the McPeters and Labow 361 (2012) above-burst climatology when computing the ozonesonde TCO (as in S20). The tropical 362 (Figure 6d) stratospheric ozonesonde profiles measure slightly low relative to MLS compared to 363 the other latitude bands, a result likely compounded by the increased low bias from 2014 to 2018 364 noted in the Figure 5 top panel. As S20 showed, the dropoff appears to be confined to pressures 365 above ~50 hPa, except at Hilo and Costa Rica where there is anomalously low ozone in the 366 troposphere. With these two exceptions, tropospheric ozone data from sondes are reliable for 367 determining ozone trends in the tropics (Thompson et al., 2021). 368

Figures 2-6 show that the TCO dropoff described in S20 has only a minor effect on the overall stability of global ozonesonde network data, and that the data should be considered reliable for trends analysis. However, when considering only tropical stations, the TCO drop will potentially have a detectable effect on ozone trends. The rest of the analysis focuses on expanding the S20 analysis to characterize the effects and timing of the TCO drop found at a subset of stations.

375 **3.2 Status Update to the TCO Dropoff**

Figures 2-6 indicate that the effects of the TCO drop described in S20 are most pronounced in the tropical ozonesonde network. As yet, undetermined manufacturing changes to the EnSci ozonesonde are suspected to be a factor in the TCO drop. Because S/N is a better

indicator of a potential manufacturing change than date of ozonesonde launch, the remainder of
our analysis focuses on ECC S/Ns to pinpoint the timing of the dropoff.

Figure 7 updates a similar ECC S/N analysis that was presented in S20 (see also Figure 381 S3). The bars on Figure 7 span the 25th to 75th percentiles in percent TCO agreement with OMI 382 383 for EnSci S/Ns placed in bins of 1000, with the dots representing the median value. Total valid 384 ECC/OMI comparisons are indicated by the numbers along the top and bottom of the figure for each S/N bin of 1000. The EnSci S/Ns from the 14 S20 stations are shown on (a), and the EnSci 385 386 S/Ns from the remaining "non-S20" stations are shown on (b). Panel (a) in Figure 7 makes clear 387 the effects of the TCO drop on the ozonesonde comparisons with OMI after S/N 25000. The 388 dropoff is approximately 3 to 5% when considering the 14 stations. There is also a notable drop 389 for S/N ~21-22000s, a "recovery" for 23-24000s, and a sharp drop and persistent low bias 390 beginning with 25000. Figure 7b shows that the non-S20 dropoff stations' median TCO 391 comparisons with OMI have remained within $\pm 2\%$ for all S/Ns through the 35000s. Figure 7b 392 also illustrates to importance of ongoing ozonesonde data evaluation, as the most recent data (36000-38000) display a median low bias of up to 2.6%. 393

394 This expanded analysis of 60 global stations confirms that only the EnSci ECC displays 395 the characteristics of the ozonesonde TCO drop. Figure 8 shows an identical analysis to Figure 7 for all SPC 6A ozonesondes. Note that the similar S/N values to EnSci are a coincidence. The 396 397 variation in TCO agreement in the SPC 6A S/N bins is larger than that for the 46 non-S20 EnSci stations. This suggests that SPC ECCs are also subject to possible variations in production and 398 thus data quality. However, there are no extended periods of high or low biases similar to those 399 displayed by the S20 dropoff stations in Figure 7a. For this reason, we confine the rest of our 400 401 TCO drop analysis to the EnSci ECCs.

402	A closer examination of the individual EnSci S/Ns, rather than through binning them into
403	sets of 1000, allows a better estimate of the timing of the step change in ozonesonde TCO
404	agreement with OMI. The location of the step change was determined using the Matlab function
405	ischange, which is found at EnSci S/N 25250. We use the 25250 S/N as a reference to divide the
406	ozonesondes into two groups to quantify a single step change in ozonesonde TCO for all EnSci
407	stations. There is a nearly 4% (from +0.42 to -3.5%) TCO drop relative to OMI for the 14 S20
408	stations after S/N 25250 as shown in Figure 9a. Prior to S/N 25250, the standard deviation of the
409	EnSci/OMI comparisons is 4.3%, and after S/N 25250 it is 4.4%. This indicates that the TCO
410	drop is indeed a step change, with no change to the variance in the TCO comparisons with OMI.
411	This potentially means that the uncertainties of the affected EnSci ozonesonde measurements
412	have not increased, but future analyses are still needed to fully characterize these results.
413	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations
413 414	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean
413 414 415	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20
413414415416	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20 station step-changes in the mean values from pre- to post-S/N 25250 are statistically significant
 413 414 415 416 417 	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20 station step-changes in the mean values from pre- to post-S/N 25250 are statistically significant based on a 95% confidence interval (see text on Figures 9a and 9b). This interval is determined
 413 414 415 416 417 418 	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20 station step-changes in the mean values from pre- to post-S/N 25250 are statistically significant based on a 95% confidence interval (see text on Figures 9a and 9b). This interval is determined using 10,000 bootstrap resamples of each distribution to generate the confidence bounds around
 413 414 415 416 417 418 419 	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20 station step-changes in the mean values from pre- to post-S/N 25250 are statistically significant based on a 95% confidence interval (see text on Figures 9a and 9b). This interval is determined using 10,000 bootstrap resamples of each distribution to generate the confidence bounds around the mean value (Efron 1979; Efron and Tibshirani 1993). The 1% TCO drop for non-S20
 413 414 415 416 417 418 419 420 	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20 station step-changes in the mean values from pre- to post-S/N 25250 are statistically significant based on a 95% confidence interval (see text on Figures 9a and 9b). This interval is determined using 10,000 bootstrap resamples of each distribution to generate the confidence bounds around the mean value (Efron 1979; Efron and Tibshirani 1993). The 1% TCO drop for non-S20 stations appears to support the hypothesis posed in S20 that a production change in the EnSci
 413 414 415 416 417 418 419 420 421 	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20 station step-changes in the mean values from pre- to post-S/N 25250 are statistically significant based on a 95% confidence interval (see text on Figures 9a and 9b). This interval is determined using 10,000 bootstrap resamples of each distribution to generate the confidence bounds around the mean value (Efron 1979; Efron and Tibshirani 1993). The 1% TCO drop for non-S20 stations appears to support the hypothesis posed in S20 that a production change in the EnSci ozonesonde is a factor leading to the dropoff, which leads to station-specific preparation
 413 414 415 416 417 418 419 420 421 422 	The same analysis technique applied to all the EnSci ozonesondes at the non-S20 stations (Figure 9b) indicates that there may also be a detectable TCO drop, albeit just over 1% (mean differences with OMI change from +0.68 to -0.39%), at those stations. Both the S20 and non-S20 station step-changes in the mean values from pre- to post-S/N 25250 are statistically significant based on a 95% confidence interval (see text on Figures 9a and 9b). This interval is determined using 10,000 bootstrap resamples of each distribution to generate the confidence bounds around the mean value (Efron 1979; Efron and Tibshirani 1993). The 1% TCO drop for non-S20 stations appears to support the hypothesis posed in S20 that a production change in the EnSci ozonesonde is a factor leading to the dropoff, which leads to station-specific preparation procedures, sensing solution type, or other factors mitigating, or amplifying the effects of this

The largest TCO drop for the EnSci ECCs is found relative to OMI. The S20 station TCO drops compared to the other three satellite instruments (**Figure S4**) are smaller in magnitude at less than 3%. The TCO drops for the non-S20 stations are statistically *insignificant* for OMPS and GOME-2A (**Figure S5**). Determining whether there has been a drift in OMI TCO or one of the other three satellites is beyond the scope of this paper, but the smaller ozonesonde TCO drops relative to OMPS, GOME-2A, and GOME-2B, albeit with shorter available time series, are an important consideration.

The pre- and post-S/N 25250 percent change in TCO relative to OMI for each station is 431 432 shown in Table 2, provided that 25 valid OMI comparisons are available for both periods. When 433 considering *all* EnSci ECCs, the pre- to post-S/N 25250 TCO drop relative to OMI is 1.8%. 434 Time series of comparisons with the five satellite instruments (including GOME-2C) are posted to https://tropo.gsfc.nasa.gov/shadoz/SHADOZ PubsList.html so that users can examine the 435 ozonesonde data stability relative to satellite measurements for all 60 stations since late 2004. 436 Table 2 should be used in conjunction with the posted station time series to assess the potential 437 effects of the EnSci TCO drop, and to identify other biases or step changes in the ozonesonde 438 data at specific stations. 439

The effects of the TCO drop on the ozonesonde stratospheric profiles relative to Aura MLS measurements are shown in **Figure 10**. The S20 stations (**Figure 10a**) show roughly a 3-5% decrease in stratospheric ozone, with the median post-S/N 25250 values being lower than MLS at all pressure levels from 56.23 to 6.81 hPa. The non-S20 stations (**Figure 10b**) show a smaller drop of 1-2% ozone relative to MLS from pre- to post-S/N 25250. Oscillations in the Aura MLS ozone profiles, which have been reduced but still exist in the v5 data (**Livesey et al.**, **2022**), in the tropical upper troposphere/lower stratosphere make it difficult to exactly quantify the stratospheric ozone drop at and below the 56.23 hPa level. However, other than the Costa
Rica and Hilo stations previously mentioned, we do not find evidence that the TCO drop affects
altitudes/pressures below this pressure level or in the troposphere.

450 **3.3**

3.3 Potential Indicators of the Source of the Dropoff

451 We explore a possible relationship of the TCO drop with the SST used at each station. Three SSTs are currently in use in the global network: 1% KI, full buffer (SST1.0); 0.5% KI, 452 half buffer (SST0.5); 1.0% KI, one-tenth buffer (SST0.1; "low-buffer"). Tropical/subtropical 453 stations are where the largest and most persistent TCO drops are found. Five of the seven 454 tropical S20 EnSci stations use SST0.1 (Hilo, Costa Rica, San Cristóbal, Fiji, and Samoa) and 455 show a larger post-S/N 25250 dropoff compared to the two SST0.5 stations (Nairobi and 456 Ascension Island; 3.8% average for SST0.1 vs. 2.7% average for SST0.5; Ascension Island is 457 listed at "N/A" in Table 2 because it did not launch EnSci ECCs prior to S/N 25250). Given this 458 459 fact and the results of Figure 9b, which indicate that non-S20 stations may also show small TCO drops, it is prudent to examine SST0.1 stations outside of tropical/subtropical latitudes. 460

Figure S6a presents an analysis of the EnSci S/Ns at three stations in the Contiguous 461 U.S. (CONUS): Trinidad Head, Boulder, and Huntsville, that have used SST0.1 since 2005 462 (Sterling et al., 2018). The three stations show a TCO drop of 1.7% (significant with > 95% 463 464 confidence) relative to OMI after EnSci S/N 25250, and now average -1.43% TCO relative to OMI. Figure S6b shows the Boulder EnSci S/N comparisons with the co-located Dobson TCO, 465 which confirms the OMI results. The Boulder ozonesondes show a sharp 1.8% TCO drop (again, 466 significant with > 95% confidence) relative to the Dobson after S/N 25250. From the results 467 presented above, it appears that all EnSci stations may be subject to some change in ECC 468

469	performance related to the TCO drop, with the magnitude of effects possibly dependent on
470	station-specific characteristics such as the SST formula. Although our analysis suggests a
471	potential role for SST type in the dropoff, this must be empirically tested in the laboratory and
472	field before drawing definitive conclusions. In general, SST0.5, which is the ASOPOS-
473	recommended SST for the EnSci ECC, is apparently less affected at global network stations. We
474	point out that several stations using the low-buffer SST0.1 solution are affected by the TCO
475	drop. However, the S20 study effectively ruled out other potential sources of the sudden EnSci
476	low bias including the type of radiosonde paired with the ozonesondes and radiosonde pressure
477	offsets (Steinbrecht et al., 2008; Stauffer et al., 2014; Inai et al., 2015).
478	A large dataset of lab-measured EnSci pump efficiency corrections by Nakano and
479	Morofuji (2022) shows that changing stratospheric pump efficiencies are a potential contributor
480	to the TCO drop. Their analysis indicates that larger pump efficiency corrections above 50 hPa
481	are necessary for EnSci ECCs beginning with S/N ~25000 (see their Figure 15). Raw
482	ozonesonde ECC cell currents are processed using an average pump efficiency that is assumed to
483	not vary significantly based on ECC production and S/N. However, application of the larger
484	Nakano and Morofuji (2022) pump efficiency corrections after S/N 25000 will increase EnSci
485	ECC stratospheric ozone and TCO. Also note on their Figure 15 the lower pump efficiency
486	corrections for S/N 24000s, which corresponds to the high-biased ozonesonde TCO for S20
487	stations on Figure 7a.
488	The ASOPOS Task Team will quantify the effects that the Nakano and Morofuji (2022)

490 with the application of their lab-measured pump efficiencies. A change to the EnSci stratospheric

489

pump corrections have on EnSci ozone time series, and determine if the TCO drop is mitigated

491 pump efficiencies would explain why it appears that, on average, all EnSci stations may show at

492	least a small TCO drop coincident with S/N 25250. Furthermore, because the tropical
493	stratospheric ozone peak is found at higher altitudes/lower pressures compared to mid- and high-
494	latitude stations, larger than expected EnSci stratospheric pump efficiency corrections would
495	disproportionally affect TCO at tropical sites, potentially explaining the clustering of S20
496	stations in the tropics.

498

A discussion on our communications with the EnSci manufacturer is found in the Supplementary Material.

499

4 Summary and Discussion

We have presented the first examination of data quality from the 60-station global 500 ozonesonde network using the ASOPOS 2.0 guidelines that recommend comparison of sonde 501 TCO and stratospheric ozone profiles with consistently calibrated and updated satellite data. We 502 evaluated ozonesonde network data since late 2004 by comparing satellite TCO and stratospheric 503 ozone measurements with $\sim 40,000$ ECC profiles from the 60 stations. This investigation extends 504 our 37-station S20 study and adds measurements from 2020-2022. The expanded analysis 505 reveals that overall, the ozonesonde measurements are stable and accurate relative to satellite 506 TCO and stratospheric measurements over the past 18 years. Average ozonesonde TCO 507 comparisons with Aura OMI remain within $\pm 2\%$ for each year from 2005 to 2021. Ozonesonde 508 TCO stability is slightly better relative to OMPS and GOME-2A/B, over shorter periods. 509 Stratospheric ozone measurements from ozonesondes also agree within $\pm 5\%$ of Aura MLS data 510 for all stations and pressure levels from 50 to 10 hPa. However, the TCO dropoff affects about 511 half of tropical (±20° latitude) ECC stations, with an overall average 4-6% TCO low bias relative 512 to four satellite instruments in 2016-2017 at tropical latitudes. A new dataset of lab-measured 513

EnSci stratospheric pump efficiencies offers a promising path toward investigating the role of the
ECC pump for TCO drop-affected station data (Nakano and Morofuji, 2022).

The results described above reinforce the importance of following the ASOPOS 2.0 516 guidelines for continuous evaluation of ECC sonde data quality with satellite observations as 517 518 well as with co-located ground-based instruments: Dobson, Brewer, SAOZ, Fourier Transform 519 InfraRed (FTIR), Microwave (MW), lidar. TCO data from OMI, OMPS, GOME-2A/B, and stratospheric ozone profile data from Aura MLS are available as L2 overpass files for all 60 520 521 stations used in this analysis, and dozens more (websites in Acknowledgments and Data 522 Availability Statement). The availability of these files eliminates cumbersome downloading of 523 full satellite ozone datasets. With such streamlining, the sonde community has an "early warning 524 system" for unexpected changes to a station's instrumentation or preparation procedures. The satellite and ground-based instrument comparisons also serve as a guide for homogenizing data 525 526 from ozonesonde time series. Comparisons among ozonesonde and satellite data since the beginning of the Aura OMI record in late 2004 for all 60 stations used in this study have been 527 posted to https://tropo.gsfc.nasa.gov/shadoz/SHADOZ PubsList.html. 528

Finally, our assessment has shown that the global ozonesonde network data are of exceptionally high quality overall. This is especially true given the success of ozonesonde data homogenization that has been applied to dozens of stations, reducing or eliminating step changes and biases in the non-homogenized time series. The metric of 5% uncertainty in the ozonesonde measurement, requested by the satellite and trends communities is nearly achieved. As data from additional stations are homogenized, users will see greater uniformity in ozone profile quality throughout the global network data.

537 Acknowledgments

The data analysis that contributed to this paper is part of an ongoing effort by the 538 539 ASOPOS 2.0 Panel and ozonesonde colleagues to quantify global ozonesonde network data quality and to solve the TCO dropoff. The authors express appreciation to the Network for the 540 Detection of Atmospheric Composition Change (NDACC) Ozonesonde Working Group and 541 542 Steering Committee. The ozonesonde data collected and presented here represent the combined effort of hundreds of ozonesonde community members around the globe, for which we are 543 grateful. We are also grateful for the open communication from EnSci to help solve the source of 544 the ozonesonde TCO drop. Funding for this work was graciously provided through support of 545 SHADOZ and NDACC by the NASA Upper Atmosphere Research Program and Upper 546 Atmospheric Composition Observations Program (UARP and UACO; Dr. Kenneth Jucks 547 program manager) to NASA/GSFC (R. M. Stauffer, PI). Special thanks to Universidad San 548 Francisco de Quito (USFQ) and to Dr. María Cazorla, PI, for providing and making public the 549 550 ozonesonde data from Ecuador (Cazorla et al., 2021). 551

552 **Open Research**

553 The following URLs were accessed for ozonesonde data, and specific stations

corresponding to the various archives can be found in Table 1 of this manuscript: National

- 555 Oceanic and Atmospheric Administration (NOAA):
- 556 <u>ftp://ftp.gml.noaa.gov/data/ozwv/Ozonesonde/;</u> Harmonization and Evaluation of Ground Based
- 557 Instruments for Free Tropospheric Ozone Measurements (HEGIFTOM):
- 558 <u>http://hegiftom.meteo.be;</u> Universidad San Francisco de Quito (USFQ): <u>https://observaciones-</u>
- 559 <u>iia.usfq.edu.ec/</u>; Network for the Detection of Atmospheric Composition Change (NDACC):

- 560 <u>https://www-air.larc.nasa.gov/missions/ndacc/data.html;</u> World Ozone and Ultraviolet Data
- 561 Centre (WOUDC): <u>https://woudc.org/data/explore.php?lang=en</u>
- 562 (http://dx.doi.org/10.14287/10000008); SHADOZ:
- 563 <u>https://tropo.gsfc.nasa.gov/shadoz/Archive.html</u> (https://doi.org/10.57721/SHADOZ-V06);
- 564 Tropospheric Ozone Pollution Project (TOPP): http://www.ruf.rice.edu/~ozone/. Ground-based
- 565 TCO data were downloaded from WOUDC: <u>https://woudc.org/data/explore.php?lang=en</u>
- 566 (http://dx.doi.org/10.14287/10000004). Aura MLS v5 L2 ozone profile overpass data were
- 567 downloaded at <u>https://avdc.gsfc.nasa.gov/pub/data/satellite/Aura/MLS/V05/L2GPOVP/O3/</u>.
- 568 OMI, OMPS, GOME-2A, and GOME-2B L2 TCO overpass data were downloaded at
- 569 <u>https://avdc.gsfc.nasa.gov/pub/data/satellite/Aura/OMI/V03/L2OVP/OMTO3/</u>,
- 570 <u>https://avdc.gsfc.nasa.gov/pub/data/satellite/Suomi_NPP/L2OVP/NMTO3-L2/</u>,
- 571 <u>https://avdc.gsfc.nasa.gov/pub/data/satellite/MetOp/GOME2/V03/L2OVP/GOME2A/, and</u>
- 572 <u>https://avdc.gsfc.nasa.gov/pub/data/satellite/MetOp/GOME2/V03/L2OVP/GOME2B/</u>. Time
- series of the comparisons of satellite and ozonesonde data for all 60 stations used in this study
- 574 can be found at <u>https://tropo.gsfc.nasa.gov/shadoz/SHADOZ_PubsList.html</u>. All analyses were
- 575 performed using the MATLAB 2017b software package
- 576 (https://uk.mathworks.com/help/matlab/release-notes-R2017b.html).
- 577

578 **References**

- 579 Ancellet, G., Godin-Beekmann, S., Smit, H. G. J., Stauffer, R. M., Van Malderen, R., Bodichon,
- 580 R., & Pazmiño, A. (2022). Homogenization of the Observatoire de Haute Provence ECC
- 581 ozonesonde data record: comparison with lidar and satellite observations, *Atmospheric*
- 582 *Measurement Techniques*, 15, 3105–3120, https://doi.org/10.5194/amt-2022-7.
- Boyd, I., Bodeker, G., Connor, B., Swart, D., & Brinksma, E. (1998). An assessment of ECC
- ozone sondes operated using 1% and 0.5% KI cathode solutions at Lauder, New Zealand.

585 *Geophysical Research Letters*, 25, 2409–2412, doi:10.1029/98GL01814.

- 586 Cazorla, M., Parra, R., Herrera, E., da Silva, F., R. (2021). Characterizing ozone throughout the
- atmospheric column over the tropical Andes from in situ and remote sensing observations.
- 588 *Elementa: Science of the Anthropocene* 21, 9 (1): 00019.
- 589 https://doi.org/10.1525/elementa.2021.00019.
- 590 Cooper, O. R., Parrish, D. D., Stohl, A., Trainer, M., Nédélec, P., Thouret, V., et al. (2010).
- 591 Increasing springtime ozone mixing ratios in the free troposphere over western North
- 592 America. *Nature*, 463, 344–348. <u>https://doi.org/10.1038/nature08708</u>.
- 593 Davies, J., McElroy, C. T., Tarasick, D. W., & Wardle, D. I. (2003). Ozone capture efficiency in
- 594 ECC Ozonesondes; measurements made in the laboratory and during Balloon Flights. EGS-
- 595 AGU-EUG Joint Assembly, Abstracts from the meeting held in Nice, France, 6–11 April
- 596 2003. Abstract id: 13703.
- 597 Deshler, T., Mercer, J., Smit, H. G. J., Stuebi, R., Levrat, G., Johnson, B. J., et al. (2008).
- 598 Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers,
- and with different cathode solution strengths: The Balloon Experiment on Standards for
- Ozonesondes. *Journal of Geophysical Research*, 113, D04307, doi:10.1029/2007JD008975.

- Deshler, T., Stuebi, R., Schmidlin, F. J., Mercer, J. L., Smit H. G. J., Johnson, B. J., et al. (2017).
- 602 Methods to homogenize electrochemical concentration cell (ECC) ozonesonde measurements
- across changes in sensing solution concentration or ozonesonde manufacturer. *Atmospheric*
- 604 *Measurement Techniques*, 10, 2021–2043, doi:10.5194/amt-10-2021-2017.
- Efron, B. (1979). Bootstrap Methods: Another Look at the Jackknife." Ann. Statist. 7 (1) 1 26,
 January, 1979. https://doi.org/10.1214/aos/1176344552.
- Efron, B. & Tibshirani, R.J. (1993). An Introduction to the bootstrap. Chapman and Hall, Boca
 Raton.
- 609 Froidevaux, L., Jiang, Y. B., Lambert, A., Livesey, N. J., Read, W. G., Waters, J. W., et al.
- 610 (2008). Validation of Aura Microwave Limb Sounder stratospheric ozone measurements.

Journal of Geophysical Research, 113, D15S20, doi:10.1029/2007JD008771.

- Hao, N., Koukouli, M. E., Inness, A., Valks, P., Loyola, D. G., Zimmer, W., Balis, D. S.,
- 613 Zyrichidou, I., Van Roozendael, M., Lerot, C., and Spurr, R. J. D. (2014). GOME-2 total
- ozone columns from MetOp-A/MetOp-B and assimilation in the MACC system, *Atmos.*
- 615 *Meas. Tech.*, 7, 2937–2951, https://doi.org/10.5194/amt-7-2937-2014.
- Hassler, B., Kremser, S., Bodeker, G. E., Lewis, J., Nesbit, K., Davis, S. M., Chipperfield, M. P.,
- Dhomse, S. S., and Dameris, M. (2018). An updated version of a gap-free monthly mean
- zonal mean ozone database, *Earth Syst. Sci. Data, 10*, 1473-1490,
- 619 https://doi.org/10.5194/essd-10-1473-2018.
- Hubert, D., Lambert, J.-C., Verhoelst, T., Granville, J., Keppens, A., Baray, J.-L., Bourassa, A.
- E., Cortesi, U., Degenstein, D. A., Froidevaux, L., Godin-Beekmann, S., Hoppel, K. W.,
- Johnson, B. J., Kyrölä, E., Leblanc, T., Lichtenberg, G., Marchand, M., McElroy, C. T.,
- Murtagh, D., Nakane, H., Portafaix, T., Querel, R., Russell III, J. M., Salvador, J., Smit, H.

624	G. J., Stebel, K., Steinbrecht, W., Strawbridge, K. B., Stübi, R., Swart, D. P. J., Taha, G.,
625	Tarasick, D. W., Thompson, A. M., Urban, J., van Gijsel, J. A. E., Van Malderen, R., von der
626	Gathen, P., Walker, K. A., Wolfram, E., & Zawodny, J. M. (2016). Ground-based assessment
627	of the bias and long-term stability of 14 limb and occultation ozone profile data records.
628	Atmospheric Measurement Techniques, 9, 2497–2534. https://doi.org/10.5194/amt-9-2497-
629	2016.
630	Inai, Y., Shiotani, M., Fujiwara, M., Hasebe, F., & Vömel, H. (2015). Altitude misestimation
631	caused by the Vaisala RS80 pressure bias and its impact on meteorological profiles.
632	Atmospheric Measurement Techniques, 8, 4043-4054, https://doi.org/10.5194/amt-8-4043-
633	2015.
634	Johnson, B. J., Oltmans, S. J., Vömel, H., Smit, H. G. J., Deshler, T., & Kroeger, C. (2002). ECC
635	ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered
636	and unbuffered ECC sensor cathode solutions. Journal of Geophysical Research, 107, D19.
637	https://doi.org/10.1029/2001JD000557.
638	Killick R., P. Fearnhead, and I.A. Eckley (2012). Optimal detection of changepoints with a linear
639	computational cost. Journal of the American Statistical Association. 107, 500, 1590-1598.
640	Komhyr, W. D. (1969). Electrochemical concentration cells for gas analysis. Annales
641	<i>Geophysicae</i> , 25, 203–210.
642	Komhyr, W. D., & Harris, T. B. (1971). Development of an ECC-Ozonesonde. NOAA Technical
643	Report. ERL 200-APCL 18. Boulder, CO: U.S. G.P.O.
644	Komhyr, W. D. (1986). Operations handbook-Ozone measurements to 40-km altitude with
645	model 4A electrochemical concentration cell (ECC) ozonesondes (used with 1680 MHz
646	radiosondes). NOAA Technical Memo. ERL ARL-149, Boulder, CO: Air Resources Lab.

- 647 Komhyr, W. D., Barnes, R. A., Brothers, G. B., Lathrop, J. A., & Opperman, D. P. (1995).
- Electrochemical concentration cell ozonesonde performance evaluation during STOIC 1989.
- 649 *Journal of Geophysical Research*, 100(D5), 9231–9244. <u>https://doi.org/10.1029/94JD02175</u>.
- Liu, G., J.J. Liu, D.W. Tarasick, V.E. Fioletov, J.J. Jin, O. Moeni, X. Liu, C.E. Sioris and M.
- Osman (2013), A global tropospheric ozone climatology from trajectory-mapped ozone
- 652 soundings, Atmos. Chem. Phys. 13, 10659-10675, https://doi.org/10.5194/acp-13-10659-
- 653 2013.
- Liu, J., D.W. Tarasick, V.E. Fioletov, C. McLinden T. Zhao, S. Gong, C. Sioris, J. Jin, G. Liu,
- and O. Moeini (2013), A Global Ozone Climatology from Ozone Soundings via Trajectory
- Mapping: A Stratospheric Perspective, Atmos. Chem. Phys., 13, 11441-11464,
- 657 https://doi.org/10.5194/acp-13-11441-2013.
- Livesey, N. J., Read, W. G., Froidevaux, L., Lambert, A., Santee, M. L., Schwartz, M. J., et al.
- 659 (2021). Investigation and amelioration of long-term instrumental drifts in water vapor and
- nitrous oxide measurements from the Aura Microwave Limb Sounder (MLS) and their
- 661 implications for studies of variability and trends. *Atmospheric Chemistry and Physics*, 21,
- 662 15409–15430, https://doi.org/10.5194/acp-21-15409-2021.
- Livesey, N. J., Read, W. G., Wagner, P. A., Froidevaux, L., Santee, M. L., Schwartz, M. J., et al.
- 664 (2022). Version 5.0x Level 2 and 3 data quality and description document, JPL D-105336
- 665 Rev. B. [Available at https://mls.jpl.nasa.gov/data/v5-0_data_quality_document.pdf].
- Logan, J. A., Megretskaia, I. A., Miller, A. J., Tiao, G. C., Choi, D., Zhang, L., et al. (1999).
- 667 Trends in the vertical distribution of ozone: A comparison of two analyses of ozonesonde
- data. *Journal of Geophysical Research*, 104, 26373–26400.

669	Logan, J. A., Jones, D. B. A., Megretskaia, I. A., Oltmans, S. J., Johnson, B. J., Vömel, H.,
670	Randel, W. J., Kimani, W., and Schmidlin, F. J. (2003). Quasibiennial oscillation in tropical
671	ozone as revealed by ozonesonde and satellite data, J. Geophys. Res., 108, 4244, D8.
672	doi:10.1029/2002JD002170.
673	MATLAB. (2017). MATLAB version 9.3.0.713579 (R2017b) [Software]. The Mathworks, Inc.
674	https://uk.mathworks.com/help/matlab/release-notes-R2017b.html.
675	McPeters, R., Kroon, M., Labow, G., Brinksma, E., Balis, D., Petropavlovskikh, I., et al. (2008).
676	Validation of the Aura Ozone Monitoring Instrument total column ozone product. Journal of
677	Geophysical Research, 113, D15S14, doi:10.1029/2007JD008802.
678	McPeters, R. D. & Labow, G. J. (2012). Climatology 2011: An MLS and sonde derived ozone
679	climatology for satellite retrieval algorithms. Journal of Geophysical Research, 117, D10303
680	doi:10.1029/2011JD017006.
681	McPeters, R. D., Frith, S., & Labow, G. J. (2015). OMI total column ozone: extending the long-
682	term data record. Atmospheric Measurement Techniques, 8, 4845–4850,

https://doi.org/10.5194/amt-8-4845-2015. 683

- McPeters, R., Frith, S., Kramarova, N., Ziemke, J., & Labow, G. (2019). Trend quality ozone 684
- from NPP OMPS: the version 2 processing. Atmospheric Measurement Techniques, 12, 977-685
- 985, https://doi.org/10.5194/amt-12-977-2019. 686
- Moeini, O., Tarasick, D. W., McElroy, C. T., Liu, J., Osman, M. K., Thompson, A. M., et al. 687
- 688 (2020). Estimating boreal fire-generated ozone over North America using ozonesonde
- profiles and a differential back trajectory technique. Atmospheric Environment: X, 7, 689
- 100078. https://doi.org/10.1016/j.aeaoa.2020.100078. 690

691	Munro, R., Lang, R., Klaes, D., Poli, G., Retscher, C., Lindstrot, R. (2016). The GOME-2
692	instrument on the Metop series of satellites: instrument design, calibration, and level 1 data
693	processing – an overview, Atmospheric Measurement Techniques, 9, 1279–1301,
694	doi:10.5194/amt-9-1279-2016.
695	Nakano, T. & Morofuji, T. (2022). Development of an automated pump efficiency measuring
696	system for ozonesonde utilizing the airbag type flowmeter, EGUsphere [preprint],
697	https://doi.org/10.5194/egusphere-2022-565.
698	NASA/GSFC. (2019). Southern Hemisphere Additional Ozonesondes version 6 ozonesonde
699	profile data [Dataset]. National Aeronautics and Space Administration Goddard Space Flight
700	Center (NASA/GSFC). https://doi.org/10.57721/SHADOZ-V06.
701	NASA/GSFC. (2022). Aura MLS v5 L2 ozone profile overpass data [Dataset]. National
702	Aeronautics and Space Administration Goddard Space Flight Center (NASA/GSFC).
703	https://avdc.gsfc.nasa.gov/pub/data/satellite/Aura/MLS/V05/L2GPOVP/O3/.
704	NASA/GSFC. (2022). OMI L2 total column ozone overpass data [Dataset]. National Aeronautics
705	and Space Administration Goddard Space Flight Center (NASA/GSFC).
706	https://avdc.gsfc.nasa.gov/pub/data/satellite/Aura/OMI/V03/L2OVP/OMTO3/.
707	NASA/GSFC. (2022). OMPS L2 total column ozone overpass data [Dataset]. National
708	Aeronautics and Space Administration Goddard Space Flight Center (NASA/GSFC).
709	https://avdc.gsfc.nasa.gov/pub/data/satellite/Suomi_NPP/L2OVP/NMTO3-L2/.
710	NASA/GSFC. (2022). GOME-2A L2 total column ozone overpass data [Dataset]. National
711	Aeronautics and Space Administration Goddard Space Flight Center (NASA/GSFC).
712	https://avdc.gsfc.nasa.gov/pub/data/satellite/MetOp/GOME2/V03/L2OVP/GOME2A/.

- 713 NASA/GSFC. (2022). GOME-2B L2 total column ozone overpass data [Dataset]. National
- 714 Aeronautics and Space Administration Goddard Space Flight Center (NASA/GSFC).
- 715 https://avdc.gsfc.nasa.gov/pub/data/satellite/MetOp/GOME2/V03/L2OVP/GOME2B/.
- 716 NASA/GSFC. (2022). Ozonesonde and satellite comparison time series [Figures]. National
- 717 Aeronautics and Space Administration Goddard Space Flight Center (NASA/GSFC).
- 718 <u>https://tropo.gsfc.nasa.gov/shadoz/SHADOZ_PubsList.html</u>.
- 719 NDACC. (2022). Network for the Detection of Atmospheric Composition Change ozonesonde
- profile data [Dataset]. Network for the Detection of Atmospheric Composition Change
- 721 (NDACC). https://www-air.larc.nasa.gov/missions/ndacc/data.html.
- Newton, R., Vaughan, G., Ricketts, H. M. A., Pan, L. L., Weinheimer, A. J., & Chemel, C.
- (2016). Ozonesonde profiles from the West Pacific Warm Pool: Measurements and
- validation. Atmospheric Chemistry and Physics, 16, 619–634. <u>https://doi.org/10.5194/acp-16-</u>
- 725 <u>619-2016</u>.
- NOAA/GML. (2022). Global Monitoring Laboratory ozone/water vapor group ozonesonde
- 727 profile data [Dataset]. National Oceanic and Atmospheric Administration Global Monitoring
- Laboratory (NOAA/GML). ftp://ftp.gml.noaa.gov/data/ozwv/Ozonesonde/.
- 729 Petropavlovskikh, I., Godin-Beekmann, S., Hubert, D., Damadeo, R., Hassler, B., & Sofieva, V.
- 730 (2019). SPARC/IO3C/GAW Report on Long-term Ozone Trends and Uncertainties in the
- 731 Stratosphere. SPARC Report No. 9, GAW Report No. 241, WCRP Report 17/2018.
- [Available at https://elib.dlr.de/126666/1/LOTUS_Report_full_noSupplement.pdf].
- 733 Proffitt, M. H., & McLaughlin, R. J. (1983). Fast response dual-beam UV-absorption photometer
- suitable for use on stratospheric balloons. *Review of Scientific Instruments*, 54, 1719–1728.

- 735 Reid, S. J., Vaughan, G., Marsh, A. R. W., & Smit, H. G. J. (1996). Accuracy of ozonesonde
- measurements in the troposphere. *Journal of Atmospheric Chemistry*, 25, 215–226,

737 <u>https://doi.org/10.1007/BF00053792</u>.

- 738 Rice University. (2022). Tropospheric Ozone Pollution Project ozonesonde profile data
- 739 [Dataset]. Rice University. <u>http://www.ruf.rice.edu/~ozone/</u>.
- 740 RMI. (2022). Harmonization and Evaluation of Ground Based Instruments for Free Tropospheric
- 741 Ozone Measurements [Dataset]. Royal Meteorological Institute of Belgium (RMI).
- 742 http://hegiftom.meteo.be.
- 743 Smit, H. G. J., & Kley, D. (1998). JOSIE: The 1996 WMO International intercomparison of
- ozonesondes under quasi flight conditions in the environmental simulation chamber at Jülich.
- Geneva: World Meteorological Organization. WMO Global Atmosphere Watch Report No.

746 130, WMO TD No. 926.

- 747 Smit, H. G. J., & Straeter, W. (2004). JOSIE-2000, Jülich Ozone Sonde Intercomparison
- Experiment 2000, The 2000 WMO international intercomparison of operating procedures for
- 749 ECC-ozonesondes at the environmental simulation facility at Jülich. WMO Global
- 750 Atmosphere Watch report series, No. 158 (Technical Document No. 1225). Geneva: World
- 751 Meteorological Organization.
- 752 Smit, H. G. J., Straeter, W., Johnson, B. J., Oltmans, S. J., Davies, J., Tarasick, D. W., et al.
- (2007). Assessment of the performance of ECC-ozonesondes under quasi-flight conditions in
- the environmental simulation chamber: Insights from the Jülich Ozone Sonde
- ⁷⁵⁵ Intercomparison Experiment (JOSIE). *Journal of Geophysical Research*, 112, D19306,
- 756 doi:10.1029/2006JD007308.

- 757 Smit, H. G. J. & the Panel for the Assessment of Standard Operating Procedures for
- 758 Ozonesondes (ASOPOS) (2012). Guidelines for homogenization of ozonesonde data,
- 759 SI2N/O3S-DQA activity as part of "Past changes in the vertical distribution of ozone
- 760 assessment". [Available at http://www-
- 761 das.uwyo.edu/%7Edeshler/NDACC_O3Sondes/O3s_DQA/O3S-DQA-
- 762 Guidelines%20Homogenization-V2-19November2012.pdf].
- 763 Smit, H. G. J. & the Panel for the Assessment of Standard Operating Procedures for
- 764 Ozonesondes (ASOPOS) (2014). Quality assurance and quality control for ozonesonde
- measurements in GAW. World Meteorological Organization, GAW Report 201. [Available
- at https://library.wmo.int/doc_num.php?explnum_id=7167].
- 767 Smit, H. G. J., Thompson, A. M., & the Panel for the Assessment of Standard Operating
- 768 Procedures for Ozonesondes, v2.0 (ASOPOS 2.0) (2021). Ozonesonde Measurement
- 769 Principles and Best Operational Practices. World Meteorological Organization, GAW Report
- 268. [Available at https://library.wmo.int/doc_num.php?explnum_id=10884].
- 771 Stauffer, R. M., Morris, G. A., Thompson, A. M., Joseph, E., Coetzee, G. J. R., & Nalli, N. R.
- (2014). Propagation of radiosonde pressure sensor errors to ozonesonde measurements.
- Atmospheric Measurement Techniques, 7, 65–79, doi:10.5194/amt-7-65-2014.
- 574 Stauffer, R. M., Thompson, A. M., & Witte, J. C. (2018). Characterizing global ozonesonde
- profile variability from surface to the UT/LS with a clustering technique and MERRA-2
- reanalysis. *Journal of Geophysical Research: Atmospheres*, 123, 6213–6229.
- 777 https://doi.org/10.1029/2018JD028465.
- Stauffer, R. M., Thompson, A. M., Oman, L. D., & Strahan, S. E. (2019). The effects of a 1998
- observing system change on MERRA-2-based ozone profile simulations. Journal of

- 780 Geophysical Research: Atmospheres, 124, 7429–7441.
- 781 <u>https://doi.org/10.1029/2019JD030257</u>.
- 782 Stauffer, R. M., Thompson, A. M., Kollonige, D. E., Witte, J. C., Tarasick, D. W., Davies, J., et
- al. (2020). A post-2013 dropoff in total ozone at a third of global ozonesonde stations:
- Electrochemical concentration cell instrument artifacts? *Geophysical Research Letters*, 47,

785 e2019GL086791. <u>https://doi.org/10.1029/2019GL086791</u>.

- 786 Steinbrecht, W., Schwarz, R., & Claude, H. (1998). New pump correction for the Brewer-Mast
- 787 ozone sonde: Determination from experiment and instrument intercomparisons. *Journal of*
- 788 Atmospheric and Oceanic Technology, 15, 144–156. https://doi.org/10.1175/1520-
- 789 0426(1998)015<0144:NPCFTB>2.0.CO
- 790 Steinbrecht, W., Claude, H., Schönenborn, F., Leiterer, U., Dier, H., & Lanzinger, E. (2008).
- 791 Pressure and temperature differences between Vaisala RS80 and RS92 radiosonde systems.

Journal of Atmospheric and Oceanic Technology, 25, 909-927,

- 793 doi:10.1175/2007JTECHA999.1.
- 794 Sterling, C. W., Johnson, B. J., Oltmans, S. J., Smit, H. G. J., Jordan, A. F., Cullis, P. D., et al.
- 795 (2018). Homogenizing and estimating the uncertainty in NOAA's long term vertical ozone
- profile records measured with the electrochemical concentration cell ozonesonde.
- 797 Atmospheric Measurement Techniques, 11, 3661-3687, https://doi.org/10.5194/amt-2017-
- *798 397*.
- 799 Tarasick, D. W., Davies, J., Smit, H. G. J., & Oltmans, S. J. (2016). A re-evaluated Canadian
- 800 ozonesonde record: Measurements of the vertical distribution of ozone over Canada from
- 1966 to 2013. *Atmospheric Measurement Techniques*, 9, 195–214, doi:10.5194/amt-9-195-
- 802 2016.

- Tarasick, D. W., Galbally, I., Cooper, O. R., Schultz, M. G., Ancellet, G., LeBlanc, T., et al.
- 804 (2019). TOAR-observations: Tropospheric ozone from 1877 to 2016, observed levels, trends
- and uncertainties. *Elementa: Science of the Anthropocene*, 7(1), 39.
- 806 http://doi.org/10.1525/elementa.376.
- Tarasick, D. W., Smit, H. G. J., Thompson, A. M., Morris, G. A., Witte, J. C., Davies, J., et al.
- 808 (2021). Improving ECC ozonesonde data quality: Assessment of current methods and

outstanding issues. *Earth and Space Science*, 8, e2019EA000914.

- 810 https://doi.org/10.1029/2019EA000914.
- Thompson, A. M., Witte, J. C., Sterling, C., Jordan, A., Johnson, B. J., Oltmans, S. J., et al.
- 812 (2017). First reprocessing of Southern Hemisphere Additional Ozonesondes (SHADOZ)
- profiles (1998-2016). 2. Comparisons with satellites and ground-based instruments. *Journal*
- of Geophysical Research: Atmospheres, 122, 13000-13025,
- 815 https://doi.org/10.1002/2017JD27406.
- Thompson, A. M., Smit, H. G. J., Witte, J. C., Stauffer, R. M., Johnson, B. J., Morris, G. A., et
- al. (2019). Ozonesonde quality assurance: The JOSIE-SHADOZ (2017) Experience. Bulletin
- 818 of the American Meteorological Society, 100 (1), 155-171, https://doi.org/10.1175/BAMS-D 819 17-0311.1.
- Thompson, A. M., Stauffer, R. M., Wargan, K., Witte, J. C., Kollonige, D. E., & Ziemke, J. R.
- 821 (2021). Regional and seasonal trends in tropical ozone from SHADOZ profiles: Reference
- for models and satellite products. *Journal of Geophysical Research: Atmospheres*, 126,
- e2021JD034691. <u>https://doi.org/10.1029/2021JD034691</u>.

- Thornton, D. C., and Niazy, N. (1982), Sources of background current in the ECC ozonesonde:
- 825 Implications for total ozone measurements, *Journal of Geophysical Research*, 87 (C11),
- 826 8943–8950, doi:10.1029/JC087iC11p08943.
- Tilmes, S., Lamarque, J.-F., Emmons, L. K., Conley, A., Schultz, M. G., Saunois, et al. (2012).
- Technical Note: Ozonesonde climatology between 1995 and 2011: description, evaluation
- and applications. *Atmospheric Chemistry and Physics*, 12, 7475–7497,
- 830 <u>https://doi.org/10.5194/acp-12-7475-2012</u>.
- USFQ. (2022). Universidad San Francisco de Quito ozonesonde profile data [Dataset].
- 832 Universidad San Francisco de Quito (USFQ). https://observaciones-iia.usfq.edu.ec/.
- Van Malderen, R., Allaart, M. A. F., De Backer, H., Smit, H. G. J., & De Muer, D. (2016). On
- instrumental errors and related correction strategies of ozonesondes: Possible effect on
- calculated ozone trends for the nearby sites Uccle and De Bilt. *Atmospheric Measurement*

Techniques, 9, 3793–3816. https://doi.org/10.5194/amt-9-3793-2016.

- 837 Vömel, H., & Diaz, K. (2010). Ozone sonde cell current measurements and implications for
- observations of near-zero ozone concentrations in the tropical upper troposphere.
- *Atmospheric Measurements Techniques*, 3, 495–505. https://doi.org/10.5194/amt-3-495 2010.
- Vömel, H., Smit, H. G. J., Tarasick, D., Johnson, B., Oltmans, S. J., Selkirk, H., et al. (2020). A
- new method to correct the ECC ozone sonde time response and its implications for
- 843 "background current" and pump efficiency. *Atmospheric Measurements Techniques*, 13,
 844 5667–5680.
- 845 Witte, J. C., Schoeberl, M. R., Douglass, A. R., & Thompson, A. M. (2008). The Quasi-biennial
- 846 Oscillation and annual variations in tropical ozone from SHADOZ and HALOE.

Atmospheric Chemistry and Physics, 8, 3929–3936. https://doi.org/10.5194/acp-8-39292008.

849	Witte, J. C., Thompson, A. M., Smit, H. G. J., Fujiwara, M., Posny, F., Coetzee, G. J. R., et al.
850	(2017). First reprocessing of Southern Hemisphere ADditional Ozone-sondes (SHADOZ)
851	profile records (1998–2015): 1. Methodology and evaluation. Journal of Geophysical
852	Research: Atmospheres, 122, 6611-6636. https://doi.org/10.1002/2016JD026403.
853	Witte, J. C., Thompson, A. M., Smit, H. G. J., Vömel, H., Posny, F., & Stübi, R. (2018). First
854	reprocessing of Southern Hemisphere ADditional OZonesondes profile records: 3.
855	Uncertainty in ozone profile and total column. Journal of Geophysical Research:
856	Atmospheres, 123, 3243-3268. https://doi.org/10.1002/2017JD027791.
857	Witte, J. C., Thompson, A. M., Schmidlin, F. J., Northam, E. T., Wolff, K. R., and Brothers, G.
858	B. (2019). The NASA Wallops Flight Facility digital ozonesonde record: Reprocessing,
859	uncertainties, and dual launches. Journal of Geophysical Research: Atmospheres, 124, 3565-
860	3582. https://doi.org/10.1029/2018JD030098.
861	WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion. (2018).
862	Global Ozone Research and Monitoring Project-Report No. 58. Geneva, Switzerland, p. 588.
863	WOUDC. (2022). OzoneSonde [Dataset]. World Ozone and Ultraviolet Data Centre (WOUDC).
864	http://dx.doi.org/10.14287/10000008.
865	WOUDC. (2022). Total Ozone - Daily Observations [Dataset]. World Ozone and Ultraviolet

866 Data Centre (WOUDC). http://dx.doi.org/10.14287/10000004.

868 Table 1. Metadata for the 60 global ozonesonde stations used in this study including

869 latitude/longitude, number of profiles from August 2004-present, data source, whether the station

870 has co-located ground-based TCO data available in the WOUDC archive, and whether the

station's ozonesonde data used here have been homogenized (see text for explanation of the

872 homogenization process). The single asterisks and bold columns indicate the 14 S20 dropoff

stations used here as a reference. URLs for the respective ozonesonde data archives are given at

the bottom of the table.

<u>Station</u>	<u>Lat (°)</u>	<u>Lon (°)</u>	<u># Profiles</u>	<u>Dates</u>	<u>Source</u>	Ground-Based?	Homogenized?
Alert*	82.49	-62.34	705	2004-2020	HEGIFTOM	Y	Y
Eureka*	79.98	-85.94	1064	2004-2021	HEGIFTOM	Y	Y
Ny-Ålesund	78.92	11.93	1245	2004-2020	NDACC	Y	N
Thule	76.53	-68.74	118	2004-2016	NDACC	N	N
Resolute	74.7	-94.96	622	2004-2021	HEGIFTOM	Y	Y
Summit	72.34	-38.29	635	2004-2017	NOAA	N	Y
Scoresbysund	70.48	-21.97	849	2004-2021	NDACC	Y	N
Sodankyla	67.37	26.65	670	2004-2019	NDACC	Y	N
Lerwick	60.13	-1.18	621	2004-2016	WOUDC	Y	Ν
Churchill*	58.74	-94.07	510	2004-2021	HEGIFTOM	Y	Y
Edmonton*	53.54	-114.1	766	2004-2021	HEGIFTOM	Y	Y
Goose Bay	53.31	-60.36	761	2004-2021	HEGIFTOM	Y	Y
Legionowo	52.4	20.97	974	2004-2021	HEGIFTOM	N	N
De Bilt	52.1	5.18	862	2004-2020	HEGIFTOM	Y	Y
Valentia	51.94	-10.25	460	2004-2020	WOUDC	Y	N
Uccle	50.8	4.35	2348	2004-2020	HEGIFTOM	Y	Y
Praha	50.01	14.45	794	2004-2021	WOUDC	N	N
Kelowna**	49.93	-119.4	673	2004-2017	HEGIFTOM	N	Y
Hohenpeissenberg	47.8	11.02	2116	2004-2021	WOUDC	Y	Y
Payerne	46.49	6.57	2528	2004-2020	HEGIFTOM	N	Y
Haute Provence	43.94	5.71	800	2004-2021	NDACC	Y	Y
Yarmouth**	43.87	-66.11	754	2004-2021	HEGIFTOM	N	Y
Sapporo	43.06	141.33	387	2004-2018	WOUDC	Y	Ν
Trinidad Head	40.8	-124.16	913	2004-2022	NOAA	N	Y
Madrid	40.47	-3.58	775	2004-2021	HEGIFTOM	Y	Y
Boulder	40	-105.25	992	2004-2022	NOAA	Y	Y
Wallops Island	37.93	-75.48	850	2004-2020	SHADOZ	Y	Y
Tateno	36.06	140.13	516	2004-2021	WOUDC	Y	N
Huntsville	34.72	-86.64	777	2004-2020	NOAA	N	Y
Idabel	33.9	-94.75	149	2004-2016	ТОРР	Ν	Ν
Houston	29.72	-95.34	505	2004-2017	ТОРР	N	Ν
Izaña	28.3	-16.48	745	2004-2020	HEGIFTOM	Y	Y

Naha	26.21	127.69	419	2004-2018	WOUDC	Y	N
Hong Kong	22.31	114.17	776	2004-2020	WOUDC	Y	N
Hanoi	21.01	105.8	337	2004-2020	SHADOZ	Y	Y
Hilo*	19.43	-155.04	839	2004-2021	SHADOZ	Y (Mauna Loa)	Y
Costa Rica*	9.94	-84.04	659	2004-2021	SHADOZ	N	Y
Paramaribo	5.8	-55.21	608	2004-2021	HEGIFTOM	Y	Y
Kuala Lumpur	2.73	101.27	318	2004-2021	SHADOZ	N	Y
Quito	-0.2	-78.44	43	2004-2020	USFQ	N	N
San Cristobal*	-0.92	-89.62	176	2004-2016	SHADOZ	N	Y
Nairobi*	-1.27	36.8	641	2004-2019	SHADOZ	Y	Y
Natal*	-5.42	-35.38	472	2004-2021	SHADOZ	Y	Y
Watukosek	-7.5	112.6	124	2004-2013	SHADOZ	N	Y
Ascension*	-7.58	-14.24	490	2004-2021	SHADOZ	N	Y
Samoa*	-14.23	-170.56	568	2004-2021	SHADOZ	Y	Y
Fiji*	-18.13	178.4	236	2004-2021	SHADOZ	N	Y
Reunion	-21.06	55.48	553	2004-2020	SHADOZ	Y	Y
Irene	-25.9	28.22	233	2004-2020	SHADOZ	Y	Y
Broadmeadows	-37.69	144.95	790	2004-2020	WOUDC	Y	N
Lauder	-45	169.68	794	2004-2021	HEGIFTOM	Y	Y
Macquarie	-54.5	158.95	794	2004-2020	WOUDC	Y	N
Marambio	-64.24	-56.62	882	2004-2019	WOUDC	Y	N
Dumont d'Urville	-66.67	140	363	2004-2019	NDACC	Y	N
Davis	-68.58	77.97	473	2004-2019	WOUDC	N	N
Syowa	-69	39.58	529	2004-2021	WOUDC	Y	N
Neumayer	-70.62	-8.37	1186	2004-2021	NDACC	Ν	N
McMurdo	-77.85	166.67	174	2004-2010	NDACC	Y	Y
Belgrano	-77.87	-34.62	97	2004-2020	NDACC	Y	N
South Pole	-90	-169	984	2004-2021	NOAA	Y	Y
Total Profiles:			42042				
* Denotes the 14 S20 TCO dropoff stations							
** Kelowna and Yarmouth data corrected since S20 publication							
NOAA: ftp://ftp.gml.noaa.gov/data/ozwv/Ozonesonde/							
HEGIFTOM: http://hegiftom.meteo.be							
USFQ: https://observaciones-iia.usfq.edu.ec/							
NDACC: https://www-air.larc.nasa.gov/missions/ndacc/data.html							
WOUDC: https://woudc.org/data/explore.php?lang=en							
SHADOZ: https://trop	oo.gsfc.nas	a.gov/shadc	z/Archive.htr	nl			
TOPP: http://www.ruf.rice.edu/~ozone/							

Table 2. Additional metadata for the 60 global ozonesonde stations used in this study including

879 the primary ozonesonde type and SST used. The farthest right column indicates the average

880 EnSci ozonesonde percentage TCO change relative to OMI after EnSci S/N 25250. The average

881 EnSci ozonesonde TCO change relative to OMI pre- and post-EnSci S/N 25250 considering *all*

stations is -1.8%.

<u>Station</u>	Ozonesonde Type	<u>SST Type</u>	OMI% Change (25250)**	
Alert*	EnSci, now SPC	1.0	0.1	
Eureka*	EnSci, now SPC	1.0	-1	
Ny-Ålesund	SPC	1.0	N/A	
Thule	EnSci	0.5	N/A	
Resolute	EnSci, now SPC	1.0	-2.9	
Summit	EnSci	0.5	-1.2	
Scoresbysund	EnSci	1.0	-5.6	
Sodankyla	EnSci	0.5	-2.6	
Lerwick	SPC	1.0	N/A	
Churchill*	EnSci, now SPC	1.0	-5.8	
Edmonton*	EnSci, now SPC	1.0	-2.2	
Goose Bay	EnSci, now SPC	1.0	-1.1	
Legionowo	SPC	1.0	N/A	
De Bilt	SPC	1.0	N/A	
Valentia	SPC	1.0	N/A	
Uccle	EnSci	0.5	-0.9	
Praha	SPC	1.0	N/A	
Kelowna*	EnSci	1.0	-1.1	
Hohenpeissenberg	Brewer-Mast	N/A	N/A	
Payerne	EnSci	0.5	-1.3	
Haute Provence	EnSc	1.0	N/A	
Yarmouth*	EnSci, now SPC	1.0	-3.2	
Sapporo	EnSci	0.5	0.1	
Trinidad Head	EnSci	0.1	-1.2	
Madrid	SPC	1.0	N/A	
Boulder	EnSci	0.1	-1.5	
Wallops Island	SPC	1.0	N/A	
Tateno	EnSci	0.5	-1	
Huntsville	EnSci	0.1	-2.5	
Idabel	EnSci	0.5	-3.3	
Houston	EnSci	0.5	-1.4	
Izaña	SPC	1.0	N/A	
Naha	EnSci	0.5	1	
Hong Kong	SPC	1.0	N/A	
Hanoi	EnSci	0.5	-1.3	

Hilo*	EnSci	0.1	-2.8				
Costa Rica*	EnSci	0.1	-5.6				
Paramaribo	SPC	1.0	N/A				
Kuala Lumpur	EnSci	0.5	N/A				
Quito	EnSci	0.1	N/A				
San Cristobal*	EnSci	0.1	N/A				
Nairobi*	EnSci	0.5	-2				
Natal*	SPC	1.0	N/A				
Watukosek	EnSci	2.0	N/A				
Ascension*	EnSci	0.5	N/A				
Samoa*	EnSci	0.1	-3.6				
Fiji*	EnSci	0.1	-4.4				
Reunion	EnSci	0.5	-0.9				
Irene	SPC	1.0	N/A				
Broadmeadows	SPC	1.0	N/A				
Lauder	EnSci	0.5	-2.6				
Macquarie	SPC	1.0	N/A				
Marambio	EnSci	0.5	-0.2				
Dumont d'Urville	EnSci	0.5	N/A				
Davis	SPC	1.0	N/A				
Syowa	EnSci	0.5	1				
Neumayer	SPC	1.0	N/A				
McMurdo	EnSci	0.5	N/A				
Belgrano	SPC	1.0	N/A				
South Pole	EnSci	0.1	0				
	Average Change: -1.8						
* Denotes the 14 S20 TCO dropoff stations							
** Requires minimum of 25 valid pre- and 25 valid post-EpSci 25250 serial number OMI TCO							

** Requires minimum of 25 valid pre- and 25 valid post-EnSci 25250 serial number OMI TCO comparisons (otherwise marked N/A). Statistics consider only EnSci ozonesondes



Figure 1. Map of the 60 global ozonesonde stations used in this study. All stations except

887 Hohenpeissenberg (Brewer-Mast type) currently launch ECC ozonesondes. Stations (12 total)

identified as having a \geq 3% TCO drop relative to OMI in S20 are shown as red dots, and the two

889 Canadian stations (Kelowna and Yarmouth; see Figure S2) with corrected data for this study are

shown as orange dots. Those two stations are still grouped with the "S20" stations for this

analysis. All other stations ("Non-S20"; 46 total) are shown as blue dots.



Figure 2. Coincident ozonesonde and satellite comparisons in percent difference for all 60 893 stations used in this study. Top: Time series of comparisons among all ozonesonde and MLS O₃ 894 profiles ([ECC-MLS/ECC]). Red or blue colors indicate where the ozonesonde ozone is greater 895 896 or less than MLS. Middle: Ozonesonde and satellite TCO comparisons in percent difference ([ECC-satellite]/ECC) for OMI (blue), OMPS (red), GOME-2A (green), and GOME-2B (cyan). 897 The lines corresponding to each TCO satellite instrument indicate 500-ozonesonde centered, 898 moving averages. No average lines are plotted for the first 250 and last 250 comparisons. 899 900 Bottom: Ozonesonde and satellite TCO comparison statistics in percent difference for each individual year from 2005-2021. Bars represent the 25th to 75th percentile, with the dots 901 representing the median comparison. 902 903



Figure 3. As in Figure 2, but for ozonesonde stations poleward of 60° latitude in both
hemispheres.



Figure 4. As in Figure 2, but for ozonesonde stations within $\pm (20 \text{ to } 60)^{\circ}$ latitude (i.e.,

910 "midlatitudes" in both hemispheres).



913 Figure 5. As in Figure 2, but for stations within 20° latitude of the equator.



Figure 6. Comparisons of all coincident ozonesonde and Aura MLS ozone profiles in percent
difference for the four latitude bands (a-d) referred to in Figures 2 through 5. The shading
represents the 25th to 75th percentile, with the thick lines indicating the median (50th percentile)
difference.



Figure 7. Comparisons of ECC ozonesonde TCO with OMI in percent difference for (a) all EnSci ozonesondes at the 14 S20 TCO dropoff stations, (b) all EnSci ozonesondes launched at the other 46 global stations in this study (note that some stations have not launched EnSci ECCs). EnSci S/Ns are grouped into bins of 1000 (26 = 26000 to 26999) for analysis. The bars show the 25th to 75th percentiles for each bin, with the dots representing the median value. The total number of valid ozonesonde/OMI comparisons for each bin are shown by the numbers along the top and bottom, aligned with the bars.





Figure 8. As in Figure 7, but for all SPC 6A ozonesondes launched at any of the 60 stations. Note

that the similar S/Ns for EnSci and SPC 6A are a coincidence, and not all stations have launchedSPC 6A ECCs.



935

Figure 9. Comparisons in percent difference between ozonesonde and OMI TCO for all 14 S20
station (a) and all non-S20 station (b) EnSci S/Ns (all S/Ns are shown). The thick blue dashed
line indicates the mean value for S/Ns prior to 25250, and the thick red dashed line indicates the

mean value after S/N 25250. The mean values and their 95% confidence intervals (CI) are shown

940 in text below both figures and the 95% CIs are indicated by the thin dashed lines.

941





Figure 10. As in Figure 6, but here the comparisons are for EnSci ozonesondes only at the (a) 14 S20 stations and (b) non-S20 stations. The comparisons with Aura MLS ozone are shown for EnSci S/Ns prior to 25250 (blue) and after S/N 25250 (red). The shading represents the 25th to 75th percentile, with the median (50th percentile) difference shown by the solid lines.

- 948
- 949