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Tropospheric Ozone Assessment Report: Present-day distribution and trends of tropospheric ozone relevant to climate and global atmospheric chemistry model evaluation

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The Tropospheric Ozone Assessment Report (TOAR) is a current IGAC activity (http://www.igacproject.org/activities/TOAR) with a mission to provide the research community with an up-to-date scientific assessment of tropospheric ozone's global distribution and trends from the surface to the tropopause.

Guided by this mission, TOAR has two goals:

1) Produce the first tropospheric ozone assessment report based on the peer-reviewed literature and new analyses.

2) Generate easily accessible, documented data on ozone exposure and dose metrics at hundreds of measurement sites around the world (urban and non-urban), freely accessible for research on the global-scale impact of ozone on climate, human health and crop/ecosystem productivity.

The report is being written as a series of eight stand-alone publications to be submitted for peer-review to *Elementa: Science of the Anthropocene*, an open-access, non-profit science journal founded by five US research Universities and published by University of California Press (www.elementascience.org). Prior to submission each paper will be posted to the TOAR webpage (http://www.igacproject.org/activities/TOAR/OpenComments) for a 30-day open comment period. We invite members of the atmospheric and biological sciences communities as well as the general public to read the papers and provide comments if they wish to do so. The open comment period will last for 30 days for each paper, with the draft papers posted to the website as they become available.

To provide comments on this particular paper, please send an e-mail to lead author Audrey Gaudel: Audrey.Gaudel@colorado.edu

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Abstract. *The Tropospheric Ozone Assessment Report (TOAR)* is an activity of the International Global Atmospheric Chemistry Project. This paper is a component of the assessment report, focusing on the present-day distribution and trends of tropospheric ozone relevant to climate and global atmospheric chemistry model evaluation. Utilizing the TOAR database, which hosts the world's largest collection of global surface ozone metrics, several figures present the global distribution and trends of daytime average ozone at all available non-urban monitoring sites, highlighting the regions and seasons of the world with the greatest ozone mole fractions (nmol mol^{-1}). Similarly, ozonesonde and commercial aircraft observations reveal the global distribution of ozone throughout the depth of the free troposphere. Long term surface ozone observations are limited in their global spatial coverage, but observations at remote locations indicate that ozone in the 21st century is greater than it was in the 1970s and 1980s. While some remote sites and many sites in the heavily polluted regions of East Asia show ozone increases since 2000, many others show decreases and there is no clear global pattern for surface ozone changes since 2000. Two new satellite products provide detailed views of ozone in the lower troposphere across East Asia and Europe, revealing the full spatial extent of the spring and summer ozone enhancements across eastern China that cannot be assessed from limited surface observations. Sufficient data are now available (ozonesondes, satellite, aircraft) across the tropical region from South America eastwards to the western Pacific Ocean, to indicate a likely tropospheric column ozone increase since the 1990s. The 2014-2016 mean tropospheric ozone burden (TOB) for the latitude range 60˚N-60˚S from five satellite products is 296 Tg ± 4%. While this agreement is excellent, the products differ in their quantification of TOB trends and further work is required to reconcile the differences.

1. Introduction

1.1 The Tropospheric Ozone Assessment Report (TOAR)

Tropospheric ozone is a greenhouse gas and pollutant detrimental to human health, and crop and ecosystem productivity (LRTAP Convention, 2015; REVIHAAP, 2013; US EPA, 2013; Monks et al., 2015). Since 1990 a large portion of the anthropogenic emissions that react in the atmosphere to produce ozone have shifted from North America and Europe to Asia (Granier et al., 2011; Cooper et al., 2014; Zhang et al., 2016). This rapid shift, coupled with limited ozone monitoring in developing nations, has left scientists unable to answer the most basic questions: Which regions of the world have the greatest human and plant exposure to ozone pollution? Is ozone continuing to decline in nations with strong ozone precursor emissions controls? To what extent is ozone increasing in the developing world? Is there a change in the natural sources of tropospheric ozone? How can the atmospheric sciences community facilitate access to ozone metrics necessary for quantifying ozone's impact on climate, human health and crop/ecosystem productivity?

To answer these questions the International Global Atmospheric Chemistry Project (IGAC) developed the *Tropospheric Ozone Assessment Report (TOAR): Global metrics for climate change,*

human health and crop/ecosystem research (www.igacproject.org/activities/TOAR). Initiated in 2014, TOAR's mission is to provide the research community with an up-to-date scientific assessment of tropospheric ozone's global distribution and trends from the surface to the tropopause. TOAR's primary goals are, 1) Produce the first tropospheric ozone assessment report based on all available surface observations, the peer-reviewed literature and new analyses, and 2) Generate easily accessible and documented ozone exposure metrics at thousands of measurement sites around the world (urban and non-urban). Through the TOAR database (https://join.fz-juelich.de) these ozone metrics are freely accessible for research on the global-scale impact of ozone on climate, human health and crop/ecosystem productivity (Schultz et al., 2017, hereinafter referred to as *TOAR-Surface Ozone Database*). The assessment report is organized as a series of papers in a Special Feature of *Elementa: Science of the Anthropocene*, with this paper focusing on the present-day distribution and trends of tropospheric ozone relevant to climate and global atmospheric chemistry model evaluation (hereinafter referred to as *TOAR-Climate*).

1.2 Tropospheric ozone's relevance to climate

Tropospheric ozone has a top-of-atmosphere (TOA) long-wave radiative effect (LWRE) unevenly distributed across the globe, as shown in Figure 1.2 (estimated by the IASI instrument onboard the Metop-A and Metop-B satellites; see Section 2.5 for details). LWRE quantifies the present day tropospheric ozone greenhouse effect, and its spatial variability is due to variations in tropospheric ozone combined with other factors that affect the sensitivity of TOA radiance to ozone absorption such as surface temperature, atmospheric temperature and water vapor. As will be shown in Sections 3 and 4 of *TOAR-Climate*, satellite products vary in their quantification of tropospheric column ozone and the impact of this uncertainty on LWRE has not yet been fully quantified.

The increase of tropospheric ozone since pre-industrial times has amplified its greenhouse effect and therefore contributes to the radiative forcing (RF) of the atmosphere. Due to its relatively short lifetime tropospheric ozone is considered a 'near-term climate forcer', a class of compounds whose impact on climate occurs primarily within the first decade after their emission (IPCC AR5: Myhre et al, 2013). The global-average radiative forcing due to tropospheric ozone as calculated by global atmospheric chemistry models is estimated to be 0.40 ± 0.20 W m^{-2} (IPCC, 2013). The relatively large error bars of ± 50% are due to uncertainties in the estimate of pre-industrial concentrations of tropospheric ozone (Forster et al., 2007; Gauss et al., 2006; Mickley et al., 2001; Young et al., 2013), and uncertainties in the present-day spatial distribution of tropospheric ozone (Gauss et al., 2003; Kiehl et al., 1999; Naik et al., 2005; Portmann et al., 1997; Stevenson et al., 2006; Wu et al., 2007). Improvements to this estimate require an accurate observation-based quantification of the present-day tropospheric ozone burden (TOB: the total mass of ozone in the troposphere, Tg) and its vertical distribution, plus greater

confidence in global atmospheric chemistry model estimates of TOB in pre-industrial times. Current global atmospheric chemistry models vary in their estimates of the quantity of tropospheric ozone originating from the stratosphere or from in situ photochemistry (Wu et al., 2007), but agree that photochemistry is the dominant gross source of ozone, exceeding the flux from the stratosphere by factors of 7–15 (Young et al., 2013; Banerjee et al., 2016). Most (~ 90%) of the ozone produced in the atmosphere is also destroyed through photochemical loss processes, with the remainder deposited to the surface, which on an annual basis is similar in magnitude to the flux from the stratosphere. These same models estimate that approximately 30% of the present-day TOB is attributable to human activity and that the average present-day tropospheric ozone lifetime is approximately 22 days (Young et al., 2013). Further details on the tropospheric ozone budget are described in the TOAR companion paper by *Archibald et al.* (2017), hereinafter referred to as *TOAR-Ozone Budget*.

A key measure of tropospheric ozone's direct impact on radiative forcing is TOB, with the latitudinal and vertical distribution playing critical roles (Lacis et al., 1990; Forster and Shine, 1997; Bernsten et al., 1997; Worden et al., 2008, 2011; Gauss et al., 2003; Gauss et al., 2006; Bowman et al., 2013; Stevenson et al., 2013). Therefore, a full assessment of ozone's impact on radiative forcing requires accurate knowledge of ozone's distribution and trends throughout the full depth of the troposphere and across the entire globe. Ozone can also affect radiative forcing indirectly due to its impact on vegetation, carbon uptake (Sitch et al., 2007; Lombardozzi et al., 2015), and methane lifetime (West et al., 2007; Fiore et al., 2008).

The goal of *TOAR-Climate* is to provide a wide range of in situ and remotely sensed ozone observations that can be used to assess the present-day TOB and to evaluate the global atmospheric chemistry models that provide estimates of pre-industrial and future-scenario tropospheric ozone. Companion papers in the TOAR Special Feature of *Elementa* describe the present-day distribution and trends of ozone relevant to human health (*TOAR-Health*: Fleming et al., 2017) and vegetation (*TOAR-Vegetation*: Mills et al., 2017), and therefore focus on ozone observations at surface sites. *TOAR-Climate* also presents surface observations, but focuses on remote or non-urban sites because they are more easily compared to relatively coarse-scale global atmospheric chemistry models and because they are more broadly representative of regional-scale ozone. *TOAR-Climate* also explores ozone in the free troposphere (defined as the layer between the atmospheric boundary layer and the tropopause) as well as ozone in the full tropospheric column to quantify TOB and its vertical and horizontal distribution. Another unique aspect of *TOAR-Climate* is the intercomparison of several near-global ozone products derived from in situ observations and remote sensing. Many of these products, such as tropospheric column ozone (TCO) from the OMI and IASI satellite-borne instruments, are quite new (Payne et al., 2017, Wespes et al., 2017) and are expected to form a key component of an evolving global ozone

observational network (Bowman, 2013). TOAR's emphasis on collaboration has provided an opportunity to compare these satellite products for the first time. The purpose of the intercomparison is to determine if the various products agree in their quantification of TOB, TCO or long-term trends. The most robust results can then be used for global atmospheric chemistry model evaluation as described in *TOAR-Model Performance* (Young et al., 2017).

The results of *TOAR-Climate* are presented as follows. Ozone metrics and statistics have been selected for their relevance to understanding average tropospheric conditions and for evaluating the global atmospheric chemistry models used to estimate pre-industrial and future ozone levels. The ozone observations are made from a wide range of instruments (described in Section 2) implementing in situ (surface ozone analyzers, aircraft-based instruments and ozonesondes) and remotely sensed techniques (ground-based Umkehr and FTIR, lidar and satellite). Further details on these methods can be found in TOAR's overview of global ozone observational techniques (Tarasick et al., 2017, hereinafter referred to as *TOAR-Observations*). The present-day global distribution of ozone at the surface, in the free troposphere and in the full tropospheric column is presented in Section 3. Trends in these same regions are presented in Section 4, with time series beginning anywhere from the 1970s (where data are available) to the year 2000, and extending through 2014, 2015 or 2016, depending on data availability. Finally, Section 5 discusses ozone trends or distributions in several regions of the world and describes how the datasets used in *TOAR-Climate* can be accessed.

2. Method

2.1 Description of the ozone metrics relevant to climate and global model evaluation

TOAR-Metrics (Lefohn et al., 2017) provides descriptions of all ozone metrics included in the TOAR database. The metrics relevant to climate and global atmospheric chemistry model evaluation that were selected for *TOAR-Climate* are: 1) the seasonal daytime average (8:00 to 20:00 local time) for surface observations, 2) seasonal nighttime averages (20:00 to 8:00 local time) at mountaintop sites, 3) monthly and seasonal means for free tropospheric observations from commercial aircraft (IAGOS), ozonesondes and lidars, as well as for tropospheric column ozone retrievals from space and ground-based remote sensing instruments. In some instances 5^{th}, 50^{th}, 95^{th} and 98^{th} percentiles are also shown. The present-day ozone values at surface sites are assessed for 2010-2014, with each site required to have at least three years of data during this 5-year period. At a given surface site the magnitude of the temporal ozone trend is determined with the Theil-Sen (T-S) estimator, and the significance of the trend is determined with the nonparametric Mann-Kendall (M-K) test, as described in *TOAR-Metrics*. Statistical significance is based on an α value of 0.05, and all trends are reported with 95% confidence intervals (see Table 5.8).

TOAR uses specific units when describing ozone observations and levels of exposure. When referencing an ozone observation in ambient air, TOAR follows World Meteorological Organization guidelines (Galbally et al., 2013) and uses the mole fraction of ozone in air, expressed in SI units of nmol mol^{-1}. Under tropospheric conditions the nmol mol^{-1} is indistinguishable from the volumetric mixing ratio ppb. The same units are applied to any ozone statistic, such as median or 95th percentile values. In *TOAR-Health* and *TOAR-Vegetation*, units of parts per billion (ppb) are used for the ozone exposure metrics discussed in those papers to maintain consistency with the ozone human health and vegetation research communities.

When referring to a tropospheric column ozone (TCO) value, TOAR uses the Dobson unit (DU), where 1 DU is the number of molecules of ozone per square centimeter required to create a layer of pure ozone 0.01 millimeters thick at standard temperature and pressure (or 2.69×10^{16} ozone molecules cm^{-2}). The tropospheric column extends from the surface to the tropopause, which can be defined according to a variety of methods including temperature lapse rate, temperature cold point (tropical tropopause), trace gas thresholds or thermodynamic properties such as isentropic potential vorticity. The choice of tropopause definition varies between research groups and due to the differences in altitude between the various tropopause definitions, independently calculated TCO values for a given time and location can differ by several DU. Discrepancies in tropopause altitude are particularly common at mid-latitudes in the region of the subtropical jet stream (Bethan et al., 1996; Wirth, 2000; Rodriguez-Franco and Cuevas, 2013).

2.2 Regionally representative surface sites

The TOAR Surface Ozone Database contains climate-relevant ozone metrics at hundreds of surface sites around the world, both urban and rural (Schultz et al., 2017). For this analysis a subset of non-urban surface sites has been selected for the purposes of illustrating the spatial and temporal variability of regionally representative ozone around the globe and for straight-forward comparison to global atmospheric chemistry models. Urban sites were not considered because in spatial terms they are not representative of broad regions. Instead they are strongly impacted by very localized emissions, reflecting photochemical and deposition processes at a scale not resolved by global atmospheric chemistry models. Relying on site information derived from various global gridded datasets and stored as metadata in the TOAR database, sites were classified as urban if they met thresholds for relatively high values of human population and satellite-detected nighttime lights intensity (see *TOAR-Surface Ozone Database* for a detailed description of the site classification algorithm: Schultz et al., 2017). This selection algorithm was applied uniformly to all sites in the TOAR database to objectively identify the most highly urbanized sites, with approximately one quarter of all sites in the database classified as urban. The non-urban sites considered in this paper include suburban sites as well as rural sites surrounded by

heavily urbanized areas. At the other extreme, some of the sites are considered to be remote, either located in unpopulated coastal regions, on islands, on top of high mountains, or in low-elevation, land-locked areas remote from anthropogenic emissions.

2.3 Tropospheric ozone profiles: Ozonesondes, TOST, IAGOS, lidar

2.3.1 Ozonesondes

Ozonesondes are the most important source of vertically-resolved tropospheric ozone data for long-term climate studies due to their very long record, with regular soundings beginning in the early 1960s (Hering, 1964; Hering and Borden, 1964; 1965; 1967; Komhyr and Sticksel, 1967a,b, Attmannspacher and Dütsch, 1970). Using KI-based electrochemical detection methods similar to those developed for surface monitoring, they show good accuracy and reasonable stability over a 50-year period (Tanimoto et al., 2015; *TOAR-Observations*), and provide vertical resolution of about 100 m. Ozonesondes can be launched under cloudy conditions and therefore they are not biased towards clear-sky conditions. Ozonesonde data are particularly valuable in the upper troposphere-lower stratosphere (UTLS) region especially in the tropics where much of the upper troposphere is not sampled by instrumented commercial aircraft. The UTLS is not well-sampled by satellites either, because of a low vertical resolution.

However, ozonesonde data are temporally sparse and unevenly distributed, with only about 60 sites worldwide making regular soundings, most only once per week. For *TOAR-Climate* we have, therefore, chosen to use a derived product that addresses these issues by taking advantage of the long lifetime of ozone in the free troposphere. This product, described below (Section 2.3.2), uses trajectory calculations based on meteorological reanalyses to spatially extend the observations and fill the gaps between ozonesonde stations. The result is a global 3-dimensional dataset of observed ozone. Ozone observations at individual ozonesonde sites, for example, Lauder, New Zealand, are only assessed by *TOAR-Climate* for the purposes of evaluating remotely sensed TCO.

2.3.2 TOST

The Trajectory-mapped Ozonesonde dataset for the Stratosphere and Troposphere (TOST) is a 3-dimensional, long-term ozone dataset derived from ozone soundings using a trajectory-based ozone mapping methodology (Liu, G. et al., 2013; Liu, J. et al., 2013). This global dataset is interpolated from sparse ozone soundings, but as the interpolation is based on knowledge of actual atmospheric motion (using National Centers for Environmental Prediction (NCEP) reanalysis data) it is superior to simple linear or polynomial-based interpolation.

TOST was derived from over 50,000 ozonesonde profiles at ~116 stations from the 1960s to 2010s. Locations of these stations for the period 2008-2012 are shown in Figure S2.3.2. Taking advantage of tropospheric ozone's lifetime of a few weeks, the Hybrid Single-Particle Lagrangian

Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998) was applied to fill the gaps between ozonesonde stations, by extending each ozone record along its trajectory path forward and backward for four days. Over this 4-day period ozone production and loss is assumed to be negligible. Then, all ozone values along these trajectory paths were binned into a 3-dimensional grid of 5° x 5° x 1 km (latitude, longitude, and altitude), from sea level or ground level up to 26 km. The number of ozonesonde observations in each grid cell is typically 10-50 (*TOAR-Observations)*. TOST includes a yearly archive from 1965 to 2012 and a monthly archive for each decade (i.e., decadal mean of each month). TCO is also derived from the ozone mole fractions below the tropopause, defined according to the National Centers for Environmental Prediction (NCEP) reanalysis data using the WMO 2 K km^{-1} lapse-rate definition (WMO, 1992). TOST is latitudinally, longitudinally, and vertically resolved so that it can reveal longitudinal variations in the atmosphere that two-dimensional zonal mean ozone climatologies cannot. It also covers a longer time period, and in some cases, higher latitudes than satellite-derived tropospheric ozone data sets. TOST depends on neither a priori data nor photochemical modeling and thus provides independent information that can supplement satellite data and model simulations. TOST has been evaluated using individual ozonesondes (removed from TOST one by one) by backward and forward trajectory comparisons, and by comparisons with MOZAIC profiles and surface monitoring data (Tarasick et al., 2010; Liu, G. et al., 2013; Liu, J. et al., 2013). The agreement is generally quite good (for example, in the troposphere, r=0.91-0.99, RMS=3-5 nmol mol^{-1}, at 9 North American stations), but there are larger biases in the UTLS, over mountainous regions and in areas where ozonesonde measurements are sparse (Liu, J. et al., 2013). The accuracy of the TOST data also depends largely on the quality of HYSPLIT and the meteorological data on which it is based.

2.3.3 IAGOS

The In-Service Aircraft for the Global Observing System (IAGOS) program conducts long-term observations of atmospheric trace gases, aerosols and cloud particles on the global scale using commercial aircraft of internationally operating airlines. The origins of IAGOS lie with the MOZAIC (Measurements of OZone and water vapor on Airbus In-service airCraft) program, in which as many as five long-range Airbus A340 commercial aircraft provided in-situ measurements of ozone (as well as other species and thermodynamic parameters) along their flight routes in various regions of the world (*Marenco et al.*, 1998). Initiated in August 1994, MOZAIC continuously populated a database of both tropospheric vertical profiles (landing and takeoff phase) and upper troposphere-lower stratosphere (UTLS) observations (cruise phase), until November 2014 with the cessation of observations on the last A340 equipped with MOZAIC instruments. Ozone measurements were performed using a dual-beam ultra violet (UV)-absorption monitor (time resolution of 4 seconds) with an accuracy estimated at about ± (2 nmol mol^{-1} +2 %) (*Thouret et al.*, 1998). As the successor to MOZAIC, with the objective of long-

term sustainable operations, the first IAGOS aircraft became operational in July 2011 (*Petzold et al.*, 2015; *Nédélec et al.*, 2015). As of 2015, six IAGOS aircraft from five airlines (Air France, Lufthansa, China Airlines, Cathay Pacific, and Iberia) are in operation. The 4-year overlap of MOZAIC and IAGOS has demonstrated that the new system provides data with the same quality as the former, permitting the reliable calculation of temporal trends from 1994 to the present (*Nédélec et al.*, 2015). The MOZAIC-IAGOS data record (referred to as IAGOS hereafter) now contains over 50,000 flights, freely available through the open-access central database (http://www.iagos.org).

2.3.4 Lidar

The Ultra Violet Differential Absorption Lidar (UV DIAL) at the Observatoire de Haute Provence (OHP, 44°N, 6°E, 690 m) in southern France has recorded ozone profiles since 1991. The instrument measures ozone between 3 and 14 km above sea level (a.s.l.) using wavelengths of 289-299 nm during 1990-1993, and 289-316 nm since 1993. Ozone profiles are measured twice per week depending on cloudiness (Ancellet et al., 1997). The vertical resolution is 200 m at 2 km and 1000 m at 12 km, the precision is within 9% and the accuracy is 5 ± 5 nmol mol^{-1}. For this analysis, the lidar data set is combined with data from ECC ozonesondes launched weekly from OHP. Instrumental and meteorological biases when using the two data sets in a common database are discussed elsewhere (Gaudel et al., 2015). Considering the limited number of ECC soundings at OHP, improvement in the trend estimate is obtained in the yearly ozone trend analysis when adding the lidar data to increase the number of profiles by a factor of 2-3. An analysis based only on the lidar data is not satisfactory due to low sampling of southerly flow which is often associated with cloudy conditions.

The tropospheric ozone differential absorption lidar (DIAL) located at the Jet Propulsion Laboratory-Table Mountain Facility (TMF, 34.4°N, 117.7°W, 2285 m asl) has been operating since 1999 to contribute data to the international Network for the Detection of Atmospheric Composition Change (NDACC) and to the US-based Tropospheric Ozone Lidar Network (TOLNet). Measurements are performed routinely at nighttime, usually 2 to 4 nights per week, and 2 hours per night. The lidar instrument uses a Raman-shifted quadrupled Nd:YAG laser to emit light at 289 and 299 nm into the atmosphere, and 5 telescopes of varying size to collect the backscattered light into 3 pairs of channels of varying intensity, covering all altitudes between 4 and 18 km a.s.l. (3 and 18 km a.s.l. after 2013). The profile is extended to 25 km by combining the 299 nm high-intensity signal of the tropospheric ozone lidar with the 355 nm low-intensity signal of a co-located water vapor Raman lidar (Leblanc et al., 2012), thus covering the UTLS region with a precision of 2-5% (Leblanc et al., 2016b). More details on the system design and technical aspects can be found elsewhere (McDermid et al., 2002, Granados-Muñoz and Leblanc, 2016). Over the almost two decade-long period of measurements, the temporal sampling

has ranged between 5-min and 20-min and the vertical sampling has varied between 7.5 m and 75 m. For TOAR, the profiles routinely archived at NDACC were used. These profiles are averaged over 2-hours, with an effective vertical resolution between 150 m and 3 km, depending on altitude (Leblanc et al., 2016a). The corresponding standard uncertainty is about 5-10% throughout most of the profile, increasing to 15% at the top (Granados-Muñoz and Leblanc, 2016; Leblanc et al., 2016b).

2.4 Tropospheric Column Ozone (TCO): Satellite instruments, ground-based FTIR and Umkehr

This paper provides an intercomparison of several remotely sensed tropospheric column ozone products, as measured by satellite-borne instruments and ground-based FTIR and Umkehr instruments. Details of each product are described below with key parameters listed in Table 2.4.

2.4.1 OMI/MLS

Daily measurements of TCO and tropospheric ozone mean mole fraction were determined from the NASA Aura satellite's Ozone Monitoring Instrument (OMI) v8.5 total ozone (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI) and Microwave Limb Sounder (MLS) v3.3 stratospheric column ozone (SCO) (Livesey et al., 2011). Calculation of TCO (Ziemke et al., 2006) requires subtraction of MLS SCO from OMI total ozone (TO) for near clear-sky scenes (i.e., OMI radiative cloud fractions less than 30%) producing a gridded product at horizontal resolution of 1° latitude × 1.25° longitude. SCO was first calculated along orbit paths using standard vertical pressure integration of MLS ozone mole fraction profiles from 0.0215 hPa to the tropopause pressure (determined from NCEP analyses using the WMO 2 K km^{-1} lapse-rate definition). Daily SCO measurements were interpolated horizontally (Gaussian + linear) between orbit paths to obtain gridded SCO fields at the 1°×1.25° horizontal resolution of OMI, and then subtracted from the gridded OMI TO to derive daily gridded TCO fields.

Mean mole fraction (MF) (nmol mol^{-1}) was calculated each day from TCO in DU by the relation MF[nmol mol^{-1}] = 1270[nmol mol^{-1} hPa DU^{-1}] × TCO[DU] / ΔP[hPa], where ΔP is surface pressure minus tropopause pressure in units of hPa (Ziemke et al., 2001). The purpose of using mean MF is that it removes spatial and temporal variability in TCO caused by variations in tropopause height and terrain height. In a well-mixed atmosphere, mean MF (unlike TCO) will yield the same numbers over high mountains and nearby low terrain, and is independent of regional tropopause height fluctuations. Both TCO and MF daily measurements were averaged monthly for October 2004-December 2016. On average, 30 DU in TCO corresponds to about 42 nmol mol^{-1} in MF. Precision uncertainty for daily TCO and MF at 1°×1.25° gridding is approximately 5 DU and 7 nmol mol^{-1}, respectively. These precision numbers were estimated from one-to-one comparison of OMI/MLS TCO and ozonesonde TCO using the

same NCEP tropopause pressure. The precision numbers do not delineate potential errors in TCO coming from errors in tropopause pressures and OMI and MLS ozone. For monthly means at the same gridding, the precision numbers are about 1 DU and 1.3 nmol mol^{-1}, respectively. In this report we also calculated ozone mass in the troposphere by area integration of gridded TCO measurements. Ozone mass was calculated for specified latitude bands of 60°S-60°N, 0°-60°N, 0°-60°S, 0°-30°N, and 0°-30°S.

Biases and long-term stability of OMI and MLS ozone measurements have been evaluated in detail (Hubert et al., 2016; Schenkeveld et al., 2016). Both instruments appear very stable over the Aura decadal record. We have further tested the long-term decadal stability of OMI/MLS TCO measurements using 1-1 comparisons with daily ozonesonde TCO. Both OMI/MLS and ozonesondes used the same daily tropopause pressures from NCEP re-analyses to calculate TCO. Daily differences between OMI/MLS and ozonesonde TCO were first calculated and then averaged over the beginning and ending 5-year periods for both NH summer-only months (June-September) and also for all months of the year combined. These summer-only and all-month tests showed ending minus beginning 5-year period differences of only 0.22 DU ± 0.36 DU $decade^{-1}$ and 0.29 DU ± 0.29 DU $decade^{-1}$. That is, the decadal drift for OMI/MLS TCO based on ozonesonde TCO was found to be very small (~ 1%) and not statistically significant. Despite insignificant drift, OMI/MLS TCO had a small persistent offset with ozonesonde TCO of about 2 DU, with OMI/MLS smaller than ozonesonde TCO. MLS SCO was also tested against OMI SCO where the latter was determined using the convective cloud differential (CCD) cloud slicing method (Ziemke et al., 1998). Comparison of the 12-year time records of SCO indicated very small potential drift of 0.5 DU $decade^{-1}$ between the two instruments. A third analysis of potential drift of the OMI/MLS TCO product was also performed by generating OMI total ozone using only OMI rows 3-18 (i.e., far removed from the OMI row-anomaly errors) and testing this versus the standard OMI total column ozone product; this analysis indicated that the 0.5 DU $decade^{-1}$ amount in SCO is related to a small and subtle row anomaly flagging error in the standard total ozone product. Following these various tests, we have applied a mean adjustment of -0.5 DU $decade^{-1}$ to the OMI/MLS TCO product. This product shows that the tropospheric ozone burden (60° S – 60° N) was 265 Tg at the start of the record in October 2004 and increased to 287 Tg by September 2016, for a net increase of 8%.

2.4.2 GOME and OMI (Smithsonian Astrophysical Observatory (SAO))

Ozone profiles with 24 layers (~2.5 km thick) from the surface to 60 km (with 4 to 7 layers in the troposphere, depending on tropopause height) are retrieved from Global Ozone Monitoring Experiment (GOME; Burrows et al., 1999) and OMI (Levelt et al., 2006) radiances in the Hartley and Huggins bands using the optimal estimation technique (Liu et al., 2005, 2010; Huang et al., 2017). NCEP daily tropopause height based on the WMO 2 K km^{-1} lapse-rate definition is used as one of the retrieval levels, allowing TCO, with its retrieval errors, to be derived from the retrieved profile and its corresponding error

covariance matrix. The time series from GOME (7/1995-6/2003) and OMI (10/2004-2015) are combined to produce a nearly 20-year record with a 15-month gap during 2003-2004. GOME data prior to March 1996 are systematically higher due to the use of a shorter integration time (Burrows et al., 1999) and therefore not used in this study.

To generate monthly GOME and OMI data, only retrievals with good quality flags under near clear-sky conditions (with effective cloud fraction < 0.3) were used. Due to the limited number of GOME retrievals, selected daily retrievals were mapped directly to a common grid of 1° latitude x 1.25° longitude to derive monthly means. OMI data were similarly mapped, but on a daily basis and then averaged to produce monthly means. Due to reduced sensitivity to tropospheric ozone at higher latitudes and the lack of observations for some seasons, data are limited to 60°S-60°N.

Accurate radiometric calibration of Level 1b irradiance and radiance spectra as a function of time is critical for producing a long-term consistent data record. With these GOME retrievals, a wavelength and cross-track dependent degradation correction is derived by comparing the average reflectance for the whole latitude range 60°S-60°N with that at the beginning of GOME observations (July–December 1995) after removing the dependences on solar zenith angle and seasonal variation, and then applied to the retrieval as a function of time (Liu et al., 2007). Deviations from this assumption and the initial radiometric errors after launch can cause time-dependent systematic biases in the retrievals. For the OMI retrievals, wavelength-dependent and cross-track dependent corrections derived from comparing simulations and observations in 20°S-0° in two days is applied independent of space and time. Therefore, the retrievals are subject to time-dependent systematic biases resulting from instrument degradation especially with the occurrence of the serious row-anomaly (an anomaly that affects the quality of the level 1B radiance data at all wavelengths for a particular viewing direction of OMI) since 2009 (Huang et al., 2017). In addition, small biases between GOME and OMI are expected due to some small algorithm differences (e.g., fitting windows). As shown in Figure S2.4.2, the time series of GOME and OMI monthly mean tropospheric ozone mole fraction and their de-seasonalized values show clear systematic biases as some similar temporal patterns occur for different latitude bands where the temporal variations are expected to be different.

Both GOME and OMI TCOs show good agreement with ozonesonde TCO even without applying retrieval averaging kernels (AKs). Validation of GOME TCO during 1996-1999 at 33 individual stations showed that the retrievals capture most of the temporal variability in ozonesonde TCO with mean biases mostly within 3 DU (15%) and the standard deviations (1σ) within 3–8 DU (13–27%) (Liu et al., 2005). Validation of GOME TCO retrieval with the empirical radiometric correction for the entire GOME period against ozonesondes at Hohenpeißenberg showed similar performance after 1999 especially in mean biases (Liu et al., 2007). OMI TCOs from 2004-2014 were extensively validated with ozonesonde

observations over the globe in a recent effort by Huang et al. (2017). The TCO mean biases are within 1.5 DU (6%), with standard deviations of <~23% in the tropics and mid-latitudes during both 2004-2008 (pre row-anomaly) and 2009-2014 (post row-anomaly) periods. However, the mean biases during 2009-2014 are smaller by ~2 DU at middle latitudes and larger by ~1 DU in the tropics, and the standard deviations are larger by 3-6% than the comparisons during 2004-2008. The retrieved TCO is more stable as a function of time during 2004-2008 and contains clear latitude-dependent trend artifacts during 2009-2014. In addition, the TCO retrieval performance also shows some dependency on solar zenith angle and therefore latitude, typically with larger mean biases at larger solar zenith angles. OMI tropospheric ozone columns in the lower troposphere were also evaluated against ozonesonde observations. Surface – 750/550 hPa ozone columns also agree quite well with ozonesonde data in the tropics and at middle latitudes during summer with mean biases of less than 5% and standard deviations of 20-25%/28-36% without applying AKs. But correlation and slope decrease with lower altitude ranges due to reduced retrieval sensitivity in the lower troposphere and large smoothing errors. Analysis of OMI data shows clear ozone enhancement in the lower troposphere (surface – 750 hPa) over central and east China (Hayashida et al., 2015, 2016).

2.4.3 OMI-RAL

Global height-resolved ozone distributions spanning the stratosphere and troposphere are retrieved from satellite UV nadir sounders by the Rutherford Appleton Laboratory (RAL)'s optimal estimation scheme (Miles et al., 2015). Multi-year data sets spanning two decades (1995 – 2016) are being produced with this scheme from a series of five instruments for ESA's Climate Change Initiative (CCI) and will be updated in coming years for the EU's Copernicus Climate Change Service (C3S). RAL's scheme was the first to demonstrate tropospheric sensitivity (Munro et al., 1998). This is achieved through a three-step approach: firstly, the strong wavelength dependence of ozone absorption in the Hartley band (260-307 nm) is exploited in fitting the ratio of backscattered to direct-sun spectra to retrieve height-resolved information principally in the stratosphere; secondly, an effective surface albedo is retrieved in the 335-340 nm interval and, thirdly, temperature dependent ozone absorption in the Huggins bands (323-334 nm) is fitted to high precision (<0.1% RMS) to extend the profile retrieval into the troposphere. Ozone prior information for the first step is from a zonal mean monthly climatology (McPeters et al 2007). Retrieval outputs from the first and second steps improve the prior constraints for the third step. Precision on the 1013- 450 hPa sub-column retrieved from an individual sounding is typically ~4DU. To achieve the required spectral fitting precision and accuracy, some key instrument spectral and radiometric parameters are pre-retrieved from direct-sun irradiance spectra and a number of instrumental and geophysical parameters are co-retrieved with the ozone profile. Forward-model simulations are performed on-line with a modified version of the GOMETRAN radiative transfer model

(Rozanov et al., 1997). Among developments implemented since Miles et al. (2015) are a more rigorous representation of rotational Raman scattering to account for height-dependent filling-in of ozone absorption and significant modifications to accommodate OMI's across-track sampling by means of a 2-D detector array in place of across-track scanning by sensors of the GOME class. Spectral coverage in the Huggins bands has also been extended to 321.5-334nm. Developments are in progress to improve near-surface sensitivity through addition of the ozone visible band (Chappuis) and, for GOME-2 on Metop, improvement of UTLS vertical resolution by addition of co-located IR measurements by IASI. The scheme as adapted for OMI will be applied to new instruments in the Copernicus programme, commencing with Sentinel-5 Precursor which is due for launch in late 2017 and subsequently Sentinel-5 on Eumetsat's Metop-SG series, planned for 2021-40.

2.4.4 IASI

The Infrared Atmospheric Sounding Interferometer (IASI) is a Fourier transform spectrometer using the thermal infrared spectral range to sound the surface and the atmosphere. It is operating from the Metop series of satellites (Metop-A launched in 2006 and Metop-B launched in 2012) providing, each morning and each evening at around 9:30 local time, global and regional distributions for a range of trace gases (Clerbaux et al., 2009; Hilton et al., 2012). To achieve global coverage, the IASI instrument observes the Earth up to an angle of 48.3° on both sides of the satellite track (swath of about 2×1100 km). Each instantaneous field-of view (50 km×50 km at nadir) is composed of 2×2 circular pixels, each corresponding to a 12 km diameter footprint on the ground at nadir. *TOAR-Climate* presents several IASI ozone products, all described below.

IASI-FORLI: Ozone vertical profiles are retrieved on the global scale with the FORLI-O_3 (Fast Optimal Retrievals on Layers for IASI – v20151001) processing chain set up by the Université Libre de Bruxelles (U.L.B.) and LATMOS teams (see Hurtmans et al. (2012) for a description of the retrieval parameters and performances). FORLI-O_3 relies on a fast radiative transfer and retrieval methodology based on the optimal estimation method and it provides profiles, averaging kernels and errors on a uniform 1 km vertical grid on 41 layers from the surface to 40 km with an additional layer from 40 km to the top of the atmosphere. IASI-FORLI uses only one single ozone a priori profile and variance-covariance matrix which are built from the Logan, Labow, McPeters climatology (McPeters et al., 2007). The code was optimized to work in near real time and is now implemented in the Eumetsat ground-based facility to become the official IASI ozone product to be distributed by Eumetcast in 2017. The FORLI-O3 profiles and partial columns have undergone a series of validations against available ground-based, aircraft, ozonesonde and other satellite observations (Boynard et al., 2016, and references therein). The sensitivity of IASI in the troposphere maximizes around 4–8 km for most geophysical situations. Negative ozone trends in the troposphere at mid- and high northern latitudes for the 6-year period of 2008-2013 have been

reported, especially during summer (Wespes et al., 2016). For this study the daily tropopause height used to generate the IASI-FORLI TCO dataset relies on the WMO definition applied to the IASI level 2 temperature profiles which are provided through the Eumetcast operational processing system (August et al., 2012). Here only daytime and clear-sky ozone measurements have been considered (defined with a solar zenith angle < 80° and a fractional cloud cover per pixel below 13%), which are characterized by a good spectral fit and vertical sensitivity to the troposphere (based on quality flags using a series of criteria). Similar to other products, the IASI data were mapped on a daily basis to a grid of 5° latitude x 5° longitude, and then averaged to produce seasonal and annual means.

IASI-SOFRID: The SOftware for a Fast Retrieval of IASI Data (SOFRID) retrieves global ozone (Barret et al., 2011) and CO (De Wachter et al., 2012) profiles from IASI radiances in near-real time. SOFRID is built on the RTTOV (Radiative Transfer for TOVS, https://nwpsaf.eu/site/software/rttov/) operational radiative transfer model (Saunders et al., 1999, Matricardi et al., 2004) jointly developed by European weather forecast agencies (ECMWF, Meteo-France, UKMO and KNMI) within the NWPSAF. The RTTOV regression coefficients are based on line-by-line computations performed using the HITRAN2004 spectroscopic database (Rothman et al., 2005) and the land surface emissivity is computed with the RTTOV UW-IRemis module (Borbas et al., 2010). We use the IASI-L2 temperature profiles from EUMETSAT for radiative transfer computation by RTTOV. The retrievals are performed with the UKMO 1D-Var algorithm (Pavelin, et al., 2008) based on the optimal estimation method (Rodgers, 2000). The results presented here are based on the IASI-SOFRID v1.5 ozone product described in Barret et al. (2011). In this data version, SOFRID uses a single a priori ozone profile and associated covariance matrix based on one year (2008) of ozonesondes from the WOUDC and SHADOZ networks. The retrievals are performed for clear-sky conditions (cloud cover fraction < 25%).

IASI-SOFRID ozone retrievals enable almost independent retrievals in the lower-middle troposphere (below 225 hPa), in the UTLS (225-70 hPa) and in the stratosphere (above 70 hPa) (Barret et al., 2011). In their validation paper, Dufour et al. (2012) have shown that IASI-SOFRID ozone tropospheric columns were in good agreement with coincident ozone columns from ozonesondes for the year 2008, with correlation coefficient of 0.82 and bias of 4 ± 4% at mid-latitudes, and correlation coefficients of 0.93 and biases of 5 ± 3% in the tropics.

IASI-LISA: The retrieval of the IASI-LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques) (TP) ozone vertical profiles is performed using the radiative transfer model KOPRA (Karlsruhe Optimised and Precise Radiative transfer Algorithm), its inversion module KOPRAFIT, and a Tikhonov-Phillips (TP) altitude-dependent regularization (Eremenko et al., 2008). The retrieval constraints are optimized to both maximize the degrees of freedom in the lower troposphere and to

minimize the total error on the retrieved profile, leading to an enhanced sensitivity in the lower troposphere (Dufour et al., 2012). Two semi-independent partial columns of ozone can be determined between the surface and 12 km (especially in the case of positive thermal contrasts): the lower-tropospheric column, integrating the ozone profile from the surface to 6 km above sea level (asl); the upper-tropospheric column, integrating the ozone profile from 6-12 km a.s.l. (Dufour et al., 2010, 2012). Note that the latter column can include lower stratospheric air masses depending on the tropopause height. The averaging kernels give information on the vertical sensitivity and resolution of the retrieval. The lower-tropospheric column has a maximum sensitivity typically between 3 and 4 km with a limited sensitivity at the surface (Dufour et al., 2012). Three different a priori profiles and constraint matrices are used depending on the tropopause height (for polar, midlatitude and tropical situations; see Dufour et al., 2015). The retrieval algorithm is not optimized to provide near-real-time global data, and at present only regional data above Europe and Asia are available. For this study, only morning observations for clear-sky conditions (cloud fraction less than 15%) and high-quality pixels (based on quality flags) are used. The IASI-LISA product was mapped on a daily basis to a grid of 0.25° latitude x 0.25° longitude, and then averaged to produce seasonal means over the 2008-2014 period.

IASI+GOME2 (LISA): In order to better characterize the vertical distribution of tropospheric ozone down to the lowermost troposphere (LMT, surface to 3 km a.s.l.), a new multispectral approach called IASI+GOME2 combines the information provided by thermal IR radiances measured by the IASI instrument and earth reflectance UV spectra from GOME-2 (Cuesta et al., 2013). Both co-located spectra are fitted simultaneously for deriving vertical profiles of ozone (for effective cloud cover <0.3), providing multispectral retrievals at the IASI horizontal resolution (12-km diameter pixels spaced by 25 km at nadir). Both IASI and GOME-2 are onboard the series of Metop satellites and they offer scanning capabilities with daily global coverage. Altitude-dependent Tikhonov–Phillips-type constraints optimize sensitivity in the lowermost troposphere, which exhibits a relative maximum around 2 to 2.5 km a.s.l. over land (where thermal contrast is positive). Further details are provided in *TOAR-Observations*. The multispectral synergism of IASI and GOME-2 enhances the vertical resolution of the retrieval so as to consistently resolve ozone concentration in the lower/middle troposphere, the middle/upper troposphere and lower stratosphere. Since January 2017, global scale IASI+GOME2 observations are routinely produced at the ESPRI French National data center (http://cds-espri.ipsl.fr) of the AERIS data center (http://www.aeris-data.fr) and will be available soon for the scientific community.

2.4.5 SCIAMACHY

The SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) is a passive UV-Vis-NIR-SWIR spectrometer that operated on board the European Envisat satellite from March 2002 to April 2012 (Burrows et al., 1995; Bovensmann et al., 1999).

SCIAMACHY was designed to alternate between limb and nadir geometries so that the region probed during the limb scan could be observed about 7 minutes later during the nadir scan.

Tropospheric ozone columns are retrieved employing the Limb-Nadir-Matching (LNM) technique (Ebojie et al., 2014, Ebojie, 2014). This technique is also referred to as the tropospheric ozone residual method, which uses collocated measurements in limb and nadir viewing geometries made by the SCIAMACHY instrument. The tropospheric ozone columns are obtained subtracting the stratospheric ozone columns from the total columns of ozone. The stratospheric ozone columns are calculated by integrating the vertical profiles of ozone down to the tropopause. The tropopause was determined from the European Centre for Medium Range Weather Forecasts (ECMWF) reanalyses ERA-Interim data. The stratospheric ozone profiles are retrieved from SCIAMACHY measurements in limb viewing geometry while the total ozone columns are derived from SCIAMACHY nadir observations (Ebojie et al., 2014; Ebojie, 2014; Jia et al., 2017). When using the tropospheric ozone residual method, a good knowledge of the tropopause height (TPH) is crucial. While in the tropical band the tropopause is well above the lowest altitude of the limb measurement, this is not the case for the higher latitudes, where the tropopause can be lower than the minimum height of the limb ozone profile. In this case, extrapolation of the stratospheric ozone profiles is performed using ozonesonde climatologies (Ebojie et al., 2014; Ebojie 2014). The ground scene observed within one limb measurement is about 400 km x 240 km, while a single nadir observation covers the area of 30 km x 60 km. As a result of the ground pixel coordinates matching procedure each single value for the tropospheric ozone column is assigned to the ground scene area of about 60 x 240 km (Ebojie 2014). Only cloud free limb scenes and nadir pixels with cloud fraction < 30% were used. In addition, the analysis has been restricted to solar zenith angles (SZA) smaller than 80° and only the descending part of the orbit was used.

Main errors stem from the stratospheric ozone column. The errors in TPH are negligible even though highly variable. The errors in the total ozone columns are less variable over the globe for the tropical band and highly variable for middle latitudes showing wave structures. Total error due to these three uncertainties is approximately 5 DU in TCO (Ebojie et al., 2014; Ebojie, 2014). Since the tropospheric column is, on average, approximately 30 DU, the relative fraction of the error is around 1/6 or 16%. In the current investigation an updated and improved version of the limb nadir matching method for the ozone limb V2.9 has been used (Jia et al., 2015).

2.4.6 Ground-based FTIR

The ground-based remote-sensing Fourier Transform Infrared (FTIR) instruments currently used within the Network for the Detection of Atmospheric Composition Change (NDACC, www.ndacc.org) are the Bruker 120M, 125M, 120HR and 125HR high-resolution spectrometers, which can achieve an instrumental spectral resolution of 0.0035 cm^{-1} or better. The ozone retrievals are performed using solar

absorption spectra in the 600-1400 cm^{-1} range, and more specifically using small window(s), with many absorption ozone lines in the 1000 cm^{-1} region (see Vigouroux et al., 2015 for more details).

In addition to total ozone, the FTIR technique provides low resolution, vertical profile, mole fraction information, due to the pressure and temperature dependence of ozone's spectral absorption features. Using the Optimal Estimation technique (*Rodgers*, 2000), 4 to 5 independent layers can be resolved from the ground to about 45 km (see *TOAR-Observations*). There is at least one tropospheric layer (defined as ground to 8 km a.s.l.) that is largely independent of the rest of the atmosphere, as defined by having a degrees of freedom for signal of 0.8 to 1.0, depending on the station. This FTIR partial column ozone has expected random and systematic uncertainties of 11% and 4%, respectively (see *TOAR-Observations*). The dominating systematic uncertainties are first the spectroscopic parameters and, to a lesser extent in the troposphere, the temperature and the instrumental line shape. The total uncertainty is around 14%.

Among the FTIR stations measuring ozone, a subset provides time-series longer than 10 or even 15 years for use in ozone trend studies (*Vigouroux et al*. 2008; *García et al*., 2012; *Vigouroux et al*., 2015; *WMO*, 2010; *WMO*, 2014). A list of the stations used in *TOAR-Climate* is provided in *TOAR-Observations*. Since the measurements are solar absorption spectra, the observations are limited to clear-sky daytime conditions, which also excludes the polar night observations for the highest latitude stations. Up to 5 measurements per day are possible if conditions are sunny. On average, for all stations the number of measurements is 2.5, 7, and 15 per day, week and month, respectively, but is highly variable depending upon station location.

2.4.7 Umkehr Dobson and Brewer ozone profile retrievals

Both Dobson and Brewer spectrometers are known for their total column ozone measurement. The measurement is performed by pointing the ground-based instrument at the sun and using the optical sensor to record the spectral intensity difference (for Dobson) or photon count (for Brewer) in the UV solar spectrum. The Dobson instrument (Dobson, 1968a, 1968b) has been used to monitor the variability in total column ozone since the 1920s. The Brewer instrument was developed in the 1980s (Kerr et al., 1981), while the technique was later improved to reject the noise in the measurement at large solar zenith angles (Kerr, 2002). Both Dobson and Brewer spectrometers are capable of zenith sky measurements performed sequentially during sunrise and sunset. The result is the so-called Umkehr curve, which is analyzed to produce an ozone profile. The retrieval method is based on the optimum statistical approach that uses the a priori profile and ozone co-variance information. The method of the Dobson Umkehr measurements (Mateer, 1964; Mateer and DeLuisi, 1992; Petropavlovskikh et al., 2005) is discussed in *TOAR-Observations*. The UMK04 algorithm is recommended by the International Ozone Commission to derive ozone profiles that are optimized for trend analysis (Petropavlovskikh et al., 2005). The data are

673 archived at the World Ozone and Ultraviolet Radiation Data Centre (http://www.woudc.org/). The
674 uncertainties of the retrieval and measurements are described elsewhere (Hassler et al., 2014). The
675 discussion of the tropospheric ozone variability captured by the Umkehr retrieved profile requires
676 understanding of the configuration of the retrieval algorithm (relative contributions of the a priori
677 information and measurement) and resulting averaging kernels that describe the mapping of the vertically
678 distributed sensitivity of the measurement into the retrieved ozone profile. The UMK04 algorithm was
679 designed to represent variability in the monthly averaged time series, to minimize the impact of the a
680 priori information and to have the profile distribution equally weighted. As a result, the AKs for the
681 troposphere are fairly broad and the tropospheric layer is defined between the pressure altitude of the
682 ground station and 250 hPa. The attribution of the lowest Umkehr layer information to TCO (below the
683 tropopause) variability is therefore not well-defined as there is also a contribution from the lower
684 stratosphere that has to be taken into account. When compared to ozonesondes, integrated between the
685 Umkehr layer pressure levels, the bias can be as large as 10-20%. However, in all but the lowest layer,
686 the bias is reduced (by almost half) when the ozonesonde profiles are smoothed with the Umkehr AKs.
687 Another artifact that affects the Umkehr retrieval is the contribution from out-of-band stray light
688 (Petropavlovskikh et al., 2011). Once the correction is applied to account for this effect in the retrieval
689 algorithm, the bias relative to other ozone measurements is reduced by about 5%. The Umkehr data for
690 this study are treated for stray light. Although the bias between Umkehr and other measurements,
691 including ozonesondes and lidar (Komhyr et al, 1995; Fioletov et al, 2008; Nair et al, 2011) has been
692 identified, the data are usually de-seasonalized prior to trend analysis.

693 **2.5 Satellite observations of tropospheric ozone as a greenhouse gas**

694 TES (Tropospheric Emission Spectrometer) has operated on the NASA EOS-Aura satellite since
695 2004 and measures vertical ozone profiles using thermal infrared spectra, similar to IASI, using Fourier
696 Transform Spectrometry (FTS). TES obtained global observations from 2004 to 2009 but shifted to a
697 smaller latitude range along with targeted observations following instrument failures associated with
698 continuous operation. Since IASI observations will continue into the next decade with identical IASI
699 instruments on Metop-B and –C, there have been efforts to combine the TES and IASI data records by
700 accounting for differences in spatial coverage, spectral resolution, and a priori information in the optimal
701 estimation retrievals (Oetjen et al., 2014; 2016).

702 In addition to ozone abundance profiles, TES and IASI also produce the sensitivity of TOA
703 outgoing long-wave flux to changes in tropospheric ozone. Radiative forcing due to tropospheric ozone
704 also has significant regional variability (Shindell and Faluvegi, 2009). While satellite observations cannot
705 measure pre-industrial to present day radiative forcing of tropospheric ozone, they can measure the ozone
706 greenhouse effect of reduced TOA flux due to ozone radiance absorption. Long-wave (thermal infrared)

measurements from the TES and IASI satellite FTS instruments are used to compute instantaneous radiative kernels (IRK) for ozone in W m^{-2} nmol mol^{-1} for each vertical pressure level. IRKs are computed with the retrieved ozone vertical profiles along with the Jacobians, K, which quantify the sensitivity of the TOA radiance to each vertical profile (Worden et al., 2008, 2011; Doniki et al., 2015). Multiplying the IRK by the tropospheric ozone profile and summing the values from the surface to the tropopause gives the long-wave radiative effect (LWRE) in W m^{-2}. LWRE quantifies the present day tropospheric ozone greenhouse effect, with the annual average for December 2014 to November 2015 from IASI observations shown in Figure 1.2. The spatial variation of LWRE, with higher values over land and in the Northern Hemisphere, is due to both TOA radiance sensitivity to ozone and ozone abundance. Satellite ozone IRKs can be used to evaluate climate model estimates of the same quantities and also to predict the radiative impact of changes in ozone precursor emissions (Bowman and Henze, 2012). These measurements of the greenhouse effect of tropospheric ozone and their sensitivity to the distribution of ozone are an important benchmark for comparison to future observations.

3. Present-day distribution of tropospheric ozone

3.1 Surface ozone

Non-urban surface ozone observations for the present-day (2010-2014) are mostly found in North America, Europe and East Asia (Korea and Japan); observations beyond these regions are relatively sparse. Figure 3.1.1 shows daytime average surface ozone mole fractions at all available non-urban sites in December-January-February (DJF) and in June-July-September (JJA), the minimum and maximum seasons of ozone production in the Northern Hemisphere mid-latitudes (note that many US sites only operate during April-September, hence the fewer number of sites in DJF). In Northern Hemisphere winter (DJF), high ozone (>40 nmol mol^{-1}) is mainly confined to high elevation regions: western USA, Western Europe (Alps and Pyrenees), central Japan, central China/Nepal, Greenland, southern Algeria and Izaña (Canary Islands). Such high ozone values are less frequent at low elevations, limited to western Canada, southern California, northeastern Utah (in a region of intense oil and natural gas extraction (Oltmans et al., 2016)), Israel, islands in the Mediterranean Sea and island/coastal sites in the vicinity of South Korea, Japan, Hong Kong and Taiwan. During Northern Hemisphere summer, high ozone values (>50 nmol mol^{-1}) are concentrated in northern mid-latitudes at both high and low elevations, primarily in the western USA, southern Europe, China, South Korea and Japan. Ozone in the Southern Hemisphere is much lower with only one region (the high elevation Highveld of South Africa) exceeding 40 nmol mol^{-1}. These high ozone events occur in DJF, and September-October-November (SON), which is springtime and the peak ozone season in the Southern Hemisphere.

Figure 3.1.2 focuses on the three regions with dense surface networks (North America, Europe, East Asia) and shows daytime averages for all four seasons. In each region, maximum ozone is observed in spring/summer and the minimum ozone is observed in autumn/winter. Notably, maximum ozone values in southeastern China, South Korea and Japan occur in spring, not summer. However, ozone in the Beijing region peaks in summer. Finally, to illustrate the distribution of extreme ozone values, Figure S3.1 shows 98th percentile ozone at all available sites around the world (urban and non-urban) for the 6-month warm season (April-September in the Northern Hemisphere, and October-March in the Southern Hemisphere). Greatest values in North America are found in California and Mexico City. Europe has a strong north-south gradient with highest values in northern Italy, Spain and Greece. On the eastern edge of the Mediterranean a monitoring site at 1 km above sea level in the West Bank has ozone values as great as those found in the heavily urbanized regions of Europe. Across Asia very high ozone values (> 80 nmol mol^{-1}) are widespread (northern India, eastern mainland China, Hong Kong, Taiwan, South Korea, and Japan) despite a limited number of monitoring sites.

3.2 Free tropospheric ozone

3.2.1 Global ozone distribution in the free troposphere from aircraft and ozonesondes

Figure 3.2.1 shows seasonal mean ozone in the upper troposphere (UT) as measured by IAGOS commercial aircraft and averaged using the methodology developed by Thouret et al. (2006). Measurements are obtained from aircraft cruising altitude, typically between 9 and 12 km, and cover a large part of the Northern Hemisphere mid-latitudes and tropics, and some areas of the Southern Hemisphere. In the extra-tropics (30°S-90°S and 30°N-90°N), the UT is considered to be a layer 15-75 hPa below the local tropopause, defined as the 2 pvu (pvu=potential vorticity units) potential vorticity surface extracted from the European Centre for Medium-Range Weather Forecasts (ECMWF) operational analyses (00:00, 06:00, 12:00, 18:00 UTC) and forecasts (03:00, 09:00, 15:00, 21:00 UTC). In tropical regions (30°S-30°N), where the tropopause is typically above the aircraft cruising altitude, all observations above 8 km are assigned to the UT. Mean ozone is calculated on 5°x5° cells containing at least 300 observations over the 2009-2013 period.

The seasonal distributions of ozone in the UT show a summer maximum that coincides with the maximum photochemical activity in the northern hemisphere. Clear seasonal variations are highlighted in the northern extra-tropics, with maximum values (> 100 nmol mol^{-1}) occurring in boreal summer, and minimum values in boreal winter (< 60 nmol mol^{-1}). This is consistent with the seasonal pattern previously observed over Europe, eastern North America and the North Atlantic Ocean, based on 1994-2003 MOZAIC observations (Thouret et al., 2006). The highest ozone is observed over Eurasia (including the Middle East) (>76 nmol mol^{-1}) and to a lesser extent over the North Atlantic Ocean and Europe, similar to the upper tropospheric ozone distribution observed by the TES satellite instrument (J.

J. Liu et al., 2009). Intermediate values are measured above North America and the North Pacific Ocean, while lower values are found in the tropics (20-60 nmol mol^{-1}). Ozone is particularly low (20-40 nmol mol^{-1}) above Southeast Asia during boreal summer and autumn, likely due to deep convective uplift of low-ozone air masses. While this analysis lacks observations above SE Asia during winter and spring, a new IAGOS analysis of this region by Cohen et al. (2017) shows that upper tropospheric ozone peaks in this region during the spring biomass burning season (40-50 nmol mol^{-1}). In the tropics, high ozone values have been recorded in regions and seasons of biomass burning, particularly over South America in SON (*Yamasoe et al*., 2015), and West Africa in DJF (*Sauvage et al.*, 2005).

Figure 3.2.1 also shows seasonal mean ozone (nmol mol^{-1}) from the TOST ozonesonde climatology in the upper (7-9 km), mid- (5-7 km) and lower free troposphere (2-3 km). In comparison to the IAGOS UT climatology, the TOST 7-9 km layer generally has more ozone during DJF and MAM even though it is at a lower altitude. There are two reasons for this difference, 1) compared to IAGOS, ozonesondes are typically biased high by about 8% in the UT (*TOAR-Observations*); and 2) whereas the IAGOS product utilizes observations below the dynamical tropopause, TOST is based on the thermal (temperature lapse-rate) definition of the tropopause which is often located above the dynamical tropopause; therefore, TOST will often include additional ozone found between the thermal and dynamical tropopause (Bethan et al., 1996; Wirth, 2000). TOST shows a broad spring/summer ozone enhancement across northern mid-latitudes with a band of enhanced summertime ozone stretching from North Africa, across the Mediterranean Sea to East Asia at 5-7 km and 7-9 km. This broad feature has also been detected in the summertime upper troposphere by the TES satellite instrument (Worden et al., 2009). The ozone enhancement above the eastern Mediterranean region and Middle East in summer appears to extend from the upper troposphere down to the lower free troposphere. Peak ozone in the Southern Hemisphere occurs in the mid- and upper troposphere during SON (season of peak biomass burning), primarily in the tropics and sub-tropics stretching from South America eastwards across Africa and as far as Australia. The minimum ozone values at all three levels tend to occur over the tropical Pacific Ocean.

3.2.2 Diurnal variability

Frankfurt, Germany is the only location in the world where frequent IAGOS aircraft flights (21,000 for 1994-2012, i.e. 98 per month on average) are sufficient for building an almost complete diurnal profile of ozone throughout the depth of the troposphere (Petetin et al., 2016a). Figure 3.2.2 shows the tropospheric ozone diurnal cycle during 1994-2012, at both the seasonal and annual scale, and at several pressure levels. Only observations within the troposphere are taken into account in these diurnal profiles; the methodology employed here includes fresh stratospheric intrusions. Based on ECMWF PV fields (see Section 3.2.1), the tropopause is defined as a 30 hPa layer centered on the 2 pvu

potential vorticity surface. Data are binned by 3-hour time period, but the 0-3 UTC time period was omitted due to a small sample size. More details on the method can be found in Petetin et al. (2016a).

These results demonstrate the absence of ozone diurnal variations in the free troposphere, in contrast to the boundary layer (BL) where strong enhancements are observed in the afternoon. The coefficients of variation (standard deviation normalized by the mean) decrease from 10-30% close to the surface to less than 3% above 800 hPa. The figure clearly depicts the development of a deeper BL during summertime with ozone diurnal variations propagating up to 700 hPa (compared to 850 and 900 hPa in spring and autumn, respectively). In winter, the diurnal variation in the BL is very low due to limited photochemical activity. In the free troposphere, some fluctuations of ozone persist in the late afternoon and evening (15-24 UTC) in summer and autumn, likely due to the lower number of observations in comparison to the 3-15 UTC time interval.

3.3 Regional distribution of partial column ozone in the lower and upper troposphere

Figure 3.3.1 shows the seasonal means of two partial tropospheric ozone columns (surface-6 km and 6-12 km) over East Asia for 2010-2014 from IASI-LISA observations. Ozone peaks in the upper layer north of 35° N in DJF (when the tropopause is lowest and this layer contains a greater amount of stratospheric air), and is at a minimum in SON. South of 35° N upper tropospheric ozone has a maximum in MAM with values almost as great as in JJA. In the lower troposphere ozone generally peaks in MAM, which is in agreement with surface observations, and with TOST, except in the Beijing region where in situ surface observations peak in JJA (Figure 3.1.2). Previous analysis of IASI observations has shown that the springtime maximum in the lower troposphere above East Asia has contributions from stratosphere-to-troposphere transport and from regional photochemical ozone production (Dufour et al., 2015). Ozone diminishes from MAM to JJA at low latitudes when the summer Asian monsoon advects ozone-depleted tropical air northwards (Dufour et al., 2010; Saffiedine et al., 2016), but the decrease is not as pronounced as the seasonal cycle observed at surface sites in the same region (Figure 3.1.2).

Focusing on the year 2010, Figure 3.3.2 illustrates the new capability of IASI+GOME2 to provide the average mole fraction of ozone in the LMT (up to 3 km asl). The seasonal patterns from this remotely sensed product match the patterns revealed by the surface observational network (Figure 3.1.2), with ozone peaking in spring above southeastern China, South Korea and Japan, but peaking in summer above the Beijing region. The excellent spatial coverage of this LMT product shows that the surface summertime ozone peak observed with in situ measurements in the Beijing region extends across North and East China, where the atmospheric boundary layer typically reaches depths of 2 km (Ding et al., 2008). In absolute values, LMT ozone mole fractions derived from IASI+GOME2 are 7 nmol mol^{-1} greater than surface observations, as expected due to the column integration of higher ozone values often found above the surface (Ding et al., 2008). The seasonal evolution of LMT ozone observed by

IASI+GOME2 and averaged over the region 30-43°N, 110-129°E (confined to the land areas of eastern China and South Korea in 2010) also agrees well with IAGOS aircraft profiles (Figure 4.2.3), within 1-5 nmol mol^{-1} in winter, spring and summer (Figure S3.3).

Figure 3.3.3 shows an illustration over Europe (for August 2009) of the new observations of ozone in the LMT (up to 3 km asl) derived from IASI+GOME2. Similar to the surface observations (Figure 3.1.2) high ozone is observed across southern Europe and the Mediterranean basin in the LMT. High ozone is also observed above this region in the mid-troposphere (e.g. Safieddine et al., 2014), in agreement with the TOST ozonesonde product (Figure 3.2.1). Downward transport from the stratosphere may contribute to the enhanced mid-tropospheric ozone over the North Atlantic Ocean (Wespes et al., 2012, Škerlak et al., 2014).

3.4 Global distribution of tropospheric column ozone

Figure 3.4.1 shows TOST yearly mean TCO for the period 2008-2012 (top left panel), with similar plots for all four seasons shown in Figure S3.4.1. The TOST data show that the strongest TCO values are found in the Northern Hemisphere subtropics, stretching from the Gulf of Mexico to eastern Africa, with the maximum value found above Egypt. The seasonal plots show that the Egyptian maximum is strongest in JJA and is part of a broad enhancement that covers much of North Africa, the eastern Mediterranean region and the Middle East. The ozone enhancement above North Africa is due to extrapolation of the TOST values by trajectories and there are no independent ozone profiles above this region to evaluate this regional maximum. However, a large region of enhanced ozone above North Africa and the Middle East was detected by the TES instrument in July 2005 (J.J. Liu et al., 2009). The ozone maximum above the eastern Mediterranean has also been observed by IAGOS aircraft which show this feature to be the strongest in the Northern Hemisphere mid-latitudes during JJA (Zbinden et al., 2013); further discussion of this feature can be found in Section 5.6. Other notable Northern Hemisphere enhancements are found above northern Mexico (peak in MAM and JJA), the southeastern USA (peak in JJA), India and SE Asia (peak in MAM), the mid-latitude North Pacific Ocean (peak in MAM), much of the North Atlantic Ocean (Equator to 50° N with a peak in JJA), and the Arabian Sea (peak in MAM). The peak above India in MAM has been independently confirmed by a previous study (Lal et al., 2014). In the Southern Hemisphere ozone peaks are lower than in the Northern Hemisphere by roughly 10-20% and are confined to the tropics and subtropics above the South Atlantic Ocean and the South Indian Ocean. Peak seasonal TCO values in the Southern Hemisphere are found above the South Indian Ocean from southern Africa to western Australia during SON, which is the Southern Hemisphere's peak season for biomass burning and stratosphere-to-troposphere transport (van der Werf et al., 2010; Fishman et al., 1991; J. Liu et al. 2016, 2017).

The remaining five panels in Figure 3.4.1 show annual average TCO from five different satellite products, all for the period 2010-2014, which is a more recent time period than the data currently available from the TOST product. Seasonal TCO maps for the satellite products are shown in Figures S3.4.2 – S3.4.6. As discussed in Section 5.7 each satellite product follows a different method for retrieving ozone, resulting in different sensitivities to ozone in the lower, mid- and upper troposphere. Therefore, specific TCO features, such as the minimum above Indonesia or the enhancement over East Asia, display varying magnitudes across the five products. In the following we highlight the features that are common to the five satellite remote-sensing products and compare them to the in situ observations interpolated by TOST:

1) During DJF the satellite products tend to show a weak enhancement across the northern subtropics with a relative maximum above the Arabian Sea and western and northern India. TOST shows an ozone maximum in the same general region but its peak values of 41-44 DU are 3-6 DU greater than the satellite products.
2) During MAM TOST shows an ozone enhancement across Mexico and the Caribbean (44-47 DU), with a weaker extension across the North Atlantic Ocean. This feature is also detected by the satellites, but it is shifted further north by 5-10 degrees. Some products have similar TCO values while others are 3-6 DU less. During this season TOST also sees a broad enhancement stretching from North Africa across southern Asia into the western North Pacific Ocean, with a peak over northern India and southern China (47-50 DU). The satellites see this same general feature but with more distinctive enhancements above northern India and eastern China. We note that satellite observations, especially in the thermal infrared, have issues retrieving accurate TCO values over deserts because the associated albedo and reflection are not well-represented in radiative transfer codes.
3) During JJA all five satellite products show an ozone maximum at 30°-40° N above Asia. This feature also extends westward across the Mediterranean and the North Atlantic Ocean towards the eastern USA, but the relative intensity of this extension varies between products. TOST also sees enhanced ozone from the eastern USA eastwards across Asia, but it shows distinctive maxima above the eastern USA and the region from North Africa to the Middle East. The TOST maximum over North Africa extends southwards into the tropics, a feature not seen by any of the satellite products.
4) In the southern hemisphere during JJA TOST sees enhanced ozone from Brazil across the South Atlantic Ocean and extending across southern Africa, Madagascar and the South Indian Ocean towards Australia. These same features are even stronger during SON with peak values of 41-44 DU above Madagascar. The satellite products show the same general pattern but with peak values 3-6 DU greater.

4. Global trends of tropospheric ozone

Several studies and reviews are available in the literature that describe the observational evidence for global increases of tropospheric ozone over the course of the 20th century. *TOAR-Observations* (Tarasick et al., 2017) provides a synthesis of these results and the reader is referred to this paper for a description of surface ozone observations prior to the 1970s. In this section we focus on ozone trends since the 1970s.

4.1 Surface ozone trends

Spatially, global surface ozone trends are highly variable depending on time period, region, elevation and proximity to fresh ozone precursor emissions. We first examine long-term ozone trends at mountaintop sites and focus on nighttime (20:00-8:00 local time) data when the stable atmosphere isolates the mountaintop from the air masses below, yielding ozone observations that are largely representative of the lower free troposphere. There are eight mountaintop sites in the Northern Hemisphere that can be examined for long-term nighttime ozone trends indicative of the lower free troposphere (Table 4.1 and Figure 4.1.2). Long term trends at these important sites have been reported several times in recent years (Parrish et al., 2012, 2013, 2014; Oltmans et al., 2013; Cuevas et al., 2013; Gratz et al., 2014; Xu et al., 2016), but here we provide an update through 2015. The longest record is Mauna Loa (43 years) and the shortest is Mt. Bachelor Observatory in the northwestern USA (12 years).

We begin with observations recorded continuously since 1973 from Mauna Loa Observatory (MLO) on the Big Island of Hawaii in the central North Pacific Ocean (19.5°N, 155.6°W, 3397 m). Due to its location at the northern edge of the tropics, MLO is impacted by mid-latitude air masses which originate to the north and west and tropical air masses that originate to the south and east (Harris and Kahl, 1990; Oltmans et al., 2006). Ozone is typically greater in the mid-latitude air masses and the long term ozone trend at MLO is affected by the relative frequency of air mass transport from high and low latitudes in response to climate variability driven by ENSO and the Pacific Decadal Oscillation (Lin et al., 2014). Over shorter time periods the influence of climate variability introduces greater uncertainty on the trend, for example over 1974-2016 the ozone trend at Mauna Loa is 0.15 ± 0.06 nmol mol^{-1} yr^{-1} (p=0.00) while over the most recent 17 years (2000-2016) the trend is 0.17 ± 0.22 nmol mol^{-1} yr^{-1} (p=0.13) (p indicates the p-value, which is the probability under a specified statistical model that a statistical summary of the data would be equal to or more extreme than its observed value (Wasserstein and Lazar, 2016)) (Figure 4.1.1a).

To reduce the noise in the trend due to climate variability we apply a new method for examining ozone trends at Mauna Loa (Ziemke and Cooper, 2017). Figure 4.1.1 shows the long-term (1974-2016) ozone trend at Mauna Loa based on monthly nighttime median values using all available data (0.15 ± 0.06 nmol mol^{-1} yr^{-1}; p=0.00). The figure also shows the ozone trend calculated for the dry and moist air

masses at the site, classified according to co-located dewpoint temperature observations. The dry air masses, with greater ozone values, tend to originate to the north and west and/or from higher altitudes (implying long-range transport) and have a trend of 0.23 ± 0.06 nmol mol^{-1} yr^{-1} (p=0.00), double the trend of the moist air masses that tend to originate to the south and east and/or from lower altitudes (0.11 ± 0.06 nmol mol^{-1} yr^{-1}; p=0.00). Therefore, dry air masses that originate to the north and west make a greater contribution to the overall positive trend than the moist air masses. For the recent period of 2000-2016 ozone increased in dry air masses at the rate of 0.42 ± 0.22 nmol mol^{-1} yr^{-1} (p=0.00), whereas the moist air masses do not show a statistically significant trend. Therefore, while the overall trend at Mauna Loa for the recent period of 2000-2016 does not exhibit a statistically significant trend, the dry air masses impacting the site have experienced a very strong trend with an increase of 6.7 ± 3.5 nmol mol^{-1}, or 14% since 2000. The implication is that the ozone increase in the dry air masses is most likely being driven by the increasing ozone observed across south and east Asia, as described below.

The two sites closest to Mauna Loa (seasonal ozone trends in the range of 0.1-0.2 nmol mol^{-1} yr^{-1}) are both at mid-latitudes but on either side of the North Pacific Ocean. Mt. Waliguan (3810 m), upwind of heavily populated eastern China shows seasonal ozone increases in the range of 0.1-0.3 nmol mol^{-1} yr^{-1} since 1994, in agreement with a recent in-depth analysis of this important baseline site (Xu et al., 2016). Mt. Bachelor (2763 m) has much stronger trends in the range of 0.6-1.1 nmol mol^{-1} yr^{-1} (for spring, summer and autumn), but over a much shorter period beginning in 2004 (Fischer et al., 2011; Gratz et al., 2014). In contrast to Mauna Loa the trends in moist and dry air masses at Mt Bachelor are similar (Figure S4.1.1).

The only other remote site at low latitudes is Izaña (2367 m) in the eastern subtropical North Atlantic Ocean (Cuevas et al., 2013) with seasonal ozone trends since 1987 in the range of 0.1-0.2 nmol mol^{-1} yr^{-1}. Over the full length of the record only the dry air masses have a significant positive trend, indicating that the observed ozone increase across all air masses is driven by air of mid-latitude origin (Figure S4.1.2). But since 2000 neither air mass type has a significant trend. Note that this station is influenced by significant air-mass variability on seasonal and inter-annual time scales (Rodríguez et al., 2004). This is particularly true in summertime, when transport variability affects the transport of the Saharan Air Layer (SAL) across the North Atlantic Ocean, allowing for the possibility of ozone interactions with mineral dust (Andrey et al., 2014). During winter-spring ozone can also be influenced by transport variability associated with the North Atlantic Oscillation (Cuevas et al., 2013).

Three sites are located within large industrialized regions. Whiteface Mountain Summit (1483 m) in upstate New York (Schwab et al., 2016) shows a strong decrease of ozone in summer, in agreement with many other rural monitoring sites in the northeastern USA (as shown below). In the Alps, Jungfraujoch (3580 m) (Cui et al., 2011) shows significant increases in winter and autumn, while

Zugspitze (2962 m) (Logan et al., 2012; Oltmans et al., 2013; Parrish et al., 2012) has significant increases in all seasons except summer. Attribution of ozone trends at these high Alpine sites is complicated by changing stratospheric ozone contributions (Trickl et al., 2010; 2014, and references therein). The only high latitude site is Summit, Greenland (3212 m) with no significant trend except for a strong decrease in spring.

Since 2000 significant ozone increases at the remote sites are limited to spring at Mauna Loa, spring and autumn at Mt. Waliguan and spring and autumn at Mt. Bachelor (Table 4.1 and Figure S.4.1.3). Ozone at Izaña has been flat in all four seasons. In the northeastern USA ozone has decreased strongly in summer at Whiteface Mountain Summit. Significant decreases have occurred at Jungfraujoch and Zugspitze in spring for the period 2000-2015, with weaker and insignificant decreases in most other seasons, in general agreement with Mt Cimone in northern Italy, which has shown a levelling off or slight decrease in ozone since 2000 (Cristofanelli et al., 2015).

Beyond these mountaintop sites our knowledge of lower tropospheric ozone trends from surface observations comes from the many surface ozone monitoring networks and research sites around the world. Because these sites are not located at exceptionally high elevations compared to their immediate surroundings they cannot provide information on the lower free troposphere at night. Therefore we examine daytime ozone values at non-urban sites (as defined in Section 2.2) to focus on the well-mixed atmospheric boundary layer and to avoid ozone depletion events that occur at night, especially in urban areas with fresh NO emissions. The focus on daytime non-urban sites also increases the likelihood that the observations will be regionally representative, which allows for more straightforward comparison to coarse resolution global atmospheric chemistry models.

Figure 4.1.3 shows 2000-2014 daytime ozone trends at all available non-urban sites during DJF and JJA. The vector direction indicates the ozone rate of change and the shading indicates the significance of the trend using the p-value on the linear trend. Vectors with p-values less than 0.05 are statistically significant, while vectors with p-values in the range of 0.05-0.10 give an indication of a trend. Vectors with p-values in the range of 0.10-0.34 provide a weak indication of change, and p-values greater than 0.34 indicate weak or no change. The vectors with p-values in the range of 0.05-0.34 are very useful for understanding regional trends as they typically follow the same pattern as the statistically significant vectors (Chang et al., 2017). Ozone changes across North America in DJF are largely positive while they are mixed in Europe and East Asia. The few sites available in the Southern Hemisphere don't reveal any obvious pattern. During JJA sites in Europe and North America indicate broad regional decreases while trends in East Asia are mixed. In the Southern Hemisphere results are mixed, but with positive values exceeding negative values by more than a factor of 2:1. Figure 4.1.4 provides additional information by focusing on North America, Europe and East Asia for all four seasons.

A separate analysis applied a sophisticated statistical model to the TOAR database to quantify regional ozone trends (Chang et al., 2017). For a given region, such as eastern North America, the generalized additive mixed model (GAMM) can determine the dependence of the mean ozone level on space and time by incorporating explanatory variables from the TOAR database: latitude, longitude, elevation, population density, NO_x emissions and OMI tropospheric column NO_2. As shown in Figure S.4.1.4, the analysis using all available sites (urban and rural) finds overall decreasing trends of summertime (April-September) daytime average ozone across eastern North America and Europe, but increasing ozone over East Asia. The rate of change for rural sites in these three regions is -0.42, -0.17 and +0.23 nmol mol^{-1} yr^{-1}, respectively. A regional increase of +0.20 nmol mol^{-1} yr^{-1} was also found for southeast Asia, using all available sites. Further details on this methodology are described by Chang et al. (2017).

Because East Asia is a major ozone precursor emission region we also highlight ozone trends from two recent studies at sites that were not available for the main TOAR analysis. Mt. Tai at 1.5 km above the North China Plain is ideally situated to monitor regional scale ozone levels. Summertime data from 2003-2015 reveal very strong significant positive ozone trends during daytime and nighttime conditions in the range of 1-2 nmol mol^{-1} yr^{-1} (Sun et al., 2016). Shangdianzi is a low elevation, rural Global Atmospheric Watch station northeast of Beijing. Observations from 2003-2014 show a strong and significant increase of maximum daily 8-hour average ozone of approximately 1.1 nmol mol^{-1} yr^{-1} (Ma et al., 2016).

4.2 Free tropospheric ozone trends from in situ and ground-based instruments

4.2.1 In situ observations

Exploratory and sporadic observations of free tropospheric ozone began in the first half of the 20th century using a variety of methods from aircraft and balloon platforms as described in *TOAR-Observations*. Routine observations using ozonesondes became established at a limited number of sites in the 1960s and 1970s, with additional sites established around the world in the 1980s and 1990s (Oltmans et al., 2013; *TOAR-Observations*). Ozonesonde measurement techniques have changed somewhat, becoming much more consistent in the 1980s with the improvements in ozonesonde preparation and the widespread adoption of ECC sondes (*TOAR-Observations*). In addition, routine profiles from commercial aircraft became available from the IAGOS programs in 1994, while remotely sensed observations from ground-based lidars also became available in the 1990s.

Cooper et al. (2014) conducted a literature review of free tropospheric ozone trends based on data beginning in the 1970s or 1980s and extending through the early 2000s. Their summary is as follows: "Significant positive trends since 1971 have been observed using ozonesondes above Western Europe, Japan and coastal Antarctica (rates of increase range from 1–3 ppbv $decade^{-1}$), but not at all levels

(Oltmans et al., 2013). In addition, aircraft have measured significant upper tropospheric trends in one or more seasons above the northeastern USA, the North Atlantic Ocean, Europe, the Middle East, northern India, southern China and Japan (Schnadt Poberaj et al., 2009). Insignificant free tropospheric trends were found above the Mid-Atlantic USA (1971–2010) (Oltmans et al., 2013) and in the upper troposphere above the western USA (1975–2001) (Schnadt Poberaj et al., 2009). While the available data in the free troposphere are limited, a notable finding from the existing literature is that no site or region has shown a significant negative ozone trend since the 1970s."

Focusing on more recent years, ozonesonde analyses have found a pattern of increases in the earlier part of long-term records over most of the northern hemisphere, but a flattening or even a decline in recent decades (Oltmans et al., 2013, Logan et al., 2012). A recent analysis of Canadian trends, using reevaluated data, finds little change over the 50-year record (Tarasick et al., 2016). Increases until about 2005 were found in southern hemisphere midlatitudes, and little change over the entire record elsewhere (Oltmans et al., 2013). An update to the Lauder, New Zealand ozonesonde record (1987-2014) found increasing ozone at Lauder below 6 km, but decreasing ozone in the UT (Zeng et al., 2017).

In this section we focus on free-tropospheric ozone trends since the mid-1990s due to the widespread availability of ozonesonde and commercial aircraft observations in the 1990s, and the improved consistency among ozonesonde profiles. The TOST product is a convenient near-global composite of tropospheric ozone based on profiles from dozens of ozonesonde sites around the world. For straightforward comparison to tropospheric ozone burden estimates from satellite products, ozone trends from TOST are shown in Figure 4.3.2 in units of DU yr^{-1} in several latitude bands. TOST shows significant ozone increases from 1998-2012 in latitude bands from 30° S to 60° N, but not in the band 30° – 60° S. Regional trends of tropospheric column ozone, as quantified by TOST, will be discussed in Section 4.3 where they are compared to five different satellite products.

As described in Section 2.3.3, the IAGOS program has provided accurate and consistent ozone observations from a fleet of instrumented commercial aircraft since 1994. A new analysis of ozone trends in seven frequently sampled regions of the Northern Hemisphere upper troposphere indicates a general increase of ozone (Cohen et al., 2017). Annual mean upper tropospheric observations from 1995-2013 show a significant increase of ozone across northern mid-latitudes (Eastern US, Europe, western Mediterranean, Middle East, Siberia, northeastern Asia) in the range of 0.24 – 0. 45 nmol mol^{-1} (Figure S4.2.1). No significant trend was found above the North Atlantic Ocean. There is no seasonal dependence, but the overall trend is most likely driven by the lowest values of the distribution (5^{th} percentile), which is increasing significantly in all seven study regions, in the range of 0.30 – 0.57 nmol mol^{-1}.

Regions where IAGOS ozone profiles are sufficiently frequent for trend analysis from the surface to 200 hPa include Frankfurt, Germany, the eastern USA, south/central India, Southeast Asia and northeastern China/Korea. As reported previously (Petetin et al., 2016b), annual trends in the troposphere above Frankfurt remain insignificant over the period 1994-2012. However, seasonally, significant positive trends of about +0.3 nmol mol^{-1} yr^{-1} are found at all levels in winter. Using one more year of data (2013) Figure 4.2.1 shows the seasonal changes in ozone from the early part of the IAGOS record (1994-1999) until the most recently available 5-year period (2009-2013), based on a t-test and a 95% confidence interval. Tropospheric column ozone (surface – 300 hPa) increased by 11% in winter, 1% in spring and 5% in autumn. Ozone decreased by 2% in summer driven by decreases in the lower troposphere. This approach and that of *Petetin et al*. (2016b) agree that the strongest ozone increases above Frankfurt occur in winter.

On the other side of the North Atlantic Ocean a composite of IAGOS profiles above several cities in the northeastern USA (Figure 4.2.2) shows that ozone increased from 1994-2004 to the more recent period of 2005-2013 during winter (7%), spring (7%) and autumn (3%). Summer showed no net change despite a decrease of high ozone events in the lower troposphere.

IAGOS reveals stronger ozone increases above Asia from 1994-2004 to 2005-2014 in those regions where sufficient profiles are available (Figure 4.2.3), as first reported by Zhang et al. (2016). Above northeast China/Korea ozone has increased most strongly in the boundary layer with peak tropospheric column increases (surface – 200 hPa) of 15% in summer. Increases above south/central India are greater with a peak column increase of 31% in autumn. The strongest increases are found above southeast Asia where summertime (JJA) tropospheric column ozone increased by 70%.

4.2.2 Ground-based instruments

Ozone trends in the atmospheric boundary layer and free troposphere can also be detected from ground-based ozone lidars, with long-term records available at Observatoire de Haute Provence (OHP) in southeastern France (Gaudel et al., 2015) and Table Mountain in southern California (Granados-Muñoz et al., 2016). Tropospheric column ozone has changed little above OHP from 1994-2004 to 2005-2013 as determined from a combination of lidar and ozonesonde profiles (Figure 4.2.4). TCO increased by 3% in winter, driven by an increase in the upper troposphere, but during the other seasons ozone decreased by 2-3%, largely driven by ozone decreases in the lower troposphere. Changes in ozone above Table Mountain are more variable with a 9% decrease in winter and a 7% increase in summer (Figure 4.2.5). Ozone also decreased by 5% in autumn, driven by the lower troposphere. Spring shows no net change due to decreases in the lower troposphere being offset by increases in the upper troposphere. This lack of change is in contrast to a springtime increase of ozone observed by a composite of observations across western North America for the period 1995-2014 (Lin et al. 2015). Differences could be due to different

sampling strategies, with Table Mountain representing one location during March-April-May (2000-2015) while the 20-year composite covers most of western North America during April-May (1995-2014). Ozone time series in this region are strongly affected by shifts in transport patterns associated with climate variability, which affects the ozone trend, especially over shorter time periods (Lin et al., 2015).

FTIR and Umkehr instruments provide long-term tropospheric column ozone (TCO) observations above 14 stations around the world (Figure 4.2.6), with FTIR extending from the surface to 8 or 12 km, and Umkehr extending from the surface to 250 hPa. Because the two methods report different columns a direct comparison between collocated instruments is challenging. However, comparison of FTIR to ozonesondes and Umkehr to ozonesondes at Lauder, New Zealand shows that both instruments are similar to the sondes for the period 2001-2016 (Figure S4.2.3).

The three available FTIR instruments in the Arctic indicate weak and insignificant decreases since 1996 while the sole Arctic Umkehr instrument finds a significant increase. At northern mid-latitudes, three Umkehr and one FTIR instrument detect no significant trends. In the northern subtropics, the FTIR instrument at Izaña (*Schneider et al*., 2005) indicates an increase although the trend is not statistically significant, while in the tropics, the Umkehr instrument at Mauna Loa records a significant increase from 1995 until 2016. At southern mid-latitudes the Umkehr and FTIR instruments at Lauder, New Zealand show increasing ozone although the trends are not statistically significant. The FTIR instrument at Wollongong, Australia indicates a weak ozone decrease while the Umkehr at Perth, Australia shows an increase. Finally, the FTIR at Arrival Heights, Antarctica shows no change. In summary, these broadly scattered instruments indicate no consistent picture of ozone changes around the world. Notably, none of these stations are in Asia where IAGOS aircraft profiles indicate strong ozone increases since the mid-1990s. The station closest to Asia is Mauna Loa which shows an increase of TCO, in agreement with the lower free-tropospheric ozone increases observed at Mauna Loa Observatory. Further ground-based instrument intercomparisons are possible at specific locations such as Mauna Loa and Boulder, Colorado, USA. Sites with co-located ground-based instruments could also be used for comparison to satellite data but these studies are beyond the scope of this paper.

4.3 The global view from satellites

The Tropospheric Ozone Residual (TOR) was the first satellite product to quantify tropospheric ozone, providing tropospheric column ozone values (1° x 1.25° resolution) across much of the globe (50° S – 50° N) from 1979 through 2005 (Fishman et al., 2003). The product was derived by subtracting stratospheric column ozone measured by polar orbiting Solar Backscattered Ultraviolet (SBUV) instruments from coincident total ozone measured by Total Ozone Mapping Spectrometer (TOMS) instruments. The product was never fully evaluated to determine its accuracy for calculating trends (J. Fishman, personal communication) and, therefore, we will not attempt to draw conclusions on ozone

trends over the TOR instrument record. However, we can use the product to gain insight regarding the relative tropospheric ozone maxima at the beginning of the satellite record. Figure 4.3.1 shows TOR across the globe during June-July-August averaged over 1979-1983. In those days there were four relative ozone maxima in the Northern Hemisphere: the North American west coast, eastern USA, northern India and eastern China. In contrast, the OMI/MLS tropospheric column ozone product shows only two present-day maxima: northeastern China and the Mediterranean. The two products are derived similarly, but because they are not intercalibrated we cannot say if the present-day ozone maxima stand out because of increasing ozone in those regions, or if the intensity of ozone production in the other regions declined.

To understand how the tropospheric ozone burden has changed since the mid-1990s we now compare tropospheric column ozone by latitude band from five different satellite products, plus the TOST composite ozonesonde product (Figure 4.3.2). Reported trends are based on linear regression. As described above, TOST shows significant ozone increases from 1998-2012 in latitude bands from 30° S to 60° N, with strongest increases in the tropics and no increase in southern mid-latitudes (30° – 60° S). The OMI/MLS product shows significant increases from 2005-2016 at all latitude bands between 60° S - 60° N with strongest increases in the northern tropics and weakest trends in southern mid-latitudes (30° – 60° S). The GOME/OMI-SAO product extends from 1996 to 2015 and shows significant increases in all latitude bands with the strongest trend in the northern tropics. The OMI-RAL product shows an increase from 2005 to 2015 between 60° S - 60° N, with the strongest increases in the tropics. In contrast, the IASI-FORLI product shows a small decrease of ozone during 2008-2016 from 60° S - 60° N, with the strongest decrease at southern mid-latitudes. The IASI-SOFRID product also indicates a decrease of ozone over the period 2008-2016 from 60° S - 60° N, with the strongest decrease also occurring in the Southern Hemisphere, but in the tropics rather than mid-latitudes.

To understand how products vary in their detection of regional trends, Figure 4.3.3 compares annual trends at 5°x5° resolution across the globe between TOST and the five satellite products (Figures S4.3.1 - S4.3.6 provide seasonal comparisons). TOST, covering 2003-2012 shows strongest ozone increases above Brazil, northeastern Africa, the tropical Indian Ocean, East Asia and the western Pacific Ocean. Notable regions of ozone decreases are found over southern Africa and the Antarctic Peninsula. The satellite products span slightly different periods than TOST which may partially explain why they differ from TOST, yet the differences between satellite products can be as great as their differences from TOST. Section 5.7 discusses the various satellite ozone retrieval methods which account for some of the differences between the satellite-detected ozone trends. Due to the difficulties in comparing ozone trends between satellite products with different measurement techniques and retrieval methods, Figure 4.3.4 provides a simple assessment of the regions of the world where TOST and the five satellite products in

Figure 4.3.3 agree in their depiction of statistically significant annual ozone trends. We note that while each product has been derived differently, the three products using OMI radiances are not fully independent of one another, nor are the two IASI products. The greatest agreement in terms of positive trends is found in the tropics with the region stretching from South America eastwards to the western Pacific Ocean containing many grid cells with at least 4 products with positive trends. Regions with at least five products in agreement are Southeast Asia, equatorial Brazil, central northern Africa, the tropical South Indian Ocean and northern Australia. Southeast Asia is the most extensive region with at least five products in agreement, including five grid cells showing agreement between all 6 products.

Figure 4.3.4 also shows the agreement between products in terms of statistically significant negative trends, which is weaker than the agreement for positive trends. In the tropical region from South America eastward to Indonesia most grid cells show no decrease and at most only one product per grid cell shows a decrease. No product shows a decrease above Southeast Asia or eastern China south of 40° N. There are only two regions where three or four products agree on significant decreases, located in the Southern Hemisphere mid-latitudes above New Zealand and South America.

There are two other satellite products reported in the literature that provide information on TCO from the past decade, but are not part of the comparison described above. The first is derived from the now expired SCIAMACHY instrument which provided trend estimates for 70° S - 70° N from 2003 to 2011 (Ebojie et al., 2016). Overall the product found statistically insignificant ozone increases between 50° S and 30° N and insignificant decreases between 30° N - 70° N. On a regional basis the strongest significant ozone increase was a broad region above SE Asia, similar to the region of significant trends shown in Figure 4.3.4. The second product is a 20-year (1995-2015) composite of TCO above the tropics from the GOME, SCIAMACHY, OMI, GOME-2A and GOME-2B instruments (Heue et al., 2016). The 20-year tropical trend is 0.07 ± 0.01 DU yr^{-1}, less than half the rate of four products in Figure 4.3.2 that show increasing tropical ozone (TOST, OMI/MLS, GOME/OMI-SAO and OMI-RAL). Regionally the strongest trends were found in a band from central northern Africa eastwards to SE Asia, and in a band stretching from northern Brazil eastwards to central Africa. In the near future, additional long-term (20-years or more) composites of tropical TCO using multiple satellite instruments will be available for tropical ozone trend quantification (Leventidou et al., 2016; J. Ziemke, personal communication)

5. Discussion and Conclusions

Sections 3 and 4 have provided an up-to-date overview of tropospheric ozone's present-day distribution and trends. Many factors, both anthropogenic and natural, influence these ozone values (*Monks et al*., 2015; *Neu et al.*, 2014), and a consideration of all of these processes is beyond the scope of this paper. However, *TOAR-Ozone Budget* (*Archibald et al.* 2017) provides a new review of these processes and *TOAR-Model Performance* (*Young et al*., 2017) discusses the present-day capabilities of

global atmospheric chemistry models to simulate tropospheric ozone. To synthesize the findings from Sections 3 and 4 we focus our discussion on five regions that have experienced notable ozone changes since the 1990s at the surface and in the free troposphere: mid-latitude North America, Western Europe, East Asia, the Northern Hemisphere tropics (0°-30° N) and the Southern Hemisphere tropics (0°-30° S). We also highlight the region across the Mediterranean and Middle East, not because we have firm evidence that ozone in this region is changing, but because it contains a strong summertime tropospheric column ozone maximum that has not been fully explored or monitored with in situ observations, especially across the Middle East. The section concludes with an assessment of the tropospheric ozone burden, followed by information for accessing the ozone datasets discussed by *TOAR-Climate*.

In the discussion that follows, the peer-reviewed literature is relied upon to briefly place the observed ozone trends in the context of current understanding of the processes that control ozone in each region. As ozone trends are strongly impacted by changes in ozone precursor emissions we summarize the latest findings on global emissions of the key ozone precursor, nitrogen oxides. The Community Emissions Database System (CEDS) global bottom-up emission inventory (*Hoesly et al*., 2017) shows an increase in global anthropogenic NO_x emissions of roughly 17% from 2000 to 2010 with nearly constant emissions from 2010-2014 (*Archibald et al*., 2017). Over this period, emissions decreased in North America and western Europe and increased in Asia. The net result is a small decrease of about 5% in the 30°-90° N latitude band, and large increases of 60% in the NH tropics (0°-30° N) and a doubling of emissions in the SH tropics, with SH tropical emissions being only a quarter of NH tropical emissions. A recent top-down emission inventory using OMI-detected tropospheric column NO_2 indicates no net change in global NO_2 emissions from 2005 to 2014, but with decreases of NO_x emissions in North America and Western Europe and increases in India and China, although Chinese emissions have decreased since 2011 (*Miyazaki et al*., 2017).

5.1 Mid-latitude North America

Much has been written in recent years regarding the decrease of extreme surface ozone episodes across mid-latitude North America in response to decreasing domestic ozone precursor emissions (Lefohn et al., 2010; Cooper et al., 2012; Simon et al., 2015) as well as the impact of increasing Asian emissions offsetting some of the domestic ozone reductions (Jacob et al., 1999; Brown-Steiner and Hess, 2011; Huang et al., 2013; Strode et al., 2015; Verstraeten et al., 2015; Lin et al., 2017). Surface ozone reductions are clearly seen for daytime average ozone for June-July-August over the period 2000-2014 (Figure 4.1.4), however there is no clear mid-latitude decrease in spring or autumn, and winter shows a general increase. Free tropospheric ozone trends above North America are difficult to quantify due to a sparse sampling network with infrequent observations. The longest continuous records are from ozonesondes above Canada (Tarasick et al., 2016) and Wallops Island, Virginia (Oltmans et al., 2013)

which show no overall change since the 1970s/1980s. Focusing on April-May an analysis of all available ozone observations from multiple platforms above western North America found a significant increase of free tropospheric ozone (~0.3 nmol mol^{-1} yr^{-1}) for 1995-2014 (Lin et al., 2015). In *TOAR-Climate* analysis of high-frequency 2000-2015 lidar observations above Table Mountain in southern California shows increases in summer, no change in spring and decreases in winter and autumn. Commercial aircraft observations above the northeast USA show ozone has increased since the 1990s during winter, spring and autumn with no change during summer. Focusing on the upper troposphere, commercial aircraft have also observed significant positive annual trends above the eastern US and the North Atlantic Ocean (Cohen et al., 2017). In terms of tropospheric column ozone, the ozonesonde and satellite products summarized in Figure 4.3.4 indicate no clear trend. In summary, while clear ozone changes can be demonstrated for particular regions and seasons it is not possible to define an overall trend for mid-latitude North America.

5.2 Europe

As with mid-latitude North America, extensive air quality monitoring and analysis have shown that reductions in ozone precursor emissions have reduced extreme ozone levels across much of Europe at both rural and urban sites (Derwent et al., 2010; Simpson et al., 2014; EEA, 2016). Focusing on just the annual mean of the maximum daily average 8-h ozone values, rural background sites were generally characterized by decreasing ozone while heavily urbanized (traffic) sites showed ozone increases over 2000-2014 (EEA, 2016). The TOAR analysis found similar results, but seasonal trends of daytime average ozone revealed that non-urban sites only showed broad decreases across Europe during summer months while increasing and decreasing trends varied widely across the region during other seasons (Figure 4.1.4). In the free troposphere ozonesonde and lidar observations from southern France show essentially no change from 1994 to 2013. IAGOS commercial aircraft observations show increases above Frankfurt in winter and autumn with little or no change in spring and summer, with broad upper tropospheric ozone increases across Europe on an annual basis from 1995 to 2013. In terms of tropospheric column ozone there is no consistent trend among the ozonesonde and satellite products, and FTIR and Umkehr observations show no change between 1995 and 2016 in France and Switzerland. Similar to mid-latitude North America, ozone changes vary across Europe both spatially and seasonally, precluding any generalized statement regarding ozone trends across this region.

5.3 East Asia

In this section East Asia refers to mainland China, Hong Kong, Taiwan, South Korea and Japan; the region of Southeast Asia (i.e. Vietnam, Malaysia and Thailand) will be discussed in Section 5.4 which focuses on the Northern Hemisphere tropics. After decades of emissions increases (Zhao et al, 2013) several recent studies have documented the rapid reduction of NO_x emissions in some regions of China

since about 2011, as observed by satellites (Duncan et al., 2016; Krotkov et al., 2016; Liu et al., 2016; Miyazaki et al., 2017; Van der A et al. 2017), but from the limited in situ observations there is no evidence of a recent decrease of surface ozone in China, possibly due to ozone production being VOC limited in this region (Ma et al., 2016; Sun et al., 2016; Li et al., 2017; Wang et al., 2017). In the case of Hong Kong, expected ozone decreases due to local ozone precursor emissions reductions have been countered by transport of increasing ozone from southern and eastern China over the period 2002-2013 (Xue et al., 2014). As described in Section 4.1 the three long-term ozone monitoring sites available on mainland China show ozone increases since the 1990s and early 2000s. As shown in Figure 4.1.4 there are 3 non-urban sites in Hong Kong which show weak or no trends in all four seasons during 2000-2014, however analysis of daytime average ozone at these sites based on yearly data shows ozone increases at two out of three sites. Trends across Taiwan, South Korea and Japan vary by season but positive trends outweigh negative trends, and during the warm months of April-September the overall spatially weighted trend at rural sites is positive (Chang et al., 2017). Trends in the free troposphere are generally positive since the 1970s and 1980s through 2010, as recorded by Japanese ozonesondes from Tsukuba and Sapporo (Oltmans et al., 2013), and positive since the 1990s as recorded by IAGOS commercial aircraft above eastern China and South Korea (Ding et al., 2008; see also Figure 4.2.3), as well as in the upper troposphere across a broad region of East Asia (Cohen et al., 2017). In terms of tropospheric column ozone, the TOST ozonesonde product shows widespread ozone increases across east Asia between 2003 and 2012, however the 5 satellite products in Figure 4.3.3 do not indicate a consistent trend; at most 4 of the 6 products (TOST, OMI/MLS, OMI-RAL, OMI-SOA) in Figure 4.3.3 indicate positive trends over portions of south and east China (Figure 4.3.4), while only one product (IASI-FORLI) indicates negative trends, confined to Japan and portions of northern China. In contrast to mid-latitude North America and western Europe, the majority of observational evidence for East Asia points towards a general increase of ozone since the 1990s or the year 2000, however further research is required to assess the impact of recent ozone precursor reductions on long-term ozone trends.

5.4 Northern Hemisphere tropics

Outside of the southern United States there are very few surface ozone monitors in the Northern Hemisphere tropics (here defined as 0°-30° N), and these sites gives no indication of a clear surface trend across this latitude band in either summer or winter (Figure 4.1.3). In the free troposphere IAGOS commercial aircraft show strong ozone increases above India and Southeast Asia from the period 1994-2004 to 2005-2014 (Figure 4.2.3). Increases in the 0-12 km column reached as high as 70% above Southeast Asia during summer, however this apparently large increase should be kept in perspective because the initial ozone values during 1994-2004 were very low compared to other regions of the world, especially mid-latitudes. The TOST ozonesonde product shows widespread TCO increases from the

Arabian Sea eastwards to the dateline (Figure 4.3.3). Ozone increases in this region are also detected by many of the satellite products, especially over Southeast Asia (Figure 4.3.4), with five grid cells above this region showing a significant positive ozone trend by all six products in Figure 4.3.3. For the IASI-FORLI product the increase is tied to climate variability over its short record (2008-2016) associated with the well-known ozone fluctuations in this region associated with ENSO (Ziemke et al., 2015; Wespes et al., 2017). However, for the products with longer records (OMI-RAL and OMI/MLS since 2005, TOST since 1998, and GOME/OMI since 1996) the increase persists over several ENSO cycles.

5.5 Southern Hemisphere tropics

Long-term surface ozone monitoring in the Southern Hemisphere tropics is even more limited than in the NH tropics, with only American Samoa in the western South Pacific Ocean showing a significant increase in DJF and JJA (Figure 4.1.3). The TOST ozonesonde product across this region largely reflects observations from NASA's Southern Hemisphere ADditional OZonesondes (SHADOZ) network (Thompson et al., 2007; Witte et al., 2017) showing significant ozone increases of TCO since 2003 above the Amazon and from Madagascar eastwards to the dateline. Most of the satellite products also show ozone increases across these same general regions but with a high degree of spatial variability. Figure 4.3.4 shows that 4-5 out of the six ozonesonde and satellite products indicate increasing ozone above the Amazon, and much of the area from southern Africa eastwards to the dateline. TCO decreases are indicated by 1-2 products above South Africa and the eastern South Pacific. The evidence seems to indicate a general increase of ozone across much of the Southern Hemisphere tropics through 2016. Attribution analysis has not yet been conducted to investigate these recent trends but previous observational and modelling work focusing on this region provides insight into the dominant ozone sources. Enhanced ozone and ozone precursors above the tropical South Atlantic Ocean as well as adjoining regions of South America and Africa have been observed and studied for the past 30 years (Logan et al., 1985,1986; Fishman et al., 1991; Jacob et al., 1996; Moxim et al., 2000; Thompson et al., 2000, 2007; Swap et al., 2003; Sauvage et al., 2005, 2007). Very recent work has used an atmospheric chemistry model to quantify the contribution of the stratosphere, biomass burning and anthropogenic emissions on the SH ozone enhancements (J. Liu et al., 2016, 2017). Briefly, the enhancement centered on 30° S stretching from Africa to Australia (most prominent in SH spring (SON), see Figures S3.4.1 – S3.4.6) is primarily due to ozone in the upper troposphere originating from stratosphere-troposphere exchange along the subtropical jet. The stratosphere also makes strong contributions to upper tropospheric ozone across the South Atlantic Ocean from 20°-30° S, but stratospheric influence is much less north of 20° S (i.e. beyond the subtropical jet). Beyond these regions of stratospheric influence, the SH ozone enhancement is produced from ozone precursors of anthropogenic, biomass burning and lightning origins with relative contributions that vary seasonally. In the past, quantification of ozone changes in this region

has been limited by spatially and temporally sparse in situ observations. However, the IAGOS program now has increased availability of flights from the NH to South America and Australia. These observations, when combined with SHADOZ ozonesonde profiles, may provide a sufficient density of observations to allow for robust trend evaluation of both ozone and ozone precursors.

5.6 Mediterranean and Middle East summertime ozone maximum

Some of the world's greatest summertime TCO values are found above the Mediterranean basin (Zbinden et al., 2013; see also Figure 4.3.1 and Figures S3.4.1 - S3.4.6), especially over the eastern half, with an extension towards the Persian Gulf. A more detailed view of satellite-detected ozone across the Mediterranean is also available from the TES and GOME-2 instruments (J. J. Liu et al., 2009; Worden et al., 2009; Richards et al., 2013) and the IASI instrument (Safieddine et al., 2014 and Doche et al., 2014). Aircraft profiles above the eastern Mediterranean show that summertime ozone has typical values of 36, 51 and 67 nmol mol^{-1} (10^{th}, 50^{th} and 90^{th} percentiles, respectively) at the surface, increasing to 40, 65 and 110 nmol mol^{-1} (respectively) at 300 hPa (Kalabokas et al., 2007). Similarly, lidar/ECC profiles at OHP on the western side of the Mediterranean summer maximum show typical values of 35, 50, 70 nmol mol^{-1} (5^{th}, 50^{th}, 95^{th}) at the surface, increasing to 55, 80, 95 nmol mol^{-1} (Figure 4.2.4) at 300 hPa. Previous research has characterized the summertime Mediterranean region (Lelieveld et al., 2002), as well as the adjoining Middle East (Li et al., 2001), as a crossroads where ozone from many different sources can accumulate. Much of this understanding was derived from the August, 2001 Mediterranean INtensive Oxidant Study (MINOS), a time when northern hemisphere ozone precursor emissions were much different from today (Archibald et al., 2017). Scientists determined that Asia, particularly India and Southeast Asia, was a source for upper tropospheric pollution above the eastern Mediterranean (Scheeren et al., 2003). This pollution was linked to the Asian summer monsoon followed by transport across northern Africa and a southerly approach to the Mediterranean. In spite of high pollution levels in the Asian plume over the eastern Mediterranean, the mole fractions of ozone were relatively low (55 nmol mol^{-1}) compared to the seasonal median, but were similar to ozone observed in the upper troposphere above South and Southeast Asia during 1994-2004. Ozone in the Asian plume showed no clear relationship with higher hydrocarbons, suggesting a NO_x-limited photochemical regime (Scheeren et al., 2003), but modeling indicated that the quantity of ozone from South and Southeast Asia would increase over time with increasing emissions. Ozone enhancements in the mid-troposphere were much greater, with a variety of sources including the stratosphere, lightning NO_x and North America (Roelofs et al., 2003). The model-estimated TCO above the eastern Mediterranean was 50 DU (similar to present-day satellite retrievals) with contributions from the stratosphere (30%), lightning (13%), Asia (7%), North America (8%) and Europe (14%).

In the boundary layer, the area is influenced by western and eastern European pollution via frequent northerly flow. Model experiments show that lower tropospheric summertime ozone throughout the region has greatest sensitivity to locally emitted NO_x, particularly in the west. High summertime rural surface ozone can occur over the eastern Mediterranean, especially on its eastern edge, affecting the air quality of major urban centers in the area (Zerefos et al., 2002; Kalabokas and Repapis, 2004). Analysis of MOZAIC commercial aircraft ozone profiles reveals that ozone is strongly influenced by synoptic meteorology (Kalabokas et al., 2007; Kalabokas et al., 2013; Kalabokas et al., 2015). During the highest ozone days over the eastern Mediterranean a large surface anticyclone is centered over N. Africa, extending over central and western Europe. In addition, strong summer anticyclonic subsidence in the lower troposphere, leading to enhanced ozone, has been reported over the eastern Mediterranean (Eremenko et al., 2008; Foret et al., 2009; Liu et al., 2009; Coman et al., 2012; Richards et al., 2013; Doche et al., 2014; Kleanthous et al., 2014; Safieddine et al., 2014; Zanis et al., 2014; Tombrou et at., 2015). Summer anticyclones in the area are also associated with the downward transport of upper tropospheric ozone, especially at the interface with adjacent low pressure systems located over the eastern Mediterranean and Middle East (Kalabokas et al., 2013; Zanis et al., 2014; Tyrlis et al., 2014; Kalabokas et al., 2015). Summertime stratospheric intrusions are also common events above this region influencing both the upper and mid-troposphere (Stohl et al., 2003, Škerlak et al., 2014; Akritidis et al., 2016), as found for the other season (Galani et al., 2003). In addition, a frequent midsummer peak of upper tropospheric ozone is observed above northern Europe and the adjacent North Atlantic Ocean (Thouret et al., 2006; see also Fig. 3.2.1), which could serve as an ozone reservoir for the lower troposphere and boundary layer over the eastern Mediterranean through large-scale subsidence. Similarly, enhanced ozone during anticyclonic conditions has also been observed at rural locations in the central and western Mediterranean region (Kalabokas et al., 2008; Sanchez et al., 2008; Schurmann et al., 2009; Velchev et al., 2011; Cristofanelli et al., 2015; Kalabokas et al., 2017), where summer subsidence seems to be weaker than over the eastern Mediterranean, but where frequent stagnant conditions enhance local photochemical ozone production.

TOAR-Climate has no clear evidence for a trend in the summertime ozone maximum across the Mediterranean and the Middle East. The five ozonesonde and satellite products (Figures S4.3.1 – S4.3.5) with trends calculated for summertime show no consensus on the sign or magnitude of the ozone change. Surface ozone monitoring is limited across the Mediterranean with the few available sites generally showing decreasing ozone along the northern edge of the region and decreasing ozone at Cyprus (Figure 4.1.4c). Of the five sites in the eastern Mediterranean one shows a significant increase of ozone and the other four show no sign of a significant decrease. East of Israel and the West Bank there are no sites available for trend evaluation. Improved understanding of the magnitude, extent and trends of this ozone

feature requires additional surface ozone monitoring in Egypt and in the Middle Eastern nations east of Israel. The IAGOS program provides infrequent aircraft profiles above this region which are inadequate for establishing trends, and routine profiling will be required to assess long term trends.

5.7 Tropospheric ozone burden

The Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) calculated the present-day radiative forcing due to tropospheric ozone using a model ensemble of global ozone simulations for the years 1850 and 2000 (Young et al., 2013). The 15-model mean of the year 2000 global tropospheric ozone burden (TOB) was 337 Tg, with a range of 302-378 Tg. Model performance for the present-day (2000) horizontal ozone distribution (tropospheric column ozone in units of DU) and TOB was evaluated using only the OMI/MLS product. Through TOAR we now have 6 products (TOST and the five satellite products) for quantifying present-day TOB.

Figure 5.7.1 compares TOB (60° S - 60° N) among the five satellite products discussed above with the addition of SCIAMACHY (2002-2012) and GOME (1996-2003) to provide as much information as possible on ozone prior to the operational periods of OMI and IASI. Across the globe and in both hemispheres (see also Figures S5.7.1 and S5.7.2) the products come into closer agreement after 2014. Table 5.7 shows TOB for the period 2010-2014 (corresponding to Figure 3.4.1) in the latitude range of 60° S - 60° N. The mean of the six products (including TOST) is 299 Tg with a range of 281-318 Tg, or roughly ± 6%. The mean of just the five satellite products is 297 Tg with a range of 281-318 Tg, or roughly ± 6%. The ozone burden from the five satellite products for the most recent period of 2014-2016 is 296 Tg, with an even narrower range of 285-311 Tg, or ± 4%.

The TOB results discussed so far are limited to the 60° S - 60° N latitude range and therefore do not provide estimates of the true global TOB. However, TOST covers the polar regions and provides a full global TOB estimate of 337 Tg (for 2010-2012), which means the TOST estimate of TOB in the range of 60° S - 60° N is 91% of the global TOB. Therefore, the polar regions, although they represent 13% of the globe, contain 9% of the global TOB. The IASI-SOFRID and IASI-FORLI products provide polar coverage and their full latitude range TOB values are 333 and 345 Tg, respectively, but these results are underestimates as only daytime IASI retrievals are used in this study, which excludes regions under polar night conditions (see Section 2.4.5).

While the satellite products have excellent agreement for the present-day TOB, they differ in their quantification of TOB trends. The OMI/MLS, GOME/OMI and OMI-RAL products indicate an increase of TOB through 2015-2016, while IASI-FORLI and IASI-SOFID indicate a TOB decrease. As described below, the satellite products have differing vertical sensitivities and therefore the trends reflect ozone changes at different levels of the troposphere. At this time we are unable to provide a definitive statement regarding the change in TOB over the past decade and future work is required to reconcile the different

satellite products. However many of the products indicate TCO increases across the portion of the tropics stretching from South America eastwards to the western Pacific Ocean, a region that deserves further investigation as it has experienced rapid changes in ozone precursor emissions and is sensitive to dynamical controls (e.g ENSO) on ozone interannual variability.

Ozone abundance retrievals: Satellite and ground based remote sensing relies on retrieval algorithms that model the expected measured radiance with a forward model (FM) and then invert this model using the measurement, usually with optimal estimation (Rodgers et al., 2000), to produce an estimated vertical distribution of abundance (nmol mol^{-1}) or sub-columns (DU) along with a posteriori error covariance and averaging kernel (AK) matrices. The AK quantifies the relative sensitivity of the radiance and retrieval to the "true state" for vertical retrieval layers and varies with observation type (land/ocean, day/night), the spectral range (e.g., thermal infrared or UV) being measured, spectral resolution, measurement noise and choice of a priori covariance. For example, OMI/MLS, OMI-SOA and the two products from IASI are more sensitive to the upper troposphere, while OMI-RAL is more sensitive to the lower half of the troposphere (Figures S5.7.1, S5.7.2 and S5.7.3). In this report, we have taken care to use common parameters, where possible, such as tropopause height to determine tropospheric ozone columns. However, fundamental differences remain due to the different measurement techniques and retrieval algorithms. Algorithm implementation details in addition to the choice of a priori, such as the choice of spectroscopic data and other forward model parameters can also have significant impacts on the retrievals, even for the same measurements using the same inversion technique (Liu et al., 2007; Liu et al., 2013). Finally, satellite ozone retrievals from various instruments differ due to sampling strategy, both spatially and diurnally (see Table 2.4). Despite these potentially large differences for different satellite observations of a single airmass, the global tropospheric ozone burden in Table 5.7 is remarkably consistent for the satellite observations.

Ozone trend estimation: Trend determination can have errors due to time-varying instrument biases that are not completely removed, if at all, by time dependent corrections in the retrievals. Understanding how much of the trend differences for remotely sensed measurements is due to instrument biases requires further validation using in-situ observations, such as ozonesondes, with sufficiently long records, as has been done for the stratosphere (Steinbrecht et al., 2017). Differences in vertical sensitivity and sampling will also affect trend estimation. For example, tropospheric column ozone observations with greater sensitivity to the upper troposphere have trends with greater influence from this region. This sensitivity difference might help to explain the trend differences observed for UV and thermal infrared measurements (see Figures 4.3.2 and 5.7.1). Resolving trend differences due to these measurement traits requires characterizing the effects of sampling and vertical sensitivity on trend estimates. This can be

taken into account by sampling and applying the AKs of each measurement type to a common model simulation with a known trend in tropospheric column ozone to find the resulting trend bias, if any. These validation and model sampling exercises will be the focus of future intercomparisons of remotely sensed tropospheric column ozone data products.

5.8 Data Availability

The goal of TOAR-Climate is to assess the present-day distribution and trends of tropospheric ozone for the purposes of quantifying the tropospheric ozone burden and to identify additional observations well-suited for the evaluation of global atmospheric chemistry models. Our current observation-based knowledge of ozone's distribution and trends has been covered as succinctly as possible in Sections 3, 4 and 5 and those findings will not be repeated here. Instead we highlight the fact that the global ozone observational network has enormous spatial gaps with respect to surface observations and in situ vertical profiles. While several new satellite products now provide near global coverage of TCO further work is required to determine why the satellite products differ with regard to trends. Therefore, global atmospheric chemistry models will continue to be critical tools for our understanding of not only the global distribution of tropospheric ozone but also the photochemical and dynamical processes that drive photochemical ozone production and loss, surface deposition and transport from the stratosphere (see *TOAR-Model Performance*; Young et al., 2017). The ozone data sets described in TOAR-Climate are ideal for evaluating the performance of global atmospheric chemistry models and access to these valuable data is described in Table 5.8.

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Data Accessibility: Information to access all datasets used in the TOAR-Climate analyses can be found in Table 5.8.