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Methods to homogenize ECC ozonesonde measurements across changes in sensing solution concentration or ozonesonde manufacturer

Terry Deshler[1], Rene Stübi[2], Francis J. Schmidlin[3], Jennifer L. Mercer[1,7], Herman G. J. Smit[4], Bryan J. Johnson[5], Rigel Kivi[6], and Bruno Nardi[1,8]

1. Department of Atmospheric Science, University of Wyoming, Laramie, Wyoming, USA
2. Meteo Swiss, Payerne, Switzerland
3. NASA Goddard Space Flight Center, Greenbelt, Maryland, USA
4. Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research: Troposphere, Jülich, Germany.
5. Finnish Meteorological Institute, Arctic Research, Sodankylä, Finland.
6. National Oceanic and Atmospheric Administration, Boulder, Colorado, USA
7. Now at National Science Foundation, Geosciences Directorate, Division of Polar Programs, Arlington, Virginia, USA
8. Nardi Scientific, LLC, Denver, Colorado, USA

Correspondence to: T. Deshler (deshler@uwyo.edu).

Abstract.

From the mid 1990s to the late 2000s the consistency of electrochemical cell ozonesonde long term records has been compromised by differences in manufacturers, Science Pump and ENSCI, and differences in recommended sensor solution concentrations, 1.0% potassium iodide (KI) and the one half dilution 0.5%. To investigate these differences a number of organizations independently undertook comparisons of the various ozonesonde types and solution concentrations, resulting in 197 ozonesonde comparison profiles. The goal is to derive transfer functions to allow measurements outside of standard recommendations, for sensor composition and ozonesonde type, to be converted to a standard measurement and thus homogenize the data to the expected accuracy of 5% (10%) in the stratosphere (troposphere). Subsets of these data have been analyzed previously and intermediate transfer functions derived. Here all the comparison data are analyzed to compare: 1) differences in sensor solution composition for a single ozonesonde type, 2) differences in ozonesonde type for a single sensor solution composition and 3) the World Meteorological Organization's (WMO) and manufacturer's recommendations of 1.0% KI solution for Science Pump and 0.5% KI for ENSCI. From the recommendations it is clear that ENSCI ozonesondes and 1.0% KI solution result in higher amounts of ozone sensed. The results indicate that differences in solution composition and in ozonesonde type display little pressure dependence at pressures ≥ 30 hPa and thus the transfer function can be characterized as a simple ratio of the less sensitive to the more sensitive method. This ratio is 0.96 for both solution concentration and ozonesonde type. The ratios differ at pressures < 30 hPa such that $OZ_{0.5\%}$ / $OZ_{1.0\%}$ = 0.90 +0.041 ● $\log_{10}(p)$ and $OZ_{SciencePump}$ / OZ_{ENSCI} = 0.764 + 0.133 ● $\log_{10}(p)$. For the manufacturer recommended solution concentrations the dispersion of the ratio (SP-1.0/EN-0.5), while significant, is generally within 3% and centered near 1.0, such that no changes are recommended. For stations which have used multiple ozonesonde types with solution concentrations different from the WMO's and manufacturer's recommendations, this work suggests that a reasonably homogeneous data set can be created if the quantitative relationships specified above are applied to the non-standard measurements. This result is illustrated here in an application to the Nairobi data set.

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1. Introduction

Ozone is one of the critical atmospheric trace gases. Ozone contributes to the oxidizing capacity of the troposphere, to the absorption of terrestrial IR radiation, and to the absorption of solar UV in the stratosphere. An overabundance of ozone in the troposphere causes air quality problems, while a deficit in the stratosphere leads to enhanced exposure to UV. Ozone measurements are thus required to maintain our understanding of these processes and are required over times scales of hours to years, and from single point measurements to vertical profiles to the mid stratosphere. Measurements are required over hours at single locations to characterize air quality, while regular profiles over decades are required to characterize stratospheric ozone loss and to contribute to climate modeling.

Historically, the first ozone profile information was extracted from the Dobson measurements with the discovery of the Umkehr effect in the 1930s [Götz et al., 1934]. In optimal (blue sky) conditions at sunrise and at sunset two coarse resolution ($\delta z \approx 7$ km) vertical ozone profiles from about 15 to 50 km could be retrieved by this technique and the first stratospheric ozone climatology created [Dobson et al., 1927]. Since this manual measurement method was demanding in personal resources it is only since the mid 1950s that continuous Umkehr measurements are available and the technique continues to be improved [Fioletov et al., 2006; Petropavlovskikh et al., 2005]. In the 1960s, wet-chemical ozonesondes were developed providing *in situ* high vertical resolution ($\delta z \approx 0.3$ km or less) ozone profiles from the ground to the mid stratosphere [Brewer and Milford, 1960; Komhyr, 1965]. Datasets more than 30 years long are available based on this technique [Harris et al., 1998; Stähelin et al., 2001; Jeannet et al., 2007]. In the 1970s, the satellite epoch began providing global coverage of the total ozone column [e.g. Labow et al., 2013]. In the 1990s, the active lidar and the passive microwave were developed with an improved time resolution and an extended altitude range up to the mesosphere [Beekman et al., 1994; Calisesi et al., 2003; Moreira et al., 2015]. Today, the full suite of ground based, balloon-borne, and satellite instruments provide significant spatio-temporal coverage of global ozone. Maintaining this coverage requires all three platforms. Satellite instruments have limited life times and require comparison measurements with other instruments for algorithm development and reference measurements. Balloon-borne instruments provide the highest vertical resolution and the highest sensitivity but are limited in spatial and temporal coverage. Ground based instruments are required for long time series with single reference instruments and for daily measurement capability [e.g. Guirlet et al., 2000]. Modeling activities ranging from weather forecasts to climate studies benefit from ozone distribution measurements from all three platforms [Stein et al., 2000, Cionni et al., 2011].

Ozone is recognized as an Essential Climate Variable (ECV) and target observation requirements for satellite based products for climate are defined by the Global Climate Observing System (GCOS), which is a joint undertaking of the World Meteorological Organization (WMO), the United Nations Environmental Program, and others [GCOS, 2010]. The measurement requirements for an ECV represent a challenge even for ground based instruments:

1. Accuracy: 10% (troposphere), 5% (stratosphere).
2. Spatial resolution: Horizontal: 5-50 km (troposphere), 50-100 km (stratosphere).
3. Vertical resolution: 0.5 km (troposphere), 0.5-3 km (stratosphere).
4. Three hourly observing cycle everywhere.
5. Stability: 1 % (troposphere), 0.6% (stratosphere).

Since the late 1960s the vast majority of vertical ozone profile information is from individual ozonesonde flights. The instruments used are all based on measurements of an electrical current from an electrochemical galvanic cell which is a measure of the amount of ozone sampled. The current is generated when ozone in the air, which is bubbled through an electrolytic solution, reacts with iodide ions in the electrolyte in the cell. Variations of this principle, described in detail in section 2.1, led to the Brewer-Mast (BM) ozonesonde [Brewer and Milford, 1960), the Japanese KC ozonesonde [Komhyr and Harris, 1965; Kobayashi and Toyama, 1966], and the electrochemical concentration cell (ECC) ozonesonde [Komhyr, 1969]. The BM ozonesonde consists of a single electrochemical cell with a potential applied across the silver anode and platinum cathode immersed in an alkaline potassium iodide (KI) solution. The KC ozonesonde has a platinum cathode and carbon anode immersed in a pH neutral KI solution. The ECC ozonesonde consists of two half cells each containing a platinum electrode, and differing concentrations of iodide I^- in the form of KI, saturated at the anode

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and dilute at the cathode. From these three electrochemical cell possibilities, the ECC ozonesonde has emerged as the preferred technology. One station continues using the BM ozonesonde for data continuity. The KC ozonesonde is no longer in use. Here we focus on the ECC ozonesonde.

While the ECC was under development different concentrations of KI in the cathode were investigated and the results compared with corresponding total column measurements. In the 1980s solution concentrations of 1.5 and 1.0% were in use [Barnes et al., 1985; Komhyr et al., 1995a]. By the mid 1980's a 1.0% solution of KI became the standard recommendation for Science Pump (SP) ozonesondes [Komhyr, 1986]. SP was the only manufacturer of ECC ozonesondes until the mid 1990s, when the company ENSCI (EN) was formed, which began manufacturing an alternate ECC ozonesonde. Initially ENSCI also recommended a KI concentration of 1.0% for the cathode; however, this was changed to 0.5% after unpublished comparisons of EN and SP ozonesondes using 1.0% KI indicated that EN ozonesondes recorded more ozone than the SP ozonesondes at the same solution concentration.

These changes created some confusion as recommendations in the preparation of ECC ozonesondes changed. The first results comparing ozonesondes flown with 1.0% and 0.5% KI cathode solution were based on only a few comparisons [Boyd et al., 1998]. More extensive results were obtained from comprehensive intercomparisons in the laboratory [Smit et al., 2007], and in the field [Kivi et al. 2007; Deshler et al., 2008]. These comparisons led to the current WMO recommendations for ECC ozonesonde preparations [Smit and ASOPOS Panel, 2014]; however, between the mid 1990s and late 2000s the ozonesonde community was using several variations between 1.0% and 0.5% KI cathode cell concentrations in SP and EN ozonesondes. To homogenize these records to a single standard requires transfer functions to convert measurements made with any of the various combinations to one of the two WMO recommended standard preparations: 1.0% for SP and 0.5% for EN for the KI concentrations of the cathode electrolyte. Obtaining these transfer functions is the goal of this paper.

The transfer functions will be derived from published and unpublished measurements which compare directly the response of SP and EN ECC ozonesondes using 1.0 and 0.5% concentrations of KI in the cathode cells under identical environments of ozone, pressure, and temperature. These comparisons were done in an environmental simulation chamber in Jülich, Germany [Smit et al., 2007], henceforth JOSIE09, on a multiple ECC ozonesonde gondola [Deshler et al., 2008], henceforth the BESOS experiment, on other multiple ozonesonde balloon flights [Kivi et al., 2007], and on unpublished dual ozonesonde flights from Payerne, Switzerland; McMurdo Station, Antarctica; Sodankylä, Finland; Wallops Island, Virginia, USA; and Laramie, Wyoming, USA. Together 197 comparisons of the different possible combinations have been made at these sites with the goal to develop transfer functions to convert measurements made with either manufacturer and with either 1.0 or 0.5% KI concentration to one of the WMO recommendations: SP with 1.0% KI, EN with 0.5% KI.

2. ECC ozonesonde description

2.1. ECC ozonesonde principles

Ozonesondes are based on an electrochemical cell where the chemical potential difference is maintained by differences in the iodide (I^-) concentration in each half cell. Ozone introduced into the dilute iodide half reacts with iodide and converts it to iodine (I_2) in the following reaction [Komhyr, 1969]:

$$KI + O_3 + H_2O \rightarrow 2\,KOH + I_2 + O2, \quad (1)$$

followed at the cathode by the reduction of iodine back to potassium iodide:

$$I_2 + 2\,e \rightarrow 2\,I^-. \quad (2)$$

The two electrons arise from the electrolyte saturated in iodide at the anode by the oxidation of iodide:

$$3\,I^- \rightarrow I_3^- + 2\,e. \quad (3)$$

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The outer electrical circuit consists of two platinum electrodes immersed in the half cell electrolytes which are aqueous solutions of KI. The electrolyte is saturated with KI on the anode side and with a dilute KI concentration on the cathode side. Besides KI, the electrolytes also contain potassium bromine and sodium phosphate buffers to maintain a neutral pH solution. The decomposition of each ozone molecule in the dilute electrolyte produces a transfer of electrons (Eq. 2) in the outer circuit following Faraday's law of electrolysis. Converting the mass of ozone decomposed to partial pressure with the ideal gas law and substituting $e \bullet N_A$ for Faraday's constant results in the following relationship between ozone partial pressure and electrical current:

$$O_3(p) = \frac{R}{(z \bullet e \bullet N_A)} \bullet \frac{\phi(p)}{P_E(p)} \bullet \frac{T_P(p)}{FR} \bullet (i(p) - i_0). \quad (4)$$

R is the universal gas constant, z the number of electrons required to convert the iodine in the dilute electrolyte back to iodide, e the elementary charge, N_A Avogadro's number, $i(p)$ the measured cell current as a function of atmospheric pressure, p, i_0 the background current, $\varphi(p)$ the effective stoichiometry factor of the chemical conversion of ozone into iodine, $T_P(p)$ the pump temperature, a surrogate for the temperature of the air sampled, FR the flow rate, $P_E(p)$ the pump efficiency correction to account for decreasing flow rate at low pressures. Operationally, for $i(p)$ in units of µA, z = 2, and FR in units of ml s^{-1}, the leading term in Eq. 4, $R/(z\ e\ N_A)$ is replaced by 4.3085 x 10^{-6} which gives ozone partial pressure in mPa.

Each of the terms in Eq. 4 has an uncertainty deduced from the measurement method but they also have an additional uncertainty which is more difficult to quantify, especially at high altitude (low pressure) levels. The background current, i_0, the flowrate, FR, the pump temperature, $T_P(p)$, and the stoichiometry of ozone to iodine, $\varphi(p)$, require special mention.

The back ground current i_0 is a measure of the residual signal with "zero-air" (no ozone) at the ozonesonde inlet. Originally, i_0 was attributed to side chemical reactions with oxygen and therefore, expected to decrease with altitude; however, Thornton and Niazy [1982] and Thornton [1983] and other empirical evidence from laboratory tests, suggested that i_0 is constant independent of altitude. Figure 1 gives the range of i_0 measured at the different stations prior to the measurement flights considered in this analysis. A mid value of 0.03 µA from Figure 1 corresponds to 0.1 mPa and produces an offset of the ozone profile and a diminution of the ozone column by 5.4 DU, 0.1 mPa integrated from 1000 hPa to 1 hPa, or 1.8% for a 300 DU ozone column. These i_0 values will be discussed again in section 3.2, but the value of i_0 does not affect comparisons between cells with similar backgrounds, and is thus less important for the work here.

The flow rate FR is well characterized in the laboratory preparation at surface pressure as shown in the box and whisker plot of the flow rates, Figure 2, measured at the different stations. The median values for each ozonesonde type are within 0.3 ml s^{-1}, < 10%, showing the good concordance between stations, although there is a 0.2 ml s^{-1} systematic difference between the majority of SP and EN ozonesondes. The real flow rate is much less certain at low pressure (high altitude) conditions where the pump efficiency decreases and pressure against the flow from the height of the solution in the ECC cell, on the order of 1-2 hPa, becomes non-negligible. Thus a pump efficiency correction is applied through the factor $P_E(p)$; however, there is still disagreement on the correct $PE(p)$ to use [Johnson et al., 2002]. The pumps are designed for a constant rotation speed during a flight, a characteristic which has been checked by several investigators here but not published.

The effective stoichiometric factor, $\varphi(p)$ as formulated in Eq. 4, is composed of two factors: the absorption of ozone in the electrolytic solution, and the stoichiometric efficiency of the reaction of O_3 and KI to produce I_2. This latter factor is more difficult to characterize. In theory it is close to 1. The absorption efficiency has been measured in the laboratory with two ECC ozonesondes measuring in series. These tests have shown that the absorption of ozone is somewhat dependent on the amount of solution used (e.g. 2.5 ml vs. 3.0 ml) [Tarasick et al., 2016; Davies et al., 2003], with the absorption increasing from 0.96 as the amount of solution increases from 2.5 ml. The increase of the gas diffusion rate during balloon ascent due to the pressure decrease should limit this ozone conversion efficiency loss to the lower part of the profile [Davies et al., 2003].

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All these factor are eventually time and pressure dependent and they superpose each other which makes their individual contribution particularly difficult to determine. The factors which are of particular concern for the issue of varying ozonesonde manufacturer and cathode solution concentration are contained in the terms z and $\varphi(p)$. The details of the differences in ozonesonde manufacturer and how they affect these terms can only be speculated on at this time. The differences in cell manufacturer may affect the efficiency of electron release at the anode and electron gain by iodine at the cathode, or may affect reactions of ozone and the cell walls. Either of these would affect z. Differences in KI concentration in the dilute electrolytic solution likely affects the efficiency of the conversion of O_3 into I_2 through reaction with KI, thus affecting $\varphi(p)$.

2.2. Review of the standard WMO recommendations

The preparation before the flight of an ECC ozonesonde is crucial for its performance. The Standard Operating Procedures (SOPs) for ECC ozonesondes have been established by a group of experts under the guidance of the World Calibration Center for Ozonesondes (WCCOS) of the WMO [Smit and the ASOPOS panel, 2014]. These results are from a ten year coordinated process to improve the different aspects of ECC ozonesonde preparation and data processing. Operating the ECC ozonesondes under these prescribed rules has been tested extensively in different JOSIE experiments at the Jülich Research Center [Smit et al., 2007]. The large balloon experiment BESOS was designed as an extension in the real atmosphere of these laboratory developments [Deshler et al., 2008]. In addition to 18 ozonesondes, the BESOS gondola included also the Jülich reference UV spectrometer [Proffitt et al., 1983, Smit et al., 2007] to replicate as far as possible the test procedure of the JOSIE experiments. The two experiments agree on the following conclusions:

1. ECC ozonesondes prepared according to the SOPs provide very reproducible (<2-3%) measurements.
2. The results depend on the ozonesonde manufacturer (e.g. EN vs. SP) and on the sensing solution concentration (e.g. 0.5% vs. 1.0%). The order of magnitude of the differences is 5%.
3. The combinations "EN-0.5%" and "SP-1.0%" as "provider-solution" agree with each other to within 2%, but overestimate the reference UV photometer in the stratosphere by 5-10%. However, the total ozone column estimated from these combinations on the BESOS gondola agreed with a collocated Dobson spectrophotometer.
4. It is possible to reconcile the measurements made with other "provider-solution" combinations and the photometer with the help of a simple linear in ln (p) transfer function.

JOSIE and BESOS were completed under conditions not reflecting directly the diversity of the operational services around the world. Each sounding station has specific instrumentation and operators even though they follow the same procedures. It is therefore important to verify that the conclusions from JOSIE and BESOS are also reflected in results of several operational stations. At the stations, it is not possible to fly a reference UV instrument so only relative differences can be derived from dual or multiple ozonesonde flights. In the present analysis the JOSIE and BESOS results will be analyzed in a similar way as the other dual multi instrument flights.

2.3. Review of previous solution concentration and provider comparisons

In the mid 1990s the problems of differences in "provider-solution" combinations were still of marginal importance [SPARC, 1998]. The EN-SCI company had entered the market only a few years earlier and the disparate preparation procedures prevented clearly identifying problems. The conclusions at that time were that the effect of changes in ECC KI solution concentrations were complex and required further study before clear recommendations could be provided.

McPeters et al. [1999] reports a 2% consistency from five triple ECC flights during a validation campaign at Mauna Loa in 1995 using EN 1.0% ozonesondes. The authors report that the ozonesondes overestimate the Dobson measurements by an average of 5%. In profile, above 25 km, the ozonesonde measurements are greater than the lidar and microwave measurements by a similar amount. Boyd et al. [1998] presented ozone profile differences from EN ozonesondes with 1.0 and 0.5% KI solutions at Lauder, New Zealand. A 5-6% systematic overestimation of ozone by the 1% solution compared to the 0.5% with the EN ozonesondes is evidenced by comparison of the ozone profile and total column collocated lidar and Dobson measurements.

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For an analysis of the transition from Brewer Mast to ECC (EN - 1.0%) ozonesondes, the ECC data were normalized to the Dobson column to be consistent with the Brewer Mast SOPs [Stübi et al., 2008]. Stübi et al. found that the ECC ozonesondes systematically overestimated the total ozone column with a mean normalization factor of 0.95 for more than 100 dual flights between ECC and BM indicating an overestimation of 5% of the ozone column by EN-1.0 ozonesondes.

Kivi et al. [2007] analyzed a series of dual and multiple ozonesonde flights with SP and EN instruments using 0.5% and 1.0% sensing solutions. For the homogenization of ozone profiles from the Northern high latitude stations the authors derived a third order polynomial correction based on altitude to correct the overestimation of ozone from EN-1.0% compared to SP-1.0%.

The laboratory work (Smit et al. [2007] along with the several field measurements (Boyd et al. [1998]; McPeters et al. [1999]; Stübi et al. [2008]; Kivi et al. [2007]; Deshler et al. [2008] all indicate a relatively consistent systematic bias, on the order of 5%, between the different ozonesonde manufacturers with the same electrolytic concentration, and between different electrolyte concentrations in ozonesondes from a single manufacturer.

2.4. Chemistry of the ECC ozonesonde

The early stoichiometric work on the yield of iodine from ozone showed varying results with much of the uncertainty arising from the variety of KI sensing solutions, pH buffers, and sensors used [Saltzman and Gilbert, 1959; Boyd et al., 1970; Dietz et al., 1973; Pitts et al., 1976; Lanting, 1979]. Common to many of the references was the suggestion of a secondary reaction producing additional iodine perhaps from reactions of iodide with the phosphate buffers. Johnson et al. [2002] showed that the same type of ECC ozonesonde operated with differing amounts of KI, and corresponding changes in the phosphate buffers, provide slightly different stoichiometric ratios of iodine to ozone. In fact these differences were very apparent in the initial development of the ECC ozonesondes [Komhyr, 1969; 1986].

More difficult to identify are the reasons for the differences between the SP and EN ozonesondes which are in principle the same, yet the EN ozonesondes consistently indicate a higher ozone amount when compared to an SP ozonesonde with the same sensor KI electrolyte concentration. This may be related to differences in the platinum electrode sensitivity, the ion bridge conductance, or the inner surface proprieties of the cells. A detailed study of the reasons for the differences has not been performed and is beyond the scope of this paper. As will be shown the effect is very similar to the effect of differences in KI concentration.

2.5. Need for homogenization for data comparison

The Montreal protocol signed in 1991 has established the publication every four years of an Ozone Assessment [e.g. WMO, 2010; 2014]. One of the most comprehensive reports regarding measurement techniques was the SPARC-IOC-GAW study [WMO, 1998]. An update of this study, the SI2N (SPARC/IGACO/IOC/NDACC) initiative to report the present state of knowledge of the different techniques and to reprocess long time series accordingly is being covered in a special issue of Atmos. Chem. Phys., Atmos. Meas. Tech., and ESSD. A parallel European Space Agency-CCI (Climate Change Initiative) project was established in 2011 to improve the satellites' products for the prominent "Essential Climate Variables", one being ozone. Comparisons with current satellite measurements of ozone, and future instrumental improvements for new satellite generations, require more accurate ground based data series for validation [Liu et al., 2006; Hubert et al., 2016]. Such comparisons have a rich heritage in previous field campaigns comparing various methods to measure ozone [Hilsenrath et al., 1986; Kerr et al., 1994; Margitan et al., 1995; Komhyr et al., 1995b; Meijer et al., 2004].

The MOZAIC datasets [e.g. Thouret et al., 1998; 2006] obtained from in-service aircraft provide a comparison to tropospheric ozonesonde measurements especially at the tropopause where ozone profiles are at their minimum values. Staufer et al. [2013; 2014] found a systematic difference with ozonesondes when aircraft measurements were compared to ozonesonde measurements determined by matching balloon and aircraft measurements via air parcel trajectory calculations, concluding an overestimation by the ozonesondes on the order of 5-10 % in the upper troposphere - lower stratosphere region. Logan et al. [2012] extensively analyzed tropospheric ozonesonde data by

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comparison to MOZAIC aircrafts' ascent/descent profiles and to high altitude ground based measurements, pointing out biased and suspicious datasets.

Clear improvement of ozonesonde measurement precision for properly prepared and analyzed instruments is shown in recent comparison experiments for both the EN and SP instruments [Smit et al., 2007; Deshler et al., 2008]. A good sign of the stability of these results in the last ten years is confirmed in recent studies, e.g. Logan et al. [2012]. These results are not the case for the accuracy of measurements with "provider-solution" combinations which differ from the recommendations. Such combinations typically deviate from trusted ozone measurements by 5-10%. These latter deviations are now reasonably well characterized by a large set of comparison measurements, Table 1. Thus, it is time to apply corrections to ozonesonde data measured with provider-solution combinations differing from the standard WMO recommendations. Such applications will homogenize these data sets and thereby improve data quality, usefulness for trend analysis, global homogeneity, and references for satellites and models. The appropriate corrections to apply, using the large comparison data set available, are developed in sections 3 and 4.

3. Methods to establish the transfer function

3.1. Summary of datasets considered in the present analysis.

The present analysis of dual ozonesonde measurements is an extension of the JOSIE and BESOS experiments to link short term instrument comparison campaigns to routine operations at regular sounding stations. JOSIE and BESOS used the same reference UV photometer [Proffitt et al., 1983] for the final comparisons and the results of those comparisons confirmed the high precisions and good accuracy of well-prepared ozonesondes. For the extensive additional data presented here an independent (e.g. photometric) reference is not available, rather the ozonesondes are compared pairwise. The JOSIE and BESOS data are included here also pairwise, Table 2. The first of these dual ozonesonde comparisons began in the late 1990s at different locations. Although there was no coordinated effort, the motivation at each station was similar. The need for homogenization of the long term ozonesonde record at the station. Table 1 summarizes the datasets used for the present analysis. Differences in the details of these comparisons at the different stations are described below.

3.1.1 JOSIE09 – Ozone profile simulation chamber, Jülich, Germany

The JOSIE experiments have been described by Smit and Kley [1998], Smit and Sträter [2004a, b] and Smit et al. [2007] so only the experimental principles are reviewed here. Four ozonesondes can be placed simultaneously in the atmospheric simulator. Pressure and temperature can be regulated from surface conditions to 10 hPa and -70ºC. The ozone flow is controlled in a glass cavity and measured in parallel by the ozonesondes and a reference UV photometer. Different types of "temperature-pressure-ozone" profiles are generated to simulate high-, middle- or tropical-latitude profiles. In the present analysis, only pairs of ozonesondes, representing different provider-solution combinations, simultaneously operated in the chamber are considered. This explains the low number of comparisons available for these data.

3.1.2. BESOS – Balloon-borne multi instrument gondola, Laramie, Wyoming

The BESOS experiment was described fully by Deshler et al. [2008]. A collaborative team of ozonesonde experts prepared a balloon gondola (100 kg) with 16 ozonesondes, the Jülich UV photometer [Proffitt et al., 1983], a Vaisala radiosonde, and a data acquisition system. Dobson and Brewer spectrophotometers were available at the launch site. The flight to 32 km was completed on 13 April 2004 from Laramie, Wyoming. The data from this flight are used here similarly to the JOSIE data by considering the ozonesondes pairwise. The payload had a set of 12 standard ozonesondes, 6 from EN and 6 from SP; out of each set of 6 ozonesondes, 3 had a 0.5% and 3 a 1.0% KI solution concentration. Thus, a set of nine pairs are available for each "provider-solution" combination, Table 2.

3.1.3. Payerne, Switzerland – Balloon-borne dual ozonesonde gondolas

The Payerne station is run under the responsibility of MeteoSwiss and the radiosondes used were the SRS model from the Swiss company Meteolabor. SRS radiosondes are not capable of interfacing two ozonesondes, so for the dual flights two independent receiving systems were used. These were

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synchronized at the time of the launch to better than one second and the sampling frequency was about 7 seconds. For the analysis, the data are interpolated to a common time scale to avoid any problems related to a difference of the pressure readings from the two ozonesondes. The datasets consist in two campaigns embedded in the operational service as a dual flight for the Wednesday sounding. The reference (operational) ozonesonde being the EN-0.5%. The data sets consist of:

1) 48 pairs EN-0.5% and EN-1.0% - June 2002 - July 2003.
2) 26 pairs EN 0.5% and SP 1.0% - May 2005 - December 2006.

3.1.4. McMurdo Station, Antarctica – Balloon-borne dual ozonesonde gondolas

Measurements from McMurdo Station, Antarctica, were conducted by the University of Wyoming during the ozone hole period, August –November, 1986-2010 [Mercer et al., 2007]. From this record 18 flights with two EN ozonesondes interfaced to a single microprocessor and Vaisala RS80 radiosonde were completed. The years (number of flights) are: 1996 (3), 1999 (1), 2000 (1), 2002 (6) and 2006 (7). In each case EN-1.0% and EN-0.5 % KI concentration solutions were compared. The low temperature conditions in Antarctica require a heater near the cells to prevent the solution freezing at high altitude. This preventive action is visible on Figure 3 with a mean pump temperature which stays close to 24ºC at high altitude. The background currents are low with a slightly higher value for the ozonesondes with 1.0% solution compared to the 0.5%, Figure 1. This dataset is characterized by a large variety of ozone profiles from typical ozone hole to more conventional polar conditions; ozone column ranges are 126 - 423 DU.

3.1.5. Sodankylä, Finland – Balloon-borne dual and multi ozonesonde gondolas

The Sodankylä station is run by the Finnish Meteorological Institute. The radiosondes used for the dual sonde and multiple sonde measurements were the Vaisala RS80. In the dataset used here there is a mix of 5 dual flights and 4 larger balloon flights with "6-sonde" payloads. The larger balloon payloads were recovered and flown again the next day with reused ozonesondes. The mean pump temperature profile shown in Figure 3 is characterized by the leveling of pump temperature at about 22ºC due to the use of a heater in case of the comparisons made under cold stratospheric conditions. For both the multiple and dual ozonesonde payloads a single RS80 radiosonde was applied per two ozonesondes, using interface extension boards provided by EN-SCI. Thus one receiving system was involved per two ozonesondes. The data set consists of

1) 6 pairs EN 0.5% and EN 1.0% - September 2003 - July 2004.
2) 5 pairs EN 0.5% and SP 1.0% - May 2003 - March 2005.
3) 8 pairs EN 1.0% and SP 1.0% - September 2003 - July 2004.

3.1.6. Wallops Island, Virginia - Balloon-borne dual ozonesonde gondolas

Resources for ozonesonde measurements, with Sippican radiosondes, from Wallops Island have been, and continue to be, provided by NASA Headquarters. The Wallops Island practice is to use the background current measured during the day-of-flight preparation prior to exposing the ECC to moderate ozone (5μA) for 5 minutes; these backgrounds are smaller than the others shown in Figure 1. The values of i_o are, however, close to each other within the pairs so this difference has a negligible effect on the comparison measurements which were coordinated by matching the elapsed times of flight of the two systems, similar to the procedure for Payerne. The data sets consist of:

1) 7 pairs SP 5A-ECC's 0.5% vs. 1.0% in 1996.
2) 11 pairs SP 6A-ECC's 0.5% vs. 1.0% in 2004.

3.1.7 Laramie, Wyoming – Balloon-borne multi ozonesonde gondola

These results were obtained from a collaboration between the Climate Monitoring and Diagnostic Laboratory (CMDL) of the National Oceanic and Atmospheric Administration and the University of Wyoming. CMDL prepared the gondola and the University of Wyoming conducted the flight operation. The measurements were obtained from a gondola containing 6 EN ozonesondes, 3 with 0.5% KI and 3 with 1.0% KI. The instruments were synchronized to a common data system and an RS80 Vaisala radiosonde. The flight occurred on 20 June 1996 and reached an altitude of 32 km.

3.2. Data Processing

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The ozone data processing from the measured current is based on Eq. 4 with little variability among the datasets. The major difference is in the sampling frequency of the measurements which ranged from 0.2 to 1.0 Hz. The typical e-folding response of an ozonesonde is of the order of 0.05 Hz [Smit and Kley, 1998]. All the sampling rates here are faster than this, but are the same for every pairwise comparison so the sampling rate will not affect a comparison. However, since the data analysis is based on the individual pair differences, it is necessary to average the high frequency measurements to a common time scale to avoid unduly weighting the high frequency data relative to the lower frequency measurements. Ultimately the high frequency data were averaged to a frequency of 0.2 Hz so that when the data weighted means of the comparisons were calculated each comparison profile was weighted about equally.

3.2.1. Back ground current i_0

In Figure 1, the background currents measured for the different data sets are summarized as box and whisker plots. For all sites except Wallops Island, these are the background currents after exposure to moderate ozone and just prior to flight. The i_0 used at Wallops Island was prior to exposure to moderate ozone on the day of flight preparations. This may explain the slightly lower backgrounds obtained at Wallops Island. The medians of i_0 from the various sites are all below 0.03 µA indicating the quality and consistency of the ozonesonde preparations. The i_0 values for the 1.0% solution tend to be slightly higher compared to the 0.5% solution suggesting the impact of the larger buffer amount [Johnson et al., 2002]. Boyd et al. [1998] argue that the large difference between their ascent and descent ozone (tropospheric) profiles is attributable to an increase in the background current after exposure to high ozone in the stratosphere. They have observed this increase with the 1% solution but not with the 0.5%. Similarly in the laboratory preparation, the ozonesondes are exposed to high ozone for ten minutes and the slightly higher i_0 values for the 1.0% solution could be related to such a memory effect. The origin of the background current is still poorly understood [Smit et al., 2007]. Vömel and Diaz [2010] measured the rate at which ozonesondes approach background in the laboratory, with some implications for measurements in the tropics of very low tropospheric ozone concentrations.

3.2.2. Pump flow rate

The pump flow rate is the second parameter measured in the laboratory preparation of each ozonesonde. Figure 2 shows the coherency of the pump flow rates at the 5 field measurements sites. In about half the measurement sets, the inner quartiles of the variations amongst the instruments measured are less than 3% of the median, and in all cases except one the inner quartiles are less than 6% of the median. The figure also shows a systematically 0.2-0.3 ml s^{-1} higher flow rate for SP pumps compared to EN pumps.

3.2.3. Pump efficiency correction

The application of pump efficiency corrections vary amongst the datasets. In general Komhyr [1986] is used for SP and Komhyr et al. [1995a] is used for EN ozonesondes. Since the comparisons analyzed are amongst pairs of identical ozonesondes, the pump efficiency does not play an important factor unless significantly different pump efficiencies were applied separately to the ozonesondes in a measurement pair. In most cases the same efficiency factors were applied to both ozonesondes of a pair. The one exception is the Wallops Island data, where individual pump efficiency curves were applied prior to mid 2000 when the system failed. The pairwise comparisons of these data, however, were quite similar to the Wallops Island data where identical pump efficiencies were used, and to the pairwise comparisons from the other data sets.

3.2.4. Pump temperature

For the data processing, individual pump temperatures are used as illustrated in Figure 3 for the mean pump temperature profiles for each dataset. The standard deviations of the temperature range from 1ºC for McMurdo Station to 5ºC for Sodankylä. The pump temperature decrease over a profile is around 7-10ºC for the ozonesondes with a heater and 20-23ºC for the ozonesondes without a heater. This parameter also is reproducible within the ozonesondes pairs and thus doesn't impact significantly the pairwise comparisons.

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457 **4. Comparisons of ozone partial pressure**

458 In Figure 4, an example of a dual flight from Payerne is illustrated. The two ozonesondes
459 separated by a 1.5 m long boom were hanging under the same balloon and the data transmitted to two
460 independent receiving systems on the ground. The ozone profiles have identical structures and
461 differences increase near the ozone maximum at pressures less than 50 hPa, indicating some
462 dependence on both ozone partial pressure and atmospheric pressure. The increased sensitivity of the
463 1.0% solution is clear throughout the profile.

464 **4.1. Differences between 1.0% and 0.5% KI cathode solutions for EN and SP ozonesondes**

465 The simplest way to analyze the data is to compare ozone partial pressures measured by
466 ozonesonde pairs operated simultaneously, either in the atmosphere or in the simulation chamber.
467 Scatter-plots of ozone partial pressure measured with ECC ozonesondes with 1.0% solution, x-axis,
468 against simultaneous measurements with a 0.5% solution, y-axis, are shown in Figure 5 for EN
469 ozonesondes flown from a) Payerne and b) McMurdo Station, and SP ozonesondes from c) BESOS
470 and d) JOSIE09. The color coding distinguishes four pressure ranges to highlight the altitude
471 (pressure) dependence. Only ozone partial pressures > 0.5mPa have been considered to remove large
472 differences resulting from comparisons of small numbers near the measurement limit of the
473 ozonesondes. Figure 5 demonstrates a near linear relationship between the 0.5 and 1.0% ozonesonde
474 measurements in the four pressure ranges considered, independent of the ozonesonde manufacturer.
475 The mean and standard deviation of the measurement ratios in the various pressure intervals are given
476 in the legends. The mean ratios are used to construct linear fits, which pass through the origin, to the
477 measurements in each pressure range and are displayed in the Figure. The mean ratios and standard
478 deviations for all the measurements from JOSIE09, BESOS, Payerne, and McMurdo Station at the
479 four pressure intervals are given in Table 2. Table 2 also contains bulk fits to all data from Sodankylä,
480 Wallops Island, and Laramie without differentiation according to pressure. Figure 5 and Table 2,
481 upper two boxes, display the remarkable consistency amongst all the data from the varied sources.
482 Note the consistency of the mean ratios and their standard deviations from all data sources. Figure 5
483 and Table 2 also indicate a consistent 3-4% underestimation of ozone from a 0.5% KI solution
484 compared to a 1.0% solution from the ground up to 30 hPa for both SP and EN ozonesondes. An
485 increase of the difference to 6-8% at pressures below 30 hPa is also shown by the four data sets,
486 Figure 5.

487 Table 2 also shows additional analysis in three other comparison groups: the third and fourth
488 boxes correspond to a change of provider keeping the same concentration and the final box a fit to a
489 mix of SP 1.0% and EN 0.5%. The tendency of a decrease of the linear term at lower pressures is
490 present in most data sets except for this last group where the linear fit is not statistically different than
491 the fits at pressures above 30 hPa. The correlation coefficients for the data are all above 0.9. There are
492 four cases in Table 2, two in the Payerne and two in the BESOS datasets, with standard deviations >
493 0.1. These are all in the column for pressures > 500 hPa. The origin of the large standard deviations for
494 Payerne, EN-1.0 vs EN-0.5, probably lies in the outliers apparent in Figure 5a) at pressures > 500 hPa.
495 Such discrepancies are less obvious in the other Payerne comparison and in the BESOS data. The
496 cause of these larger standard deviations was not investigated further in light of small standard
497 deviations in all datasets at pressures less than 500 hPa.

498 Considering the strong linear relationship of the dual measurements for the differences in
499 concentration in the same ozonesonde type, and differences in ozonesonde type with the same sensor
500 concentration, it is natural to simply use a single ratio to characterize the relationship of the two
501 measurements at pressures above a certain threshold pressure, and then to use a linear relationship in
502 $\log_{10}$ (p) to fit the ratio at lower pressures, insuring that the two systems merge at the threshold
503 pressure. The ratio of the measurements from a single manufacturer at two cathode concentrations is
504 illustrated in Figure 6 as an ensemble of red dots for the same data sets as in Figure 5. The dual flight
505 measurements at Payerne and McMurdo Station, Figure 6a), 6b), show a larger spread of the data but
506 the number of measurements are considerably larger and the atmospheric conditions more diverse than
507 in the BESOS and JOSIE experiments, Figure 6c), 6d). Occasionally, individual flights from Payerne
508 and McMurdo Station deviate from the majority of comparisons, seen as a set of points separated from

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the main cloud of points. These few comparisons are clear outliers compared to the majority of measurements.

These comparisons suggest that measurements from ozonesondes using a 1.0% KI concentration in the cathode can be used to derive measurements which would have been obtained from measurements with a 0.5% KI solution if the measurements using the 1.0% KI solution are modified using a pressure independent ratio at pressures above some threshold pressure and a pressure dependent ratio below the threshold pressure. Different values for the threshold pressure to switch from a single ratio to a pressure dependent ratio were tested but the results were not very sensitive to this value and it has been fixed at 30 hPa.

With the threshold pressure level established each data set was used to calculate a mean concentration ratio at pressures, p, $\geq$ 30 hPa and a linear, in $\log_{10}(p)$, fit at p < 30 hPa. The results of this analysis are displayed in the upper two boxes of Table 3 for all datasets listed in Table 1. The second column provides the concentration ratio and its standard deviation for p $\geq$ 30 hPa, the third column the number of individual ozonesonde to ozonesonde comparisons (N). Recall each dataset was standardized to a sampling frequency of 0.2 Hz to balance the weights of the high frequency and low frequency data equally. Thus the number of data points represents primarily the number of individual ozonesonde to ozonesonde comparisons within each dataset. For p < 30 hPa columns 4, 5, and 6 list the fitting parameters providing the slope in $\log_{10}$ (p) and then the offset, corresponding to the value of the concentration ratio at 1 hPa. Two offsets are listed. The first is the one used. The second offset is derived without a requirement to match the p $\geq$ 30 hPa transfer function. The small differences between these two offsets reflects the fact that the function chosen is doing a good job of representing the data even without a fitting constraint. Column 7 provides the number of data points (N) at p < 30 hPa, column 8 the number of dual ozonesonde measurements.

The coefficients for the transfer function representing the ratio of ozone sensed at the differing concentrations were calculated as a weighted mean (according to sample size) of the individual parameters given in Table 3 for all datasets considered in the analysis. These values comprise the final row in each box in Table 3. Not all data from each dataset were used due to unstable ratios at particularly low ozone concentrations, or during clearly deficient ozonesonde performance. The primary examples of the data excluded are displayed as the dark areas in Figure 6. These data were excluded for the following specific reasons:

1. McMurdo Station : Some of the dual measurements were completed in ozone hole conditions, and in these cases ozone drops to near zero producing highly divergent ratios,
2. JOSIE: At three points during the simulated profiles, the ozone flow was stopped to measure the residual signal and the response time, producing very low ozone and thus likewise ratio divergences.
3. BESOS: in the first minutes of the flight, the data acquisition unit was unstable and too noisy to consider in the present analysis.

The common transfer function to analyze differences in KI concentration, OZ_{conc}, is given in Eq. 5 and presented in Figure 6 as a blue line for p $\geq$ 30 hPa and a black line for p < 30 hPa. The function displayed in Eq. 5 accounts for a change of solution concentration independently of the ozonesonde provider.

$$\frac{OZ_{0.5\%}(p)}{OZ_{1.0\%}(p)} = 0.96, \quad \text{for } p \geq 30 \text{ hPa}, \tag{5}$$

$$\frac{OZ_{0.5\%}(p)}{OZ_{1.0\%}(p)} = 0.90 + 0.041 \bullet \log_{10}(p), \quad \text{for } p < 30 \text{ hPa}.$$

4.2. Difference between EN and SP with the same solution concentration

In Figure 7, profiles of the ratio of SP and EN ozonesondes with the same KI solution concentration are shown in the same format as Figure 6. The upper panels show the difference between the SP and EN ozonesondes with a 1.0% solution concentration while the lower panels are for

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the 0.5% solution concentration. Figure 7a) is from multiple dual flights at Sodankylä over the period 1995-2002 while the other panels present the analysis of the JOSIE and BESOS experiments. Using these data, and following the procedure used to reconcile the two solution concentrations in the same ozonesonde provider, section 4.1, the common transfer function to correct a change from one provider to the other was derived. Similar to the analysis in section 4.1 the results from fits to each data set and their weighted mean are provided in the third and fourth box in Table 3. Combining the results from the boxes comparing EN and SP ozonesondes at 1.0% and EN and SP ozonesondes at 0.5% results in the transfer function, OZ_{prov}, given in Eq. 6.

$$\frac{OZ_{SP}(p)}{OZ_{EN}(p)} = \begin{cases} 0.96, & \text{for } p \geq 30 \text{ hPa} \\ 0.764 + 0.133 \bullet \log_{10}(p), & \text{for } p < 30 \text{ hPa} \end{cases} \quad (6)$$

As for OZ_{conc}, the coefficients of the transfer function OZ_{prov} were calculated individually for the five data sets and an overall mean, weighted by the number of comparisons and flights, calculated. The JOSIE data present a larger spread than in the previous case and individual simulator runs are visible. Aside from the BESOS data for 0.5% KI at p > 150 hPa, Figure 7d), where there is a tropospheric bias of 2%, the OZ_{prov} curve reproduces the results from the different data sets. The $\log_{10}(p)$ coefficient is slightly larger in OZ_{prov} than in OZ_{conc} producing a lower value for the constant term (intercept at 1 hPa) since the constant ratio terms are the same ($ratio(OZ_{conc}) = ratio(OZ_{prov}) = 0.96$) for the $p \geq 30$hPa domain, while the decrease in the ozone ratio between the providers increases at lower pressures comparable to the decrease in ozone ratio at differing solution concentrations, Figure 6.

4.3. Similarity between the combinations EN-0.5% and SP-1.0%

With the similarity of the two transfer functions OZ_{conc} and OZ_{prov}, it is natural to counterbalance them and compare EN ozonesondes with 0.5% solution and SP ozonesondes with 1.0% solution. The results are given in Figure 8 for a) Payerne, b) Sodankylä, c) BESOS, and d) JOSIE09. The horizontal axis of Figure 8 is expanded compared to Figures 6 and 7 and the number of comparisons are low for JOSIE (3 cases) and Sodankylä (5 cases). The agreement between the ozonesonde pairs is not as clear as for the previous cases as illustrated by the Payerne data which present a somewhat larger dispersion (10%) in Figure 8 compared to Figure 5 (5%). The BESOS data have a distinct behavior below and above the tropopause (200 hPa) while the five Sodankylä flights show a constant 3% overestimations by the SP ozonesondes. However, if no simple transfer function would allow to reconcile these observations, it is noticeable that the majority of the points are within 3% around 1.0 illustrated by the gray zone in Figure 8. Table 3 last 3 lines also reveal no marked departure from unity.

The present conclusion is that the interchange between the EN-0.5% and SP-1.0% combinations would not have a negative impact on the continuity of a time series. It may increase the variability, but no noticeable break should appear at the transition between these two systems.

4.4. Transfer function application on the Nairobi data set

The Kenyan Meteorological Department (KMD), in collaboration with MeteoSwiss, operates the Nairobi aerological station, within the SHADOZ (Southern Hemisphere ADditional OZone station) network, [Thompson et al., 2012]. Weekly ozone soundings began in 1996. In summer 2010, due to interruption of the Vaisala RS80 radiosonde production, new equipment based on the RS92 was installed at Nairobi. Coincidently, the ozonesonde solution concentration was changed from 1.0% to 0.5%, keeping the same ozonesonde provider, EN. This data set is used here to illustrate the application of the transfer function OZ_{conc} defined in Eq. 5. In Figure 9, a time series on three pressure levels is illustrated. Color separates the measurements with the different solution concentrations. In the troposphere, the ozone partial pressure is low (2.5 mPa) and the variability is too high to detect

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changes of a few percent. Therefore the 500 hPa data illustrated in Figure 9 do not show the change of sensor concentration. At 30 hPa, the quasi biennial oscillation is the dominant signal and this requires at least a complete cycle after the change to correctly see the effect; however, there is a clear decrease of the mean ozone value before and after the change of concentration. Finally at 10 hPa, the lower variability and the absence of geophysical cycles in the data allow the effect of the concentration change to be clearly seen.

To quantify the concentration change, the mean ozone profiles before and after 2010 have been calculated and appear in Figure 10, with black squares for 1996 to 2010 and blue circles after 2010. Red triangles correspond to the 1996 - 2010 data after correction of each profile with the transfer function OZ_{conc}. The difference profiles are illustrated on the right side of Figure 10 in black for the original data and in red for the corrected data for the period 1996 - 2010. The error bars combine the variabilities of the two original mean profiles. Even though the differences were not significant for the pressure >30 hPa, the correction shows a net improvement for the higher levels.

For a total ozone column comparison three estimations are available for Nairobi station: the ozonesonde integrated profile, a Dobson D018 co-located spectrophotometer and the OMI (Ozone Monitoring Instrument) satellite overpass measurements. The change of sensing solution and the corrections shown in Figure 10 have affected the ratios of the total column ozone as shown in Table 4.

5. Discussion

There has been a significant effort to reconcile ozonesonde measurements completed with instruments from the two ozonesonde providers, Science Pump and ENSCI, with various combinations of the recommendations for the KI sensor solution concentrations 1.0% and 0.5%. The motivation for this effort rests on characterizations of the precision and accuracy achievable with well-prepared ozonesondes through laboratory tests [Smit and Sträter, 2004a; 2004b; Smit et al., 2007] and field tests [Logan et al., 1999; 2012; Kivi et al., 2007; Deshler et al., 2008]. These results have shown that the precision of an ECC ozonesonde is better than observed systematic differences between ozonesonde type or solution concentration. The results presented here demonstrate that the differences in ozonesonde type, with the same solution concentration, are quite systematic and thus can be characterized, to within experimental uncertainties, with a single relationship for both 0.5 and 1.0% KI concentrations. Similarly, systematic differences between sensor solution concentrations in the same ozonesonde for both SP and EN ozonesondes can also be characterized by a single relationship. These results attest to the consistency in ozonesonde manufacturing for both companies and that both ozonesonde types have similar differences in performance when the KI solution concentration is varied, pointing again to the strength of the instrumental technique and the instruments.

The rationale employed in this analysis was to find a simple set of relationships which could be applied throughout all the data analyzed. Clearly there are differences in the various datasets as shown in Figure 6. In this case the recommended relationship, Eq. 5, for the relationship between 0.5% and 1.0% KI does not optimally fit the BESOS SP data, Figure 6c), but it does quite well against the Payerne and McMurdo Station data, Figure 6a), 6b). The overestimation of the BESOS SP data is counterbalanced by the under estimation of the JOSIE09 SP data, Figure 6d). This relationship does well against the BESOS EN 0.5 – 1.0% and the Wallops Island SP 0.5-1.0% comparisons (not shown). The relationship is not steep enough for the Sodankylä measurements at pressures < 30 hPa. Differences such as these led to the alternate transfer functions using first to third order polynomials in log pressure derived by Kivi et al. [2007] and Deshler et al. [2008]. Neither of these relationships, however, would do well across the full data set analyzed here. In particular the third order polynomial provided by Kivi et al. was required due to the significant ratio decrease at pressures below 50 hPa.

Similar comments may arise from the analysis of the ozonesonde type comparisons, Figure 7, although in general the proposed relationship requiring a more significant decrease in the ozonesonde type ratio at pressures below 30 hPa is better at reproducing the ozonesonde type comparisons. The only dataset not shown in this comparison is from JOSIE09 comparing the ozonesonde types at 1.0%. That ratio profile compared to the relationships recommended is quite similar to the comparison at 0.5%, Figure 7c).

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The reasons behind the increase in ozone sensed with increase in KI concentration has not been fully explored and is beyond the scope of this paper. The discussions of this effect have centered on the importance of the sodium phosphate hydrate buffers used to maintain the pH of the solution. These buffers, which vary in proportion to the KI concentration, may lead to secondary reactions between iodide ions and the buffer leading to excess iodine, thus indicating additional ozone [Saltzman and Gilbert, 1959; Johnson et al., 2002]. Similarly there have been discussions on the reasons behind the increased sensitivity of the EN ozonesondes compared to SP ozonesondes. Speculation has centered on the efficiencies of the platinum electrode in scavenging the iodine, the conductance of the ion bridge, or the surface properties of the SP Teflon cells versus the EN molded plastic cells, but there has been no systematic investigation of this effect. This also remains beyond the scope of the work presented here.

For a transfer function to have wide acceptance within the community it must have reasonable application to the widest possible set of comparisons. Specialized transfer functions have been derived for particular subsets of the data [Kivi et al., 2007; Deshler et al., 2008] but it has not been demonstrated that these functions are useful beyond the specific data from which they were derived. The analysis here sought to develop as simple a relationship as possible based on the full comparison data set available. This was achieved through weighting of the ratio fits by the number of profile comparisons to arrive at the final four relationships described in Eqs. 5 and 6. Once derived the individual datasets were compared against the derived transfer functions and a subset of these shown in Figures 6 and 7. While Kivi et al. [2007] did not show such a comparison, Deshler et al. [2008] did. Figure 5 from Deshler et al. could be compared here against Figures 6c), 7b), and 7d). Compared to Deshler et al. the fits proposed here improve the comparisons of ozonesonde type while not significantly diminishing the comparisons of sensor concentration. Coupling this with the ability of the fits to reproduce nearly all data sets within the uncertainty of the fits provide strong support for the validity of the proposed transfer functions. This is not to argue that the relationships proposed here should be used instead of results of an individual investigation of a particular comparison dataset; however, such an individual transfer function must be supported by the appropriate measurement set, and made available publicly through the refereed literature. For investigators without access to the resources to conduct such a study, the transfer functions proposed here will do an adequate job of data homogenization.

The final comparison investigated here is between the two manufacturer's recommendations. This was done through 43 comparison profiles summarized in Figure 8. There was no attempt to derive a fitting function for these data and as the figure illustrates such an exercise would be difficult. The ratio of SP-1.0 to EN-0.5 has a wide dispersion, which is amplified in the figure by the reduced axes for the ratios, from 0.8 – 1.2 compared to Figures 6 and 7. Figure 8 suggests some bias in the smaller datasets investigated, with ratios > 1 for Sodankylä and BESOS, but < 1 for JOSIE09, while Payerne, by far the largest dataset, shows no systematic bias. The objective analysis shown in Tables 2 and 3 quantify these differences but also show that the differences are on average generally not different than 1.0 in contrast for the results of the solution concentration and ozonesonde type comparisons. Thus the data here suggest that the two, manufacturer and WMO, recommended ozonesonde type and solution concentration packages can be used directly and should be widely comparable.

6. Summary and Conclusions

Measurements with various combinations of ozonesonde type, Science Pump or ENSCI, and with differing combinations of the KI solution concentration, 1.0% or 0.5%, have led to variations in ozonesonde preparation at a number of ozonesonde stations throughout the world. These changes began in the mid 1990s and played a role in the analysis of ozonesonde data between then and the late 2000s [Mercer et al., 2007; Tarasick et al., 2016]. Recognizing that these differences exceeded the accuracy and precision that is possible from ozonesondes [Smit et al., 2007; Deshler et al., 2008] led many investigators to independently explore the differences that occur when the same ozonesonde is operated with differing solution concentrations, and when differing ozonesonde types are operated with the same solution concentrations [Johnson et al., 2002; Kivi et al., 2007; Smit et al., 2007; Deshler et al., 2008]. Measurements from these investigators and other unpublished comparisons have been analyzed in this paper. The analysis has focused on three basic comparisons: 1) Sensor solution

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composition differences in ozonesondes of the same type, 2) Ozonesonde type differences using the same sensor solution concentration, and 3) Differences of the manufacturer and WMO recommendations, Science Pump 1.0% and ENSCI 0.5% KI solution concentrations. Using the published and unpublished data has resulted in the analysis here of 116 profile comparisons for solution concentration differences, 38 profile comparisons for ozonesonde type differences, and 43 profile comparisons of the manufacturer's solution concentration recommendations. The datasets used in the comparisons have been obtained from the laboratory (JOSIE09), multi-sonde balloon-borne gondolas (BESOS, Sodankylä), and dual ozonesonde balloon-borne gondolas (Payerne, McMurdo Station, Sodankylä, Wallops I., Laramie), involving at least 6 different scientific groups.

Overall the measurements display a satisfying coherence when solution concentrations or ozonesonde type are compared. At pressures above 30 hPa, the surface to 30 hPa, the two measurements can be characterized with a simple ratio displaying almost no pressure dependence. In addition this ratio is, within experimental uncertainty, the same, 0.96, whether the difference is in solution concentration with the same ozonesonde type, or ozonesonde type with the same solution concentration. Ozone concentrations are higher for 1.0% versus 0.5% KI and for ENSCI compared to Science Pump ozonesondes. At pressures below 30 hPa there is a pressure dependence which is linear in $\log_{10}$ of pressure. This pressure dependence is more pronounced for differences in ozonesonde type. The results arrived at here are simpler than previous recommendations, but are based on a much more comprehensive dataset and include all of the data used in deriving the previous transfer functions [Kivi et al., 2007; Deshler et al., 2008] both of whom arrived at a relationship requiring a polynomial in altitude or log of the pressure for all pressures. As evidenced here, when the full datasets are investigated, the complexity of these relationships is not justified by the data.

The conclusions arrived at from the analysis described here are the following:

For differences in solution concentration independent of ozonesonde type:

$$OZ_{0.5\%} = 0.96 \bullet OZ_{1.0\%}, \text{ for } p \geq 30 \text{ hPa},$$

$$OZ_{0.5\%} = [0.90 + 0.041 \bullet log_{10}(p)] \bullet OZ_{1.0\%}, \text{ for } p < 30 \text{ hPa}.$$

For differences in ozonesonde type independent of solution concentration:

$$OZ_{SciencePump} = 0.96 \bullet OZ_{ENSCI}, \text{ for } p \geq 30 \text{ hPa},$$

$$OZ_{SciencePump} = [0.764 + 0.133 \bullet log_{10}(p)] \bullet OZ_{ENSCI}, \text{ for } p < 30 \text{ hPa}.$$

We recommend that all ozonesonde measurements completed with 1.0% KI in ENSCI ozonesondes or 0.5% KI in Science Pump ozonesondes should adjust their data according to the relationships shown above such that the final data product would be representative of 0.5% KI ENSCI or 1.0% Science Pump. This should be done for any data prepared for analysis and for public availability. The investigation of 43 profiles comparing 1.0% KI in Science Pump ozonesondes and 0.5% KI in ENSCI ozonesondes found that the dispersion in the comparisons was centered on a ratio of 1.0. Thus there is no recommendation to alter data obtained from instruments using the recommended concentrations.

If these recommendations are followed it can be expected that datasets experiencing variations in the use of ozonesonde type and solution concentration will see their long term data converge to within the expected ±5% for ozonesondes, and that offsets at the times of transition between the ozonesonde type, or solution concentration change, or both, will be minimized. This will improve significantly the reliability of long term ozone measurements derived from ozone soundings, and indirectly stabilize, in space and time, the long term series of ozone measurements obtained from satellites.

These recommendations have been implemented in the WMO/Global Atmospheric Watch (GAW)'s guidelines for the homogenization of ozonesonde data [Smit and O3S-DQA-Panel, 2012], recommended to the ozone sounding stations of the Network for the Detection of Atmospheric Composition Change (NDACC) and to SHADOZ stations. The effort for the ozonesonde investigators to accomplish these corrections will be significant, but in the end the health of the network is dependent on such quality control measures being implemented, and it will greatly add to the value of the measurements. All future measurements should use the WMO/GAW recommendations for

solution composition. Any deviation from these recommendations should be justified and carefully researched prior to a change.

Author contributions. T. Deshler with R. Stübi performed the data analysis. T. Deshler was responsible for the majority of the writing with input from all co-authors. R. Stübi provided the Payerne data, F. J. Schmidlin the Wallops Island data, J. L. Mercer, B. Nardi the McMurdo Station data, H. G. J. Smit the JOSIE09 data, B. J. Johnson, the Laramie data, R. Kivi the Sodankylä data, T. Deshler the BESOS data.

Data Availability. The ozonesonde measurements used in this analysis are available from the individual investigators and the majority of these data are on the NDACC data base. These data and the code used to created Figures 4-8 are also compiled at ftp://cat.uwyo.edu/pub/permanent/balloon/Manuscripts/Oz_Transfer_Functions/. The data for Figures 9 and 10 are available at the NDACC and SHADOZ data bases.

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References

Barnes, R. A., A. R. Bandy, and A. L. Torres: Electrochemical concentration cell ozonesonde accuracy and precision. *J. Geophys. Res.*, *90*:7881-7887, 1985.

Beekmann, M., G. Ancellet, G. Megie, H. Smit, and D. Kley: Intercomparison campaign for vertical ozone profiles including electrochemical sondes of ECC and Brewer-Mast type and a ground based UV-differential absorption lidar, *J. Atmos. Chem.*, *19*, 259-288, 1994.

Boyd, A. W., C. Willis, and R. Cyr: New determination of stoichiometry of the iodometric method for ozone analysis at pH 7.0, Anal. Chem., 42, 670–672, 1970.

Boyd, I., G. Bodeker, B. Connor, D. Swart, and E. Brinksma: An assessment of ECC ozondesondes operated using 1% and 0.5% KI cathode solutions at Lauder, New Zealand, *Geophys. Res. Lett.*, *25*, 2409-2412, 1998.

Brewer, A. W., and J. R. Milford: The Oxford-Kew ozondesonde, *Proc. R. Soc. Lond. A.*, *256*, 470-495, 1960.

Calisesi, Y., R. Stübi, N. Kämpfer, and P. Viatte: Investigation of systematic uncertainty in Brewer-Mast ozone soundings using observations from a ground-based microwave radiometer, *J. Atmos. Ocean. Technol.*, *20*, 1543-1551, 2003.

Cionni, I., Eyring, V., Lamarque, J. F., Randel, W. J., Stevenson, D. S., Wu, F., Bodeker, G. E., Shepherd, T. G., Shindell, D. T., and Waugh, D. W.: Ozone database in support of CMIP5 simulations: results and corresponding radiative forcing, *Atmos. Chem. Phys.*, *11*, 11267-11292, doi:10.5194/acp-11-11267-2011, 2011.

Davies, J., McElroy, C. T., Tarasick, D. W., and Wardle, D. I.: Ozone Capture Efficiency in ECC Ozonesondes; Measurements made in the Laboratory and during Balloon Flights, EAE03-A-13703, Geophysical Research Abstracts, Vol. 5, 13703, EGS-AGU-EUG Joint Assembly, Nice, France, 6–11 April 2003.

Deshler, T., J. Mercer, H. G. Smit, S. J. Oltmans, B. J. Johnson, R. Stübi, G. Levrat, J. Davies, A. Thompson, J. Witte, F. Schmidlin, G. B. Brothers, S. Toru, and M. Proffitt: Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers, and with different cathode solution strengths: The Balloon Experiment on Standards for Ozonesondes, *J. Geophys. Res.*, *113*, D04307, doi: 10.1029/2007JD008975, 2008.

Dietz, R. N., J. Pruzansky, and J. D. Smith: Effect of pH on the stoichiometry of the iodometric determination of ozone, Anal. Chem., 45, 402–404, 1973.

Dobson, G.M.B., D.N. Harrison, and J. Lawrence: Measurements of the Amount of Ozone in the Earth's Atmosphere and Its Relation to Other Geophysical Conditions, Part II, *Proc. Roy. Soc., A, 114*, 521-541, 1927.

812 Fioletov, V., D. Tarasick, and I. Petropavlovskikh: Estimating ozone vari-ability and instruments
813 uncertainties from sbuv(/2), ozonesondes, umkehr, and sage ii measurements: Short-term
814 variations, *J. Geophys. Res., 111*, D02305, doi: 10.1029/2005JD006340, 2006.
815 GCOS: Implementation Plan for the Global Climate Observing System (GCOS) in Support of the
816 UNFCCC (2010 Update), GCOS-138 (GOOS-184, GTOS-76), World Meteorological
817 Organization, Geneva, Switzerland, 2010.
818 Götz, F. W. P., A. R. Meetham, and G. M. B. Dobson: The vertical distribution of ozone in the
819 atmosphere, *Proc. Roy. Soc. A 145, 416*.
820 Guirlet, M., P. Keckhut, S. Godin, and G. Megie: Description of the long-term ozone data series
821 obtained from different instrumental techniques at a single location: The Observatory de Haute-
822 Provence (43.9°N, 5.7°E), *Ann. Geophys., 18*, 1325-1339, 2000.
823 Harris, N., R. Hudson, and C. Phillips: Assessment of trends in the vertical distribution of ozone, in
824 SPARC Rep. 1 and WMO Ozone Res. Monit. Proj. Rep. 43, World Climate Research Program,
825 Geneva, Switzerland, 1998.
826 Hilsenrath, E., R. Hagemeyer, J. Mentall, A. Torres, W. Attmannspacher, A. Bass, W. Evans, R. A.
827 Barnes, W. Komhyr, and D. Robbins: Results from the Balloon Ozone Intercomparison Campaign
828 (BOIC), *J. Geophys. Res., 91*, 13,137{13,152, 1986.
829 Hubert, D., Lambert, J.-C., Verhoelst, T., Granville, J., Keppens, A., Baray, J.-L., Bourassa, A. E.,
830 Cortesi, U., Degenstein, D. A., Froidevaux, L., Godin-Beekmann, S., Hoppel, K. W., Johnson, B.
831 J., Kyrölä, E., Leblanc, T., Lichtenberg, G., Marchand, M., McElroy, C. T., Murtagh, D., Nakane,
832 H., Portafaix, T., Querel, R., Russell III, J. M., Salvador, J., Smit, H. G. J., Stebel, K., Steinbrecht,
833 W., Strawbridge, K. B., Stübi, R., Swart, D. P. J., Taha, G., Tarasick, D. W., Thompson, A. M.,
834 Urban, J., van Gijsel, J. A. E., Van Malderen, R., von der Gathen, P., Walker, K. A., Wolfram, E.,
835 and Zawodny, J. M.: Ground-based assessment of the bias and long-term stability of 14 limb and
836 occultation ozone profile data records, Atmos. Meas. Tech., 9, 2497-2534, doi:10.5194/amt-9-
837 2497-2016, 2016.
838 Jeannet, P., R. Stübi, G. Levrat, P. Viatte, and J. Stähelin: Ozone balloon soundings at Payerne
839 (Switzerland): re-evaluation of the time series 1967 - 2002 and trend analysis, *J. Geophys. Res.,*
840 *112*, D11302, doi: 10.1029/2005JD006862, 2007.
841 Johnson, B. J., S. J. Oltmans, H. Vömel, H. G. J. Smit, T. Deshler, and C. Kroger: Electrochemical
842 concentration cell (ECC) ozonesonde pump efficiency measurements and tests on the sensitivity to
843 ozone of buffered and unbuffered ECC sensor cathode solutions, *J. Geophys. Res., 107*, 4393,
844 10.1029/2001JD000557, 2002.
845 Kerr, J. B., H. Fast, C. McElroy, S. J. Oltmans, J. A. Lathrop, E. Kyrö, A. Paukkunen, H. Claude, U.
846 Köhler, C. Sreedharan, T. Takao, and Y. Tsukagoshi: The 1991 WMO International
847 Ozondesondes Intercomparison at Vanscoy, Canada, *J. Atmos. Ocean. Technol., 32*, 685-716,
848 1994.
849 Kivi, R., E. Kyrö, T. Turunen, N. R. P. Harris, P. von der Gathen, M. Rex, S. B. Andersen, and I.
850 Wohltmann: Ozonesonde observations in the Arctic during 1989?2003: Ozone variability and
851 trends in the lower stratosphere and free troposphere, *J. Geophys. Res., 112*, D08306, doi:
852 10.1029/2006JD007271, 2007.
853 Kobayashi, J. and Y. Toyama: On various methods of measuring the vertical distribution of
854 atmospheric ozone (III) - Carbon iodine type chemical ozonesonde-. Pap. Met. Geophys., 17, 113-
855 126
856 Komhyr, W. D.: Operations handbook-ozone measurements to 40-km altitude with model 4A
857 electrochemical concentration cell (ECC) ozonesondes (used with 1680-MHz radiosondes), in
858 Technical memorandum ERL ARL-149, NOAA, Boulder, Colorado, 49pp, 1986.
859 Komhyr, W. D.: Electrochemical concentration cells for gas analysis, *Ann. Geophys., 25* (1), 203-210,
860 1969.
861 Komhyr, W. D., and T. B. Harris: Note on flow rate measurements made on Mast-Brewer ozone
862 sensor pumps, *Mon. Weather Rev., 93* (4), 267-268, 1965.
863 Komhyr, W. D., R. A. Barnes, G. B. Brothers, J. A. Lathrop, and D. P. Opperman: Electrochemical
864 concentration cell ozonesondes performance evaluation during STOIC 1989, *J. Geophys. Res.,*
865 *100* (D5), 9231-9244, 1995a.

866 Komhyr, W.D., B. Connor, I. Mcdermid, T. McGee, A. Parrish, and J. Margitan: Comparison of
867 STOIC 1989 ground-based lidar, microwave spectrometer, and Dobson spectrophotometer umkehr
868 ozone profiles with ozone profiles from balloon-borne electrochemical concentration cell
869 ozonesondes, *J. Geophys. Res., 100* (D5), 9273-9282, 1995b.
870 Labow, G. J., R. D. McPeters, P. K. Bhartia, *and* N. Kramarova: A comparison of 40 years of SBUV
871 measurements of column ozone with data from the Dobson/Brewer network, *J. Geophys. Res.*
872 *Atmos., 118*, 7370–7378, *doi:*10.1002/jgrd.50503, 2013.
873 Lanting, R. W.: Modification of the potassium iodide procedure for improved stoichiometry, *Atmos.*
874 *Environ., 13*, 553– 554, 1979.
875 Liu, X., K. Chance, C. E. Sioris, T. P. Kurosu, and M. J. Newchurch: Intercomparison of GOME,
876 ozonesonde, and SAGE II measurements of ozone: Demonstration of the need to homogenize
877 available ozonesonde data sets, J. Geophys. Res., 111 (D10), 14,305+**,** doi:
878 10.1029/2005JD006718, 2006.
879 Logan, J. A., I. A. Megretskaia, A. J. Miller, G. C. Tiao, D. Choi, L. Zhang, R. S. Stolarski, G. J.
880 Labow, S. M. Hollandsworth, G. E. Bodeker, H. Claude, D. D. Muer, J. B. Kerr, D. W. Tarasick,
881 S. J. Oltmans, B. Johnson, F. Schmidlin, J. Staehelin, P. Viatte, and O. Uchino: Trends in the
882 vertical distribution of ozone: a comparison of two analyses of ozonesonde data, *J. Geophys. Res.*,
883 *104* (D21), 26,373-26,399, 1999.
884 Logan, J.A., J. Staehelin, I. A. Megretskaia, J.-P. Cammas, V. Thouret, H. Claude, H. De Backer, M.
885 Steinbacher, H.-E. Scheel, R. Stubi, M. Fröhlich, and R. Derwent: Changes in ozone over Europe:
886 Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites.
887 *J. .Geophys. Res. Atmos., 117*, D09301, doi:10.1029/2011JD016952, 2012.
888 Margitan, J. J., R. A. Barnes, G. B. Brothers, J. Butler, J. Burris, B. J. Connor, R. A. Fer-rare, J. B.
889 Kerr, W. D. Komhyr, M. P. McCormick, I. S. McDermid, C. T. McElroy, T. J. McGee, A. J.
890 Miller, M. Owens, A. D. Parrish, C. L. Parsons, A. L. Torres, J. J. Tsou, T. D. Walsh, and D.
891 Whiteman: Stratospheric ozone intercomparison campaign (STOIC) 1989: Overview, *J. Geophys.*
892 *Res., 100*, 9193-9208, doi: 10.1029/95JD00509, 1995.
893 McPeters, R. D., D. J. Hofmann, M. Clark, L. Flynn, L. Froidevaux, M. Gross, B. Johnson, G. Koenig,
894 X. Liu, S. McDermid, T. McGee, F. Murcray, M. J. Newchurch, S. Oltmans, A. Parrish, R.
895 Schnell, U. Singh, J. J. Tsou, T. Walsh, and J. M. Zawodny: Results from the 1995 Stratospheric
896 Ozone Profile Intercomparison at Mauna Loa, *J. Geophys. Res., 104*, 23, pp. 30505-30514, 1999.
897 Meijer, Y. J., D. P. J. Swart, M. Allaart, S. B. Andersen, G. Bodeker, I. Boyd, G. Braa-then, Y.
898 Calisesi, H. Claude, V. Dorokhov, P. von der Gathen, M. Gil, S. Godin-Beekmann, F. Goutail, G.
899 Hansen, A. Karpetchko, P. Keckhut, H. M. Kelder, R. Koele-meijer, B. Kois, R. M. Koopman, G.
900 Kopp, J.-C. Lambert, T. Leblanc, I. S. Mc-Dermid, S. Pal, H. Schets, R. Stübi, T. Suortti, G.
901 Visconti, and M. Yela: Pole-to-pole validation of Envisat GOMOS ozone profiles using data from
902 ground-based and balloon sonde measurements, *J. Geophys. Res., 109* (D18), 23,305, doi:
903 10.1029/2004JD004834, 2004.
904 Mercer, J. L., C. Kroger, B. Nardi, B. J. Johnson, M. P. Chipperfield, S. W. Wood, S. E. Nichol, M. L.
905 Santee, and T. Deshler: Comparison of measured and modeled ozone above McMurdo Station,
906 Antarctica, 1989-2003, during austral winter/spring, *J. Geophys. Res*., *112*,
907 D19307, doi:10.1029/2006JD007982, 2007.
908 Moreira, L., Hocke, K., Eckert, E., von Clarmann, T., and Kämpfer, N.: Trend analysis of the
909 20-year time series of stratospheric ozone profiles observed by the GROMOS microwave
910 radiometer at Bern, *Atmos. Chem. Phys., 15*, 10999-11009, doi:10.5194/acp-15-10999-
911 2015, 2015.
912 Petropavlovskikh, I., P. K. Bhartia, and J. DeLuisi: New Umkehr ozone profile retrieval algorithm
913 optimized for climatological studies, *Geophys. Res. Lett., 32*, L16808,
914 doi:10.1029/2005GL023323, 2005.
915 Pitts, J. N., Jr., J. M. McAfee, W. D. Long, and A. M. Winer: Long-path infrared spectroscopic
916 investigation at ambient concentrations of the 2% neutral buffered potassium iodide method for
917 determination of ozone, Environ. Sci. Technol., 10, 787– 793, 1976.
918 Proffitt, M. H., and R. J. McLaughlin: Fast dual-beam uv-absorption photometer suitable for use on
919 stratospheric balloons, Rev. Sci. Instrum., 54, 1719-1728, 1983.

Saltzman, B. E., and N. Gilbert: Iodometric microdetermination of organic oxidants and ozone, resolution of mixtures by kinetic colorimetry, Anal. Chem., 31, 1914– 1920, 1959.

Smit, H.G.J., and D. Kley: The 1996 WMO international intercomparison of ozonesondes under quasi flight conditions in the environmental simulation chamber at Jülich, in WMO Global Atmospheric Watch Report, 130, World Meteorological Organization, Geneva, 1998.

Smit, H.G.J., and W. Sträter: JOSIE-1998 performance of the ECC ozondesondes of SP-6A and ENSCI-Z type, in WMO Global Atmospheric Watch Report, 157, World Meteorological Organization, Geneva, 2004a.

Smit, H.G.J., and W. Sträter: The 2000 WMO international intercomparison of operating procedures for ECC-ozondesondes at the environmental simulation facility at Jülich, in WMO Global Atmospheric Watch Report, 158, World Meteorological Organi-zation, Geneva, 2004b.

Smit, H. G. J., W. Sträter, B. J. Johnson, S. J. Oltmans, J. Davies, B. Hoegger, R. Stübi, F. Schmidlin, J. Witte, A. Thompson, I. Boyd, and F. Poisny: Assessment of the performance of ECC-ozondesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Jülich Ozondesonde Intercomparison Experiment (JOSIE), *J. Geophys. Res., 112*, D19306, doi: 10.1029/2006JD007308, 2007.

Smit, H. G. J. and the ASOPOS panel (Assessment of Standard Operating Procedures for Ozonesondes): Quality assurance and quality control for ozonesonde measurements in GAW, World Meteorological Organization, GAW Report #201, Geneva, Switzerland, 2014. available at: http://www.wmo.int/pages/prog/arep/gaw/documents/FINAL_GAW_201_Oct_2014.pdf.

Smit, H. G. J., and the O3S-DQA-Panel (Ozone Sonde Data Quality Assessment): Guidelines for homogenization of ozonesonde data, SI2N/O3S-DQA activity as part of "Past changes in the vertical distribution of ozone assessment", 2012. available at: http://www-das.uwyo.edu/%7Edeshler/NDACC_O3Sondes/O3s_DQA/O3S-DQA-Guidelines%20Homogenization-V2-19November2012.pdf

Staufer, J., J. Staehelin, R. Stübi, T. Peter, F. Tummon, and V. Thouret: Trajectory matching of ozonesondes and MOZAIC measurements in the UTLS – Part 1: Method description and application at Payerne, Switzerland, *Atmos. Meas. Tech., 6*, 3393-3406, doi:10.5194/amt-6-3393-2013, 2013.

Staufer, J., J. Staehelin, R. Stübi, T. Peter, F. Tummon, and V. Thouret: Trajectory matching of ozonesondes and MOZAIC measurements in the UTLS – Part 2: Application to the global ozonesonde network, *Atmos. Meas. Tech., 7*, 241-266, doi:10.5194/amt-7-241-2014, 2014.

Stähelin, J., N. R. P. Harris, C. Appenzeller, and J. Eberhard: Ozone trends: a review, *Rev. Geophys., 32* (2), 231-290, 2001.

Stein, A.F., D. Lamb, and R.R. Draxler: Incorporation of detailed chemistry into a three dimensional Lagrangian-Eulerian hybrid model: Application to regional tropospheric ozone, *Atmos. Environ., 34*, 4361-4372, 2000.

Stübi, R., G. Levrat, B. Hoegger, P. Viatte, J. Staehelin, and F. J. Schmidlin: Inflight comparison of Brewer-Mast and electrochemical concentration cell ozonesondes, J. Geophys. Res., 113, D13302, doi: 10.1029/2007JD009091, 2008.

Tarasick, D. W., Davies, J., Smit, H. G. J., and Oltmans, S. J.: A re-evaluated Canadian ozonesonde record: measurements of the vertical distribution of ozone over Canada from 1966 to 2013, Atmos. Meas. Tech., 9, 195-214, doi:10.5194/amt-9-195-2016, 2016.

Thornton, D. C. and N. Niazy: Effects of solution mass transport on the ECC ozonesonde background current. *Geophys. Res. Lett., 10*, 148-151, 1983.

Thornton, D. C. and N. Niazy: Source of background current in ECC ozondesonde: Implication for total ozone measurements, *J. Geophys. Res., 87*, 11, 8943-8950, 1982.

Thouret, V., Cammas, J.-P., Sauvage, B., Athier, G., Zbinden, R., Nédélec, P., Simon, P., and Karcher, F.: Tropopause referenced ozone climatology and inter-annual variability (1994–2003) from the MOZAIC programme, *Atmos. Chem. Phys., 6*, 1033-1051, doi:10.5194/acp-6-1033-2006, 2006.

Thouret, V., A. Marenco, J. A. Logan, P. Nedelec, and C. Grouhel: Comparisons of ozone measurements from the MOZAIC airborne program and the ozone sounding net-work at eight locations, *J. Geophys. Res. 103*, 25,695-25,720, doi: 10.1029/98JD02243, 1998.

974 Vömel, H. and Diaz, K.: Ozone sonde cell current measurements and implications for observations of
975 near-zero ozone concentrations in the tropical upper troposphere, *Atmos. Meas. Tech., 3*, 495-505,
976 doi:10.5194/amt-3-495-2010, 2010.
977 WMO: *SPARC-IOC-GAW Assessment of Trends in the Vertical Distribution of Ozone*, SPARC report
978 No.1, WMO Global Ozone Research and Monitoring Project, Report No. 43, Geneva,
979 Switzerland, May 1998.
980 WMO: *Scientific Assessment of Ozone Depletion: 2010*, Global Ozone Research and Monitoring
981 Project-Report No. 52, 516 pp., Geneva, Switzerland, 2010.
982 WMO: *Scientific Assessment of Ozone Depletion: 2014*, Global Ozone Research and Monitoring
983 Project-Report No. 55, 416 pp., Geneva, Switzerland, 2014.
984
985

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Table 1. Datasets used in the analysis giving experiment or location, years of the comparisons, location latitude and longitude, ozonesonde and solution strengths compared, number of comparisons, sampling frequency of the data (Hz), and the platform. The multi-sonde platforms contained from 4 to 12 ozonesondes.

Location	Dates	Lat.	Long.	Provider-Concen.		No.	Freq	Platform/
JOSIE09	1996-2000	50.9	-6.4	EN-0.5	EN-1.0	3	1	Simulator
				SP-0.5	SP-1.0	3		
				SP-1.0	EN-1.0	7		
				SP-0.5	EN-0.5	5		
				SP-1.0	EN-0.5	3		
BESOS	April 2004	41.3	105.7	EN-0.5	EN-1.0	9	0.5	Multi-sonde
				SP-0.5	SP-1.0	9		
				SP-1.0	EN-1.0	9		
				SP-0.5	EN-0.5	9		
				SP-1.0	EN-0.5	9		
Payerne	2002-2003	46.8	-6.9	En-0.5	EN-1.0	48	0.15	Dual-sonde
	2005-2006			SP-1.0	EN-0.5	26		Dual-sonde
McMurdo	1996-2006	-77.8	166.7	EN-0.5	EN-1.0	18	0.15	Dual-sonde
Sodankylä	1995-2002	67.4	-26.6	EN-0.5	EN-1.0	4	1	Multi- / Dual-
				SP-1.0	EN-1.0	8		sondes
				SP-1.0	EN-0.5	5		
Wallops I.	1995-2002	37.8	75.5	SP-0.5	SP-1.0	16	1	Dual-sonde
Laramie	1996	41.1	105.6	EN-0.5	EN-1.0	6	1	Multi-sonde
Total				EN-0.5	EN-1.0	88		KI conc. diff.
				SP-0.5	SP-1.0	28		KI conc. diff.
				SP-1.0	EN-1.0	24		Sonde diff.
				SP-0.5	EN-0.5	14		Sonde diff.
				SP-1.0	EN-0.5	43		Recommended

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Table 2. Mean and standard deviations of the various comparison measurements. The mean ratio is equivalent to the slope of a linear fit to the data which passes through the origin. For the datasets with the most data and the most varied comparisons the means and standard deviations are given for the pressure intervals indicated at the top. For the other datasets the means and standard deviations are given for all the data without regard to pressure.

Source	Sonde/KI	From	To	999>p>500	500>p>100	100>p>30	30>p
JOSIE09	EN	1.0%	0.5%	0.96±0.02	0.95±0.04	0.94±0.05	0.91±0.07
BESOS	EN			0.95±0.07	0.95±0.03	0.95±0.04	0.94±0.01
Payerne	EN			0.97±0.84	0.97±0.05	0.96±0.03	0.94±0.04
McMurdo	EN			0.97±0.04	0.96±0.06	0.96±0.09	0.92±0.06
Sodankylä	EN			0.93±0.03	All data		
Wallops I.	EN			0.92±0.06	All data		
Laramie	EN			0.96±0.04	All data		
JOSIE09	SP	1.0%	0.5%	0.97±0.02	0.97±0.02	0.98±0.03	0.93±0.06
BESOS	SP			0.97±0.02	0.96±0.02	0.95±0.02	0.93±0.02
Wallops I.	SP			0.94±0.06	All data		
JOSIE09	1.0%	SP	EN	0.96±0.02	0.94±0.05	0.94±0.12	0.93±0.05
BESOS	1.0%			0.97±0.13	0.97±0.03	0.96±0.04	0.96±0.02
Sodankylä	1.0%			0.95±0.03	All data		
JOSIE09	0.5%	SP	EN	0.96±0.03	0.95±0.04	0.96±0.06	0.94±0.05
BESOS	0.5%			1.00±0.07	0.98±0.03	0.96±0.03	0.96±0.02
JOSIE09		SP-1.0	EN-0.5	1.01±0.04	0.99±0.03	1.00±0.04	0.98±0.03
BESOS				1.02±0.13	1.03±0.03	1.01±0.03	1.02±0.02
Payerne				1.03±0.46	1.00±0.06	1.00±0.04	1.01±0.03
Sodankylä				1.02±0.03	All data		

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Table 3. Transfer function parameters summary. The second and third columns are for p ≥ 30 hPa providing the ratio and number of data points. Columns 4 – 7 are for p < 30 hPa, providing the slope of a linear fit in $\log_{10}(p)$, the offset adjusted to match the ratio at 30 hPa, the offset without constraint to the data below and number of data points. The offset is value of the ratio at p=1 hPa. The final column is the number of dual sonde measurements for each data set for each application.

Dataset	Ratio, p>30	N(p>30)	Slope	Offset	Offset no	N	No.
EN 0.5% to EN 1.0% - Compare Solution Strengths							
JOSIE09	0.943±0.056	1918	-0.176	1.203	1.052	949	3
BESOS	0.951±0.028	5003	0.041	0.981	0.882	1854	9
Payerne	0.965±0.546	34855	0.031	0.920	0.910	14744	48
Sodankylä	0.941±0.027	2291	0.109	0.780	0.762	524	4
McMurdo	0.977±0.124	15030	0.118	0.802	0.785	4197	18
Laramie	0.974±0.044	1290	0.063	0.882	0.848	378	6
Weighted	0.966±0.142	60387	0.041	0.904	0.886	22676	88
SP 0.5% to SP 1.0% - Compare Solution Strengths							
JOSIE09	0.955±0.129	1919	-0.164	1.198	1.051	949	3
BESOS	0.975±0.105	5005	0.014	0.954	0.914	1854	9
Wallops I.	0.937±0.065	10123	0.052	0.860	0.865	2083	16
Weighted	0.950±0.176	17047	-0.004	0.962	0.919	4886	28
SP 1.0% to EN 1.0% - Compare Sonde Providers							
JOSIE09	0.945±0.0.074	4475	0.133	0.749	0.744	2217	7
BESOS	0.959±0.061	5005	0.145	0.745	0.756	1854	9
Sodankylä	0.963±0.026	4041	0.112	0.798	0.784	961	8
Weighted	0.956±0.094	13521	0.133	0.757	0.756	5032	24
SP 0.5% to EN 0.5% - Compare Sonde Providers							
JOSIE09	0.954±0.054	3193	0.179	0.690	0.680	1587	5
BESOS	0.977±0.0.027	5003	0.119	0.801	0.786	1854	9
Weighted	0.968±0.040	8196	0.147	0.750	0.737	3441	14
SP 1.0% to EN 0.5% - The Provider Recommendations							
JOSIE09	0.998±0.055	1919	0.880	-0.301	0.142	949	3
BESOS	1.009±0.068	5004	0.112	0.842	0.864	1854	9
Payerne	1.008±0.251	17123	0.065	0.912	0.927	7069	26
Sodankylä	1.023±0.027	2462	0.003	1.019	1.015	642	5
Weighted	1.009±0.091	26508	0.143	0.797	0.850	10514	43

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Table 4. Ratios of total column ozone at Nairobi, Kenya, measured either with the OMI satellite instrument or a Dobson Spectrophotometer, compared to EN ozonesondes using 1.0% and 0.5% KI concentrations. The ratios are also shown after correction of the EN-1.0% to EN-0.5% (OZ_{conc}). Two approaches for the residual ozone column above the balloon burst are given: constant mixing ratio (MR) and using climatology [McPeters and Labow, 2012], the WMO recommendation.

Ratios	OMI / EN-1.0%	OMI / OZ_{conc}	OMI / EN-0.5%	Dobson/ EN-1.0%	Dobson / OZ_{conc}	Dobson / EN-0.5%
Medians Constant MR	0.93 ± 0.04	0.98 ±0.04	0.96 ±0.04	0.92 ±0.05	0.96 ±0.05	0.94 ±0.05
Medians Climatology	0.95 ±0.03	0.98 ±0.03	0.94 ±0.03	0.92 ±0.04	0.96 ±0.04	0.92 ±0.05

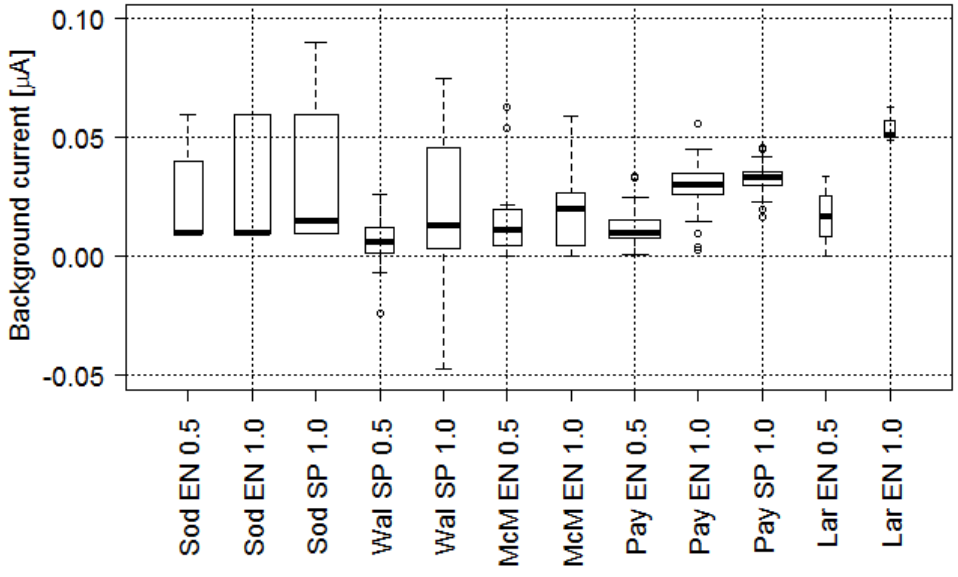

Figure 1. Boxplot of the background current (µA) measured at the five stations which flew a number of dual or multi ozonesonde gondolas: Sodankylä (Sod), Wallops Island (WaI), McMurdo Station (McM), Payerne (Pay), and Laramie (Lar). Following the station location, the ozonesonde manufacturer is identified (EN or SP) and then the KI solution concentration (0.5% or 1.0%). Medians are the thick black segments, the inter-quartile range the box height, 1.5 times the inter-quantile range the whiskers, outliers denoted as circles, the square root of the number of measurements is reflected in the box width. A value of 0.03 µA corresponds to 0.1 mPa of ozone.

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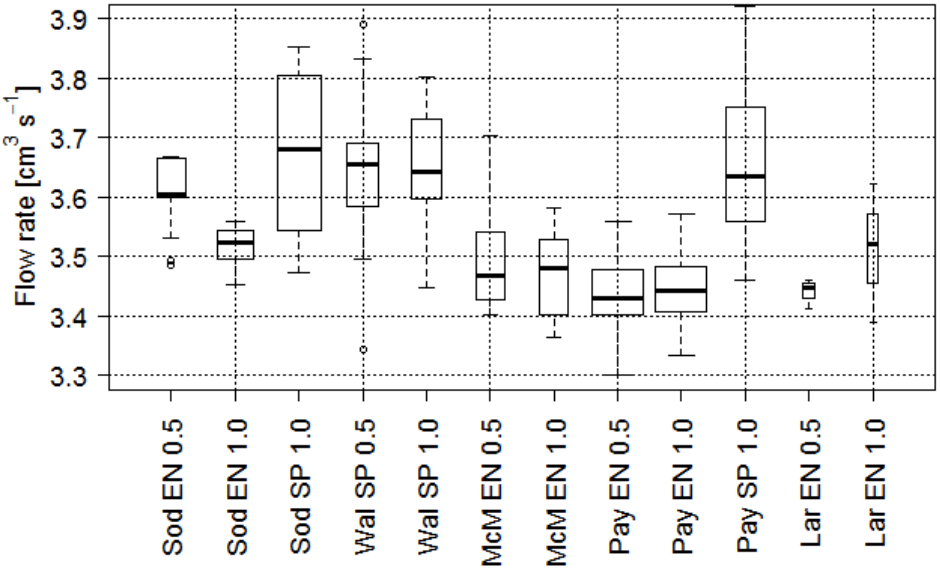

Figure 2. Ozonesonde pump flow rates (cm^3 s^{-1}) measured at the different stations, following the nomenclature of Figure 1 for the station and ozonesonde.

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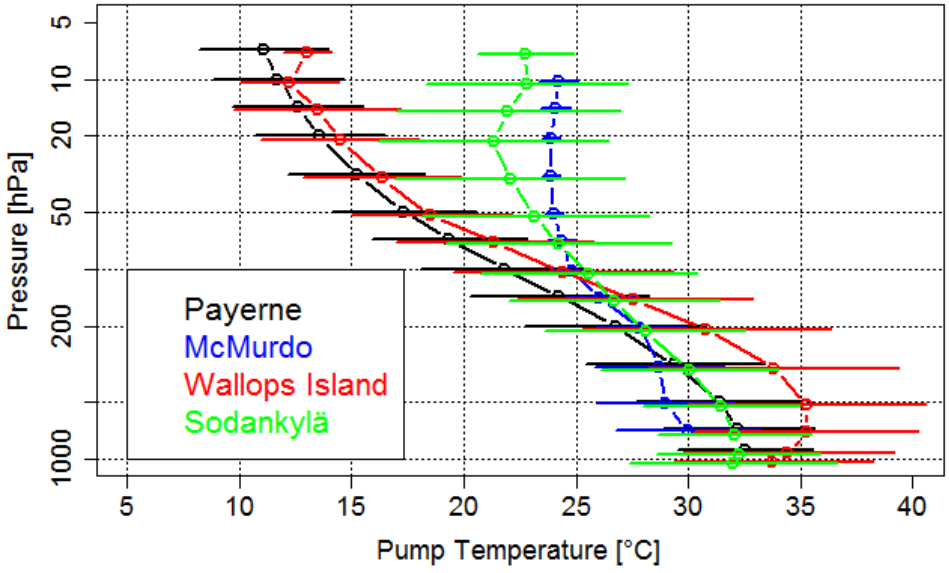

1037

1038 **Figure 3.** Mean profile of the measured pump temperature for the different dual flight data
1039 sets. The higher pump temperature at the upper part of the profiles for the McMurdo and
1040 Sodankylä stations is due to a heat source to avoid freezing of the solution. Error bars are one
1041 standard deviation of the measurements.

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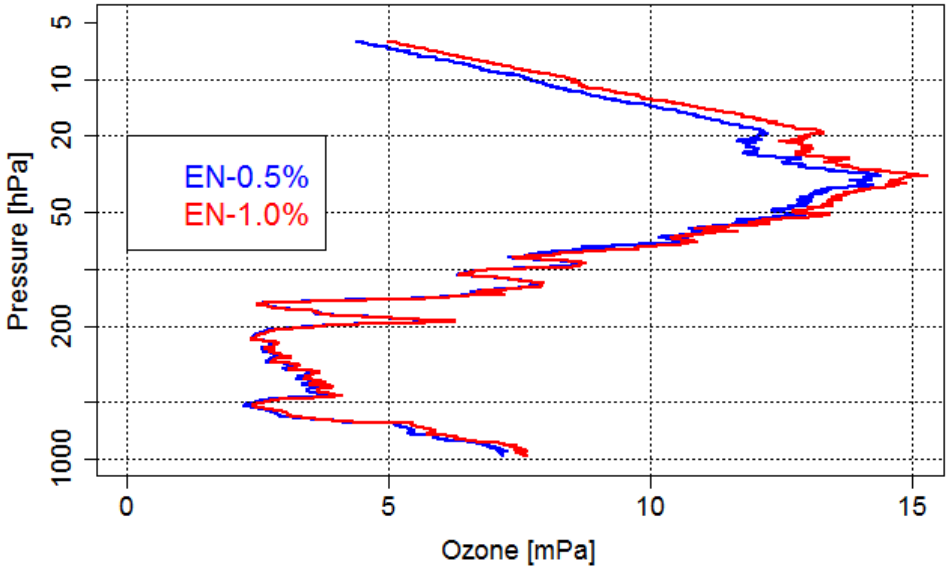

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1045 **Figure 4.** Example of the results of a dual flight profile from Payerne. The only difference
1046 between the ozonesondes is the KI solution concentration.

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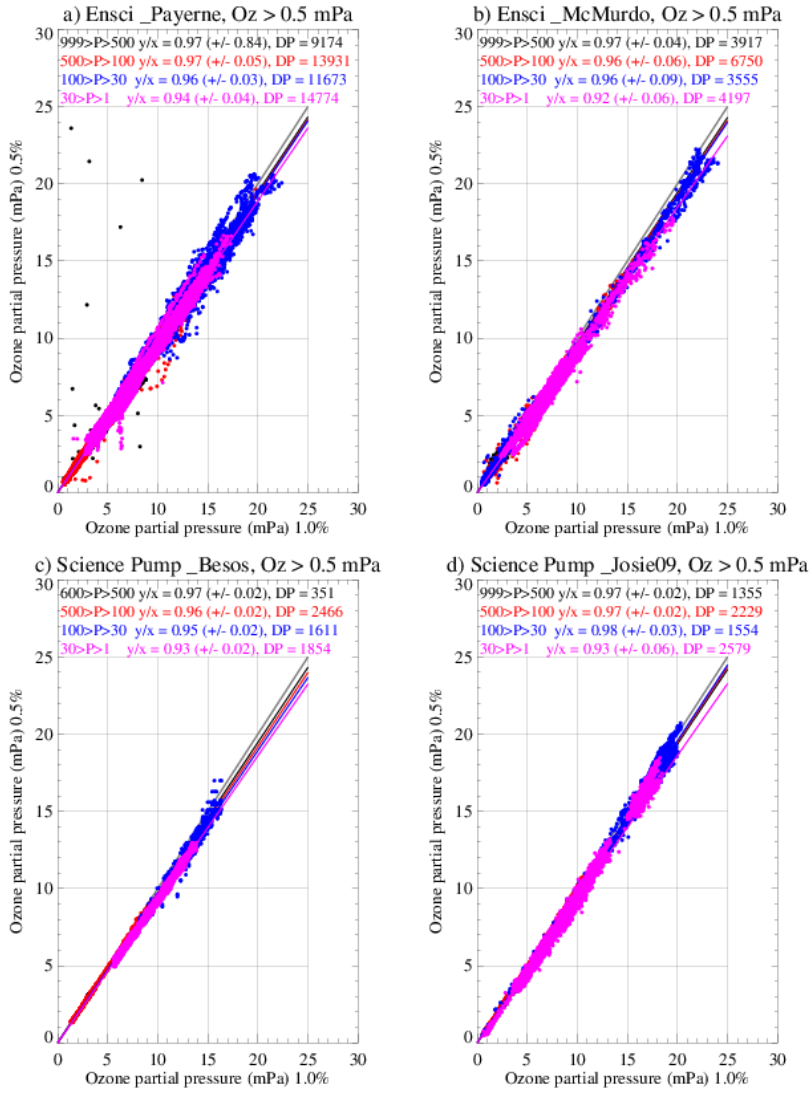

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1051 **Figure 5.** Scatter plots of ozone partial pressures measured with KI concentrations of 1.0%
1052 (x-axis) and 0.5% (ordinate-axis) using EN ozonesondes flown from a) Payerne, b) McMurdo
1053 Station, and with SP ozonesondes from c) BESOS, and d) JOSIE09. The data are subdivided
1054 into four pressure intervals and averages and standard deviations of the ratios of y:x are listed
1055 on the panels along with the number of measurements. Only ozone measurements above 0.5
1056 mPa are included. At $p \geq 30$ hPa there is little variation in the ratios either by pressure
1057 interval, location, or ozonesonde type. At $p < 30$ hPa ratios are decreasing. The 1:1 line is
1058 shown in gray.

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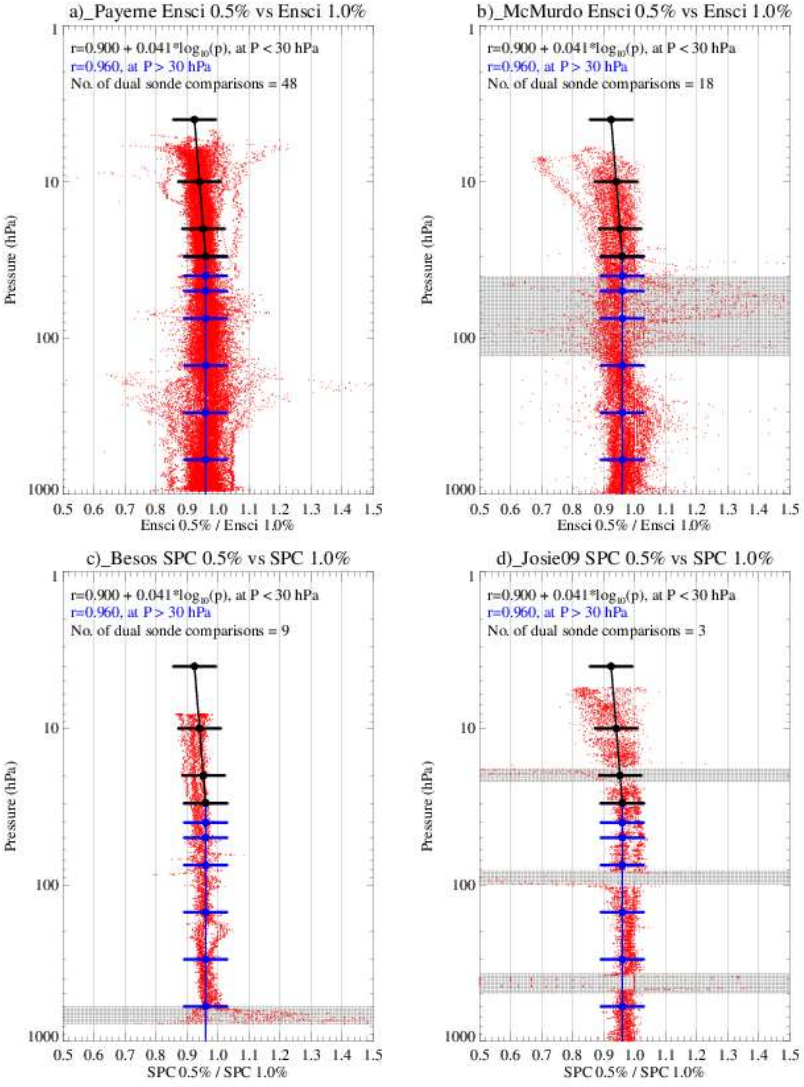

Figure 6. Vertical profiles of ratios of ozone partial pressure using ozonesondes with different KI concentrations (0.5%, 1.0%) in ozonesondes of the same manufacturer, EN or SP. a) Payerne - EN, b) McMurdo –EN, c) BESOS – SP, and d)) JOSIE09 – SP. The hashed areas are regions of low ozone in: ozone hole measurements, McMurdo; tests in the laboratory, JOSIE09; or during initial problems with the BESOS data system at the lowest altitudes.

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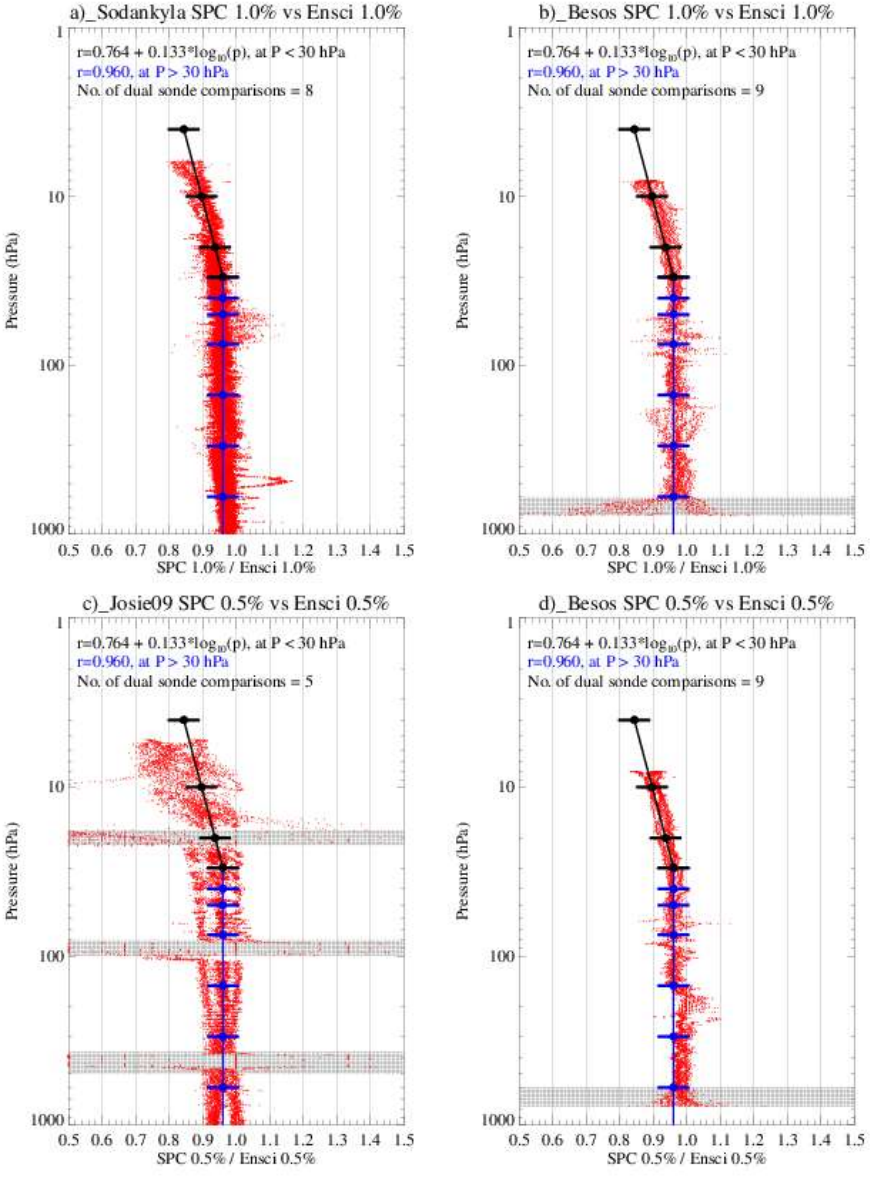

Figure 7. Vertical profiles of ratios of ozone partial pressure using ozonesondes of different manufacturer (SP, EN) with the same KI concentrations in both ozonesondes, either 1.0% (top two panels) or 0.5% (bottom two panels). a) Sodankylä – 1.0%, b) BESOS – 1.0%, c) JOSIE09 – 0.5%, d) BESOS – 0.5%. The hashed areas denote regions of low ozone in tests in the laboratory during JOSIE09, or during initial problems with the BESOS data system at the lowest altitudes.

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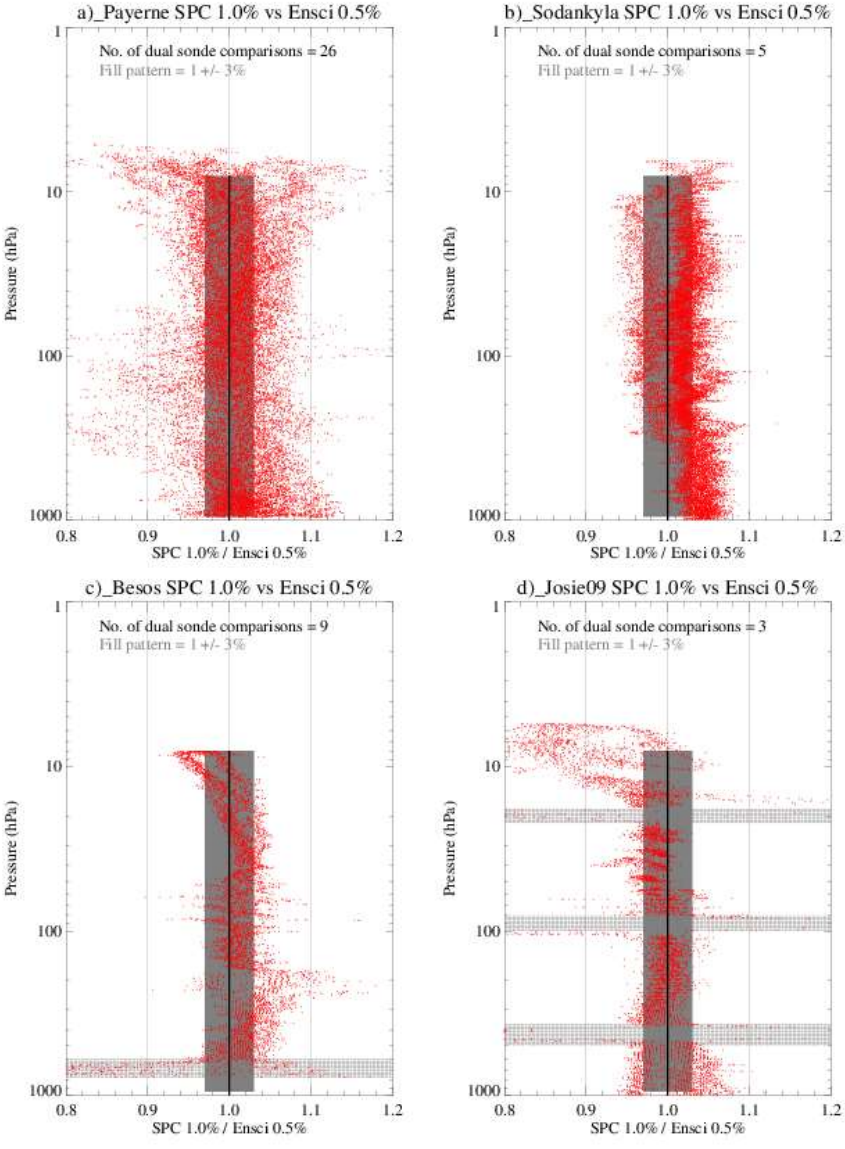

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1076 **Figure 8.** Ratios of SP-1.0% with EN-0.5% ozonesondes. The measurements are from a)
1077 Payerne, b) Sodankylä, c) BESOS, and d) JOSIE 2009. The filled regions represent 3%
1078 around 1.0. The hashed areas are as before to indicate regions of low ozone concentration
1079 during tests in JOSIE 2009 or difficulty with the data system in BESOS.

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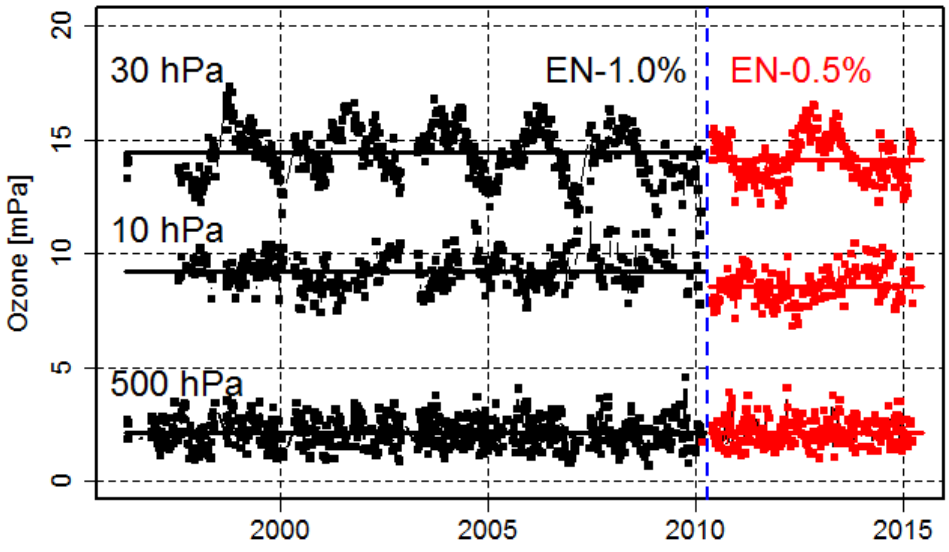

Figure 9. Ozone time series from the Nairobi station at three pressure levels: 500, 30 and 10 hPa. The black symbols correspond to the data from 1996 - 2010 (EN-1.0% solution) and the red symbols from 2010 onwards (EN-0.5%). The horizontal segments are the mean values over the two periods. No corrections to the EN-1.0% data have been made for this figure.

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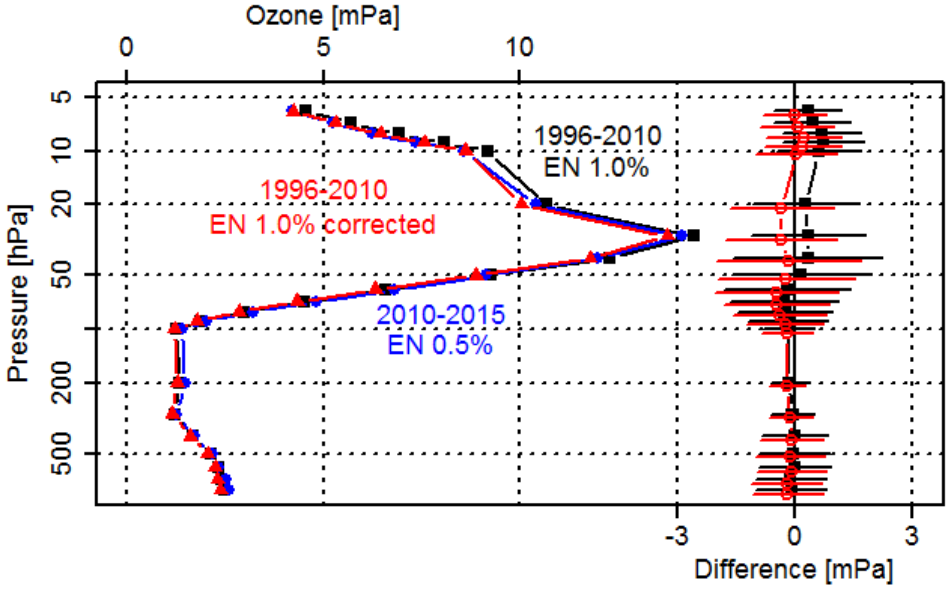

Figure 10. On the left (upper scale), mean ozone profile for the EN-1.0% period in black, EN-0.5% period in blue and corrected EN-1.0% profile using OZ_{conc} in red for the Nairobi data set. On the right (lower scale), the difference between the mean (1996-2010) ozone profiles and the mean (2010-2015) profiles before (after), black (red) correction for the change of solution concentration that occurred in 2010. A small offset of the pressure scale is used to avoid overlapping error bars.