Retrieval of ozone profiles from OMPS-LP observations and merging with SCIAMACHY and SAGE II time series to study long-term changes

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Abstract

Stratospheric ozone has been extensively studied over the last decades, as it is considered one of the most important trace gases in the atmosphere, due to its role as a protective shield against biologically harmful solar radiation. At the end of the 20th century, extensive stratospheric ozone depletion was observed, mainly caused by anthropogenic emissions of chlorine-containing substances. The discovery of the so-called Antarctic ozone hole gave a boost to the research activities in stratospheric chemistry and dynamics, which led to a better understanding of the processes governing the ozone layer, and ultimately to more reliable model simulations.

During the 21st century, an ozone recovery is expected, in response to the decreasing emissions of chlorine-containing ozone-depleting substances. This recovery is predicted to have a complex spatial structure and is modulated by the ongoing climate change. For this reason, spatially and temporally resolved observations of the stratospheric trace gases are of great significance. In this sense, the beginning of the century witnessed several new satellite missions dedicated to the study of the atmospheric composition. In particular, limb-viewing satellite instruments such as the Optical Spectrograph and Infra Red Imaging System (OSIRIS), the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) and the Microwave Limb Sounder (MLS) substantially contributed to extending our knowledge of the stratosphere. Over the last few years, significant efforts have been put into the merging of several satellite and ground-based data sets to obtain consistent long-term composites and investigate ozone changes. Thanks to these efforts, an ozone recovery over the last two decades has been identified.

Within this framework, this dissertation is articulated in three main steps:

• The set-up of an ozone retrieval algorithm to be applied to limb observations from the Ozone Mapping and Profiler Suite - Limb Profiler (OMPS-LP) and its characterization in terms of error budget;

• The comparison and the validation of the ozone profiles retrieved from OMPS-LP measurements using independent data sets;

• The merging of OMPS-LP time series with other satellite data sets (in particular SCIAMACHY) to study long term ozone changes over the last decades, as a function of altitude, latitude and longitude.

First, the retrieval algorithm applied to OMPS-LP observations is presented, from the preliminary studies to its final version. This algorithm is extensively adapted from the retrieval scheme used for SCIAMACHY measurements, maintaining a similar retrieval approach and
the same spectroscopic database. The implemented cloud screening and the retrieval of ancillary aerosol extinction profiles are also discussed. The error characterization of the retrieved ozone profiles is provided by discussing mainly the noise and parameter error components. A typical retrieved ozone profile has a vertical resolution of 2.5-3 km and its noise error component decreases from 10-20 % in the lowermost stratosphere to 2-4 % above 20 km. The parameter error is found to be larger in the lower tropical stratosphere and is generally equal to 3-5 % in the middle and upper stratosphere at all latitudes.

Afterward, a comparison of our results (IUP) with OMPS-LP ozone profiles retrieved by the NASA team is presented. Above 20 km the relative differences between the two data sets are generally below 10 % at all latitudes, with IUP profiles showing higher values in comparison with those from NASA in the upper stratosphere and around 30-35 km. Besides, an extensive validation using independent data sets is presented for the relevant altitude and latitude range. A very good agreement with respect to averaged MLS observations is found between 20 and 50 km, with discrepancies within ±7 % at all latitudes. In the lower stratosphere higher discrepancies are found, as the sensitivity of limb observations decreases and the ozone concentration drops. For this reason, a validation using collocated ozonesondes profiles is performed, focusing at altitudes below 30 km. This validation shows a good consistency within 5-7 % at mid-latitudes down to 13 km and in the tropics above 18 km.

The merging of the OMPS-LP ozone time series with the SCIAMACHY data set is then performed, obtaining the altitude-, latitude- and longitudinally resolved monthly ozone distribution in the stratosphere over the last 15 years. The merging with zonally averaged Stratospheric Aerosol and Gas Experiment (SAGE) II measurements is also addressed and ozone trends over the last 35 years are calculated, applying a multi-linear regression model to the merged time series. Over the period 1985-1997, a substantial ozone depletion is confirmed, especially in the middle and upper stratosphere. After 1997 the ozone recovery is clearly identified in the upper stratosphere, with the highest values of about 3-5 % at northern mid- and high latitudes. A changing pattern during the last 15 years in the trend in the middle tropical stratosphere is illustrated and confirmed by a chemistry-transport model simulation. In addition, by exploiting the high spatial resolution of SCIAMACHY and OMPS-LP data sets, longitudinally resolved ozone variations are also addressed, going beyond the usual zonally averaged approach. This study reveals a large longitudinal variability in the middle and upper stratosphere at mid-latitudes. The possible origins of the zonal asymmetries in ozone variations are still under investigation.
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Acronyms

ACE-FTS  Atmospheric Chemistry Experiment - Fourier Transform Spectrometer.
AK  averaging kernel.
ARRM  Absolute Radiance Residual Method.
BASIC  BAyesian Integrated and Consolidate.
BDC  Brewer-Dobson circulation.
BUV  Backscatter Ultraviolet Radiometer.
CARIBIC  Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container.
CCD  charge-coupled device.
CCI  Climate Change Initiative.
CCM  chemistry-climate model.
CCMVal  Chemistry-Climate Model Validation activity.
CDI  combined differential-integral.
CFC  chlorofluorocarbon.
CI  color index.
CIR  color index ratio.
CTM  chemical-transport model.
DIAL  differential absorption laser.
DLM  dynamical linear modeling.
ECMWF  European Centre for Medium-range Weather Forecasts.
EESC  effective equivalent stratospheric chlorine.
ENSO  El Niño Southern Oscillation.
Envisat  Environmental satellite.
ERBS  Earth Radiation Budget Satellite.

FIR   far infrared.

FOV   field of view.

FTIR  Fourier transform spectrometer.

GHG   greenhouse gases.

GMAO  Global Modeling and Assimilation Office.

GOES  Geostationary Operational Environmental Satellite.

GOME  Global Ozone Monitoring Experiment.

GOMOS Global Ozone Monitoring by Occultation of Stars.

GOZCARDS Global OZone Chemistry And Related trace gas Data records for the Stratosphere.

GROMOS GRound based Ozone MOnitoring System for Campaigns.

HALOE Halogen Occultation Experiment.

IAGOS In-service Aircraft for a Global Observing System.

IPCC Intergovernmental Panel on Climate Change.

IR   infrared.

IUP   institute for environmental physics.

L1G   level 1 gridded.

L2    level 2.

L3    level 3.

lidar light detection and ranging.

LIMS  Limb Infrared Monitor of the Stratosphere.

LORE/SOLSE Limb Ozone Retrieval Experiment/Shuttle Ozone Limb Sounding Experiment.

LOS   line of sight.


MERRA Modern-Era Retrospective analysis for Research and Applications.
**MIPAS** Michelson Interferometer for Passive Atmospheric Sounding.

**MLR** multi-linear regression.

**MLS** Microwave Limb Sounder.

**MOZAIC** Measurement of OZone and water vapour on Airbus In-service airCraft.

**NCEP** National Centers for Environmental Prediction.

**NDACC** Network for the Detection of Atmospheric Composition Change.

**NIR** near infrared.

**NOAA** National Oceanic and Atmospheric Administration.

**ODP** ozone-depleting potential.

**ODS** ozone-depleting substances.

**OHP** Observatoire de Haute-Provence.

**OMI** Ozone Monitoring Instrument.

**OMPS** Ozone Mapping and Profiler Suite.

**OMPS-LP** Ozone Mapping and Profiler Suite - Limb Profiler.

**OPAC** Optical Properties of Aerosols and Clouds.

**OSIRIS** Optical Spectrograph and Infra Red Imaging System.

**PMC** polar mesospheric cloud.

**PSC** polar stratospheric cloud.

**PWLT** piece-wise linear term.

**QBO** quasi-biennial oscillation.

**RAA** relative azimuth angle.

**RCP** representative concentration pathway.

**RSAS** Rayleigh Scattering Attitude Sensing.

**SAA** South Atlantic Anomaly.

**SABER** Sounding of the Atmosphere using Broadband Emission Radiometry.

**SAGE** Stratospheric Aerosol and Gas Experiment.
SAM  Stratospheric Aerosol Measurement.
SBUV  Solar Backscatter Ultraviolet Radiometer.
SC  seasonal cycle.
SCIAMACHY  SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY.
SHADOZ  Southern Hemisphere ADditional OZonesondes.
SME  Solar Mesospheric Explorer.
SMILES  Superconducting Submillimeter-Wave Limb Emission Sounder.
SMR  Sub-Millimeter Radiometer.
SNPP  Suomi National Polar-orbiting Partnership.
SNR  signal-to-noise ratio.
SOR  solar-ozone response.
SPARC  Stratosphere-Troposphere Processes and their Role in Climate.
SPE  solar proton event.
SSP  sub-satellite point.
SWOOSH  Stratospheric Water and OzOne Satellite Homogenized.
SZA  solar zenith angle.
TH  tangent height.
TIMED  Thermosphere Ionosphere Mesosphere Energetics Dynamics.
TOA  top of the atmosphere.
TOMS  Total Ozone Mapping Spectrometer.
TP  tangent point.
TROPOMI  TROPOspheric Monitoring Instrument.
UARS  Upper Atmosphere Research Satellite.
UTLS  upper troposphere - lower stratosphere.
UV  ultraviolet.
Vis  visible.
VMR  volume mixing ratio.
WOUxDC  World Ozone and Ultraviolet Radiation Data Centre.
List of publications

Peer reviewed papers


Conference and meeting contributions

Oral presentations


Poster presentations


Technical reports

Introduction

The importance of stratospheric ozone as a protective shield against ultraviolet (UV) solar radiation, particularly between 200 and 340 nm, was recognized by scientists already at the end of the 19th century (Hartley, 1880). A decrease in the stratospheric ozone concentration leads to an increase of UV-B radiation\(^3\) in the troposphere, directly impacting the biosphere and the tropospheric chemistry. For example, an increasing incidence of skin cancers, as well as negative effects on crops and ocean plankton are some of the consequences of such a decrease (Fuglestved et al., 1994; Norval et al., 2011). Because ozone regulates the temperature and the dynamics of the stratosphere, its variations also affect the radiative budget of the Earth (Kiehl et al., 1999). Over the last century, extensive studies have been done to understand the dynamics and the chemistry of the stratospheric ozone layer and the impact of anthropogenic emissions on it. The research activities investigating the stratospheric environment were fostered by the discovery of the so-called ozone hole (Farman et al., 1985). These studies have led to a good understanding of the chemical processes that take place in the stratosphere, including heterogeneous reactions (Solomon, 1999).

The main scientific question related to stratospheric ozone in the 21st century concerns its recovery after the severe depletion occurred in the last decades of the 20th century; this depletion is mainly attributed to anthropogenic emissions of chlorine-containing ozone-depleting substances (ODS). Over the last 30 years, the adoption of the Montreal Protocol in 1987 and its amendments led to a substantial decrease of ODS emissions, even though recent studies have highlighted that the decrease of their concentration in the stratosphere has not been as rapid as expected and that new illegal emissions have been discovered (Montzka et al., 2018). The joint effect of decreasing ODS and increasing greenhouse gases (GHG) is expected to lead to an increasing stratospheric ozone concentration in the next decades. The increase rate is expected to be influenced by the future anthropogenic emission rate of trace gases. The ozone recovery has a complex latitude and altitude pattern due to the interplay of dynamics and photochemistry. Model studies predict that the total ozone column will reach the 1980 level in the middle of the current century (CCMVal, 2010; Dhomse et al., 2018). An acceleration of the Brewer-Dobson circulation (BDC) as a consequence of the warmer troposphere is expected to cause a decreasing ozone concentration in the lower tropical stratosphere and an increase in the polar regions. The observational evidence of the ozone recovery has been established by several studies, whereas the evidence of lower stratospheric changes is still contradictory (WMO, 2018; Petropavlovskikh et al., 2019).

\(^{3}280-310\) nm
Monitoring of the ozone layer is achieved by several instruments from different platforms (Hassler et al., 2014). In this respect, satellite observations provide a unique source of highly spatially and temporally resolved data. In particular, satellite measurements in limb geometry are fundamental for studying ozone distribution with a high temporal resolution, good vertical sampling and global coverage every few days.

Despite the abundance of satellite ozone measurements, particularly with the new missions launched at the beginning of this century, it is nevertheless still challenging to study ozone trends for various reasons. Single satellite data sets are generally too short to give reliable information about long-term changes so that merging several data sets is required. Instruments are affected by systematic errors and drifts, which make the merging procedure challenging. Work is required to reduce systematic uncertainties and improve sensor stability. Several studies have been dedicated to merging satellite data sets during the last two decades, highlighting that good quality, consistency and stability of single satellite data sets are fundamental prerequisites to obtain reliable merged composites (Harris et al., 2015). The aim of this study is the creation of a long-term ozone data set, with the main focus on merging ozone profiles from the Scanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) with those from the Ozone Mapping and Profiler Suite - Limb Profiler (OMPS-LP). These two satellite instruments exploit the limb scattering technique, and the two missions have an overlap of 2.5 months. This merged data set is longitudinally resolved, enabling us to investigate zonally-resolved long-term ozone changes. A prior step to the merging is the setup of the retrieval of OMPS-LP ozone profiles. With respect to the SCIAMACHY retrieval, the same radiative transfer model and spectroscopic databases have been used. Besides, a similar retrieval approach was followed in order to ensure the best consistency between the data sets. Before merging, the retrieved OMPS-LP ozone time series was compared with the official ozone product released by NASA and validated against independent measurements.

Outline of the thesis

This thesis is structured as follows: in Ch. 1 an overview of the ozone chemistry and dynamics of the stratosphere is presented together with a review of the expected ozone recovery in the 21st century. An introduction to ozone measurements using several techniques and platforms is provided in Ch. 2. Chapter 3 concludes the introductory part, giving a detailed overview of the OMPS-LP instrument. In Ch. 4 the retrieval of ozone profiles from OMPS-LP observations is described, starting with the preliminary studies. An overview of the final algorithm settings and the retrieval characterization is then provided, including sensitivity studies to assess the parameter errors. Aerosol extinction retrieval and cloud flagging are also addressed in this chapter. In Ch. 5 a comparison with the NASA official product is presented together with the validation of our results against Aura Microwave Limb Sounder (MLS) ozonesondes and lidar profiles. Chapter 6 deals with the merging of the OMPS-LP data set with SCIAMACHY profiles, using MLS time series as a transfer function. The latitude/longitude resolved product is described here and two different approaches are introduced. A merging with monthly zonally averaged observations from the Stratospheric Aerosol and Gas Experiment (SAGE) II
instrument is also presented. Chapter 7 describes the multilinear regression model applied to the merged data sets to assess long-term ozone changes over the period 1985-2018, with a focus on the SCIAMACHY/OMPS time and on the longitudinally resolved trends. A comparison with other studies is also carried out in this part. The last chapter is dedicated to geophysical studies, in particular to the solar proton event that occurred in September 2017, the ozone hole and the quasi-biennial oscillation (QBO) disruption observed in 2015-2016.
Chapter 1

Ozone chemistry and stratospheric dynamics overview

1.1 Ozone distribution in the stratosphere

Even though ozone is a minor atmospheric constituent in terms of abundance, it plays a significant role in Earth’s atmosphere for several reasons. Its distribution peaks in the stratosphere, both in terms of number density and volume mixing ratio (VMR) where 90% of the atmospheric ozone is found, forming the so-called ozone layer (Seinfeld and Pandis, 2016). The absorption of UV radiation by O$_2$ and ozone determines the temperature structure of the atmosphere and, ultimately, the existence of the stratosphere itself. In the troposphere, ozone is also a minor greenhouse gas and is a major pollutant (IPCC, 2007).

Figure 1.1 depicts a typical yearly-averaged ozone distribution as a function of latitude and altitude, both in terms of number density (molec cm$^{-3}$) and VMR, respectively in panel (a) and (b). In these plots, ozone profiles from OMPS-LP observations are averaged over 2016 to represent a typical yearly mean distribution. Ozone concentration maxima are reached around 25 km in the tropics and at 18-20 km towards the polar regions. The absolute maximum is reached at northern mid and polar latitudes during the spring. In terms of VMR, the picture changes: the highest mixing ratio is in the tropics around 35-40 km where the ozone production is the most efficient throughout the year. Considering the time series of monthly zonally averaged ozone, we can also compute the variability of its distribution over the time series, including inter- and intra-annual oscillations. The standard deviation of ozone concentration is shown in panel (c) of Fig. 1.1 in terms of %, i.e., the standard deviation computed over 6 years of observations divided by the mean ozone profile. The largest values are found in the upper troposphere-lower stratosphere (UTLS) particularly towards polar regions, and in the lower mesosphere at mid-latitudes.

To obtain this steady-state conditions in the stratosphere, several dynamics and chemistry-related processes are involved, which are discussed in the next sections.
Chapter 1. Ozone chemistry and stratospheric dynamics overview

Figure 1.1: Yearly averaged distribution of ozone as a function of latitude and altitude from OMPS-LP observation (2016), in terms of number density (panel a) and volume mixing ratio (panel b). Panel (c) shows the variability of the ozone field in terms of the standard deviation of the monthly averaged time series at every altitude and latitude over 6 years of OMPS-LP measurements.
1.2 Stratospheric ozone chemistry

Stratospheric ozone chemistry describes the processes leading to the dynamic equilibrium of the ozone layer. It involves three main topics: the Chapman mechanism, which describes the basic scheme of ozone production and destruction, the catalytic cycles, which include several chemical species and explain the quantitative ozone distribution, and heterogeneous reactions.

1.2.1 Chapman cycle

In 1930 Chapman proposed the first consistent explanation of ozone formation and destruction in the stratosphere (Chapman, 1930), suggesting the reactions which are now referred to as the Chapman scheme:

\[
\begin{align*}
O_2 + h\nu & \rightarrow O + O \quad (\lambda < 240 \text{ nm}) \quad (1.1) \\
O + O_2 + M & \rightarrow O_3 + M \quad (1.2) \\
O_3 + h\nu & \rightarrow O_2 + O(^1D) \quad (\lambda < 320 \text{ nm}) \quad (1.3) \\
O_3 + O & \rightarrow 2O_2 \quad (1.4)
\end{align*}
\]

The energy of solar photons absorbed by ozone and oxygen molecules is converted into heat, producing the characteristic temperature profile in the stratosphere. Reaction (1.3) is the primary source of O\(^{(1D)}\) atoms in the stratosphere, which are either rapidly quenched to ground state or react with other species. Once two O atoms are formed, reactions (1.2) and (1.3) are fast so that there is a rapid interconversion between O\(_3\) and O before (1.4) can occur. Therefore, the sum of O\(_3\) and O forms the O\(_x\) family. We can then evaluate the lifetime of O\(_x\) species in the stratosphere as:

\[
\tau_{O_x} = \frac{[O] + [O_3]}{k_4[O][O_3]} \quad (1.5)
\]

where \(k_4\) is the rate coefficient of Eq. (1.4) with units \([\text{cm}^3 \text{ molec}^{-1} \text{s}^{-1}]\). Substituting the typical concentration values as a function of altitude, we obtain that the odd-oxygen lifetime is of about 12 days at 40 km, it increases to 140 days at 30 km and to 2-3 months in the lower stratosphere (Seinfeld and Pandis, 2016).

The efficiency of the Chapman cycle depends on a trade-off between the availability of photons with the suitable energy and O atoms. In the upper stratosphere, the amount of radiation is high but there are not enough O\(_2\) molecules to be photolized. On the other hand, in the lower stratosphere, the amount of available UV radiation is reduced, because of the absorption by O\(_2\) at higher altitudes. As a consequence, the ozone peak in the tropics is located around 35 km in terms of VMR and 25 km in terms of number density. Comparing the results of the Chapman model with ozone measurements, the shape of the ozone profile is reproduced reasonably well but the amount of ozone is found to be double with respect to the observations. Other mechanisms to remove ozone from the stratosphere have been studied starting from the 1960s and have highlighted the importance of catalytic cycles.
1.2.2 Catalytic cycles

Catalytic cycles provide additional chemical routes to lose odd-oxygen in the stratosphere other than reaction [1.4]. The basic scheme is the following:

\[
\begin{align*}
X + O_3 & \rightarrow XO + O_2 \quad \text{(1.6)} \\
XO + O & \rightarrow X + O_2 \quad \text{(1.7)} \\
O + O_3 & \rightarrow 2O_2 \quad \text{(1.8)}
\end{align*}
\]

For this two-steps reaction to be efficient, the bond \(X - O\) has to satisfy some constraints so that both steps are exothermic. Important species satisfying this requirement and thus representing relevant catalytic \(X\)s are OH, NO, Cl and Br. In analogy to the \(O\) group, we introduce the chemical families \(HO_x, NO_x, ClO_x\) and \(BrO_x\) to describe the species involved in the chemistry of each catalytic cycle.

The only way to stop a catalytic cycle consists in the removal of the catalyst \(X\). This can happen either via photolysis of \(XO\) in the second step, so that odd oxygen is again formed (null or holding cycle), or via reactions of \(XO\) with other species, leading to the formation of the so-called reservoir species, i.e., compounds that sequester a reactive catalyst and thereby remove it from its ozone-destructive role.

The relative contribution of each catalytic cycle to ozone destruction is a function of altitude; it is important to stress that these contributions are not additive since species from different families can react with each other and interfere. Figure [1.2] shows the relative contribution of the catalytic families to ozone destruction as a function of altitude. To understand this plot, in the rest of the section some more details of each catalytic cycle and relevant interactions between different chemical families are presented.

\[\text{FIGURE 1.2: Relative global mean ozone loss rates grouped by chemical families, computed using the NOCAR 2-dimensional model, from Portmann et al. (2012).}\]
The role of the NO\textsubscript{x} family (NO + NO\textsubscript{2}) in the stratospheric chemistry was revealed by Crutzen (1970) and Johnston (1971). The main source of NO\textsubscript{x} in the stratosphere is N\textsubscript{2}O. This greenhouse gas is emitted in the troposphere and, due to its long residence time (140 years), reaches the stratosphere via the BDC. Here, 90 % of N\textsubscript{2}O undergoes photolysis, producing O\textsuperscript{(1D)} atoms. The rest reacts as follows:

\[ \text{N}_2\text{O} + \text{O}(\text{1D}) \rightarrow \text{NO} + \text{NO} \quad (1.9) \]
\[ \text{N}_2\text{O} + \text{O}(\text{1D}) \rightarrow \text{N}_2 + \text{O}_2 \quad (1.10) \]

Reaction 1.9 is the main source of NO\textsubscript{x} in the stratosphere.

The structure of the catalytic cycle is the same as presented at the beginning of the section, namely:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (1.11) \]
\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \quad (1.12) \]

Since the rate coefficient of the reaction 1.11 is much larger than the rate coefficient of reaction 1.4, this catalytic cycle is 5 times more efficient in destroying odd-oxygen at 40 km, where NO\textsubscript{x} has the maximum ozone-depleting contribution, as seen in Fig. 1.2. A competing reaction leading to a null-cycle is the photolysis of NO\textsubscript{2} instead of its reaction with O\textsubscript{3}:

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad (1.13) \]

In the lower stratosphere, where O\textsubscript{3} is more abundant than O, the following cycle is more important:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (1.14) \]
\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (1.15) \]
\[ \text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2 \quad (1.16) \]
\[ \text{or} \quad \text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O} \quad (1.17) \]

with the last reaction faster than the third one. In addition, NO\textsubscript{3} can have a different fate:

\[ \text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (1.18) \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad (1.19) \]

Both N\textsubscript{2}O\textsubscript{5} and HNO\textsubscript{3} are reservoir species; however, reaction 1.19 occurs mainly at the surface of aerosol particles. HNO\textsubscript{3} is particularly relevant, as it stores almost half of the nitrogen compounds of the stratosphere and it can also be formed via the following gas-phase reaction:

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (1.20) \]
Chapter 1. Ozone chemistry and stratospheric dynamics overview

which involves the interaction between HO\textsubscript{x} and NO\textsubscript{x} families.

The HO\textsubscript{x} family plays an important role in the ozone chemistry in the stratosphere and it was the first discovered ozone-destroying catalytic cycle (Bates and Nicolet, 1950). The HO\textsubscript{x} family includes two species: OH and HO\textsubscript{2} which inter-convert very fast between themselves. OH is produced in the stratosphere as follows:

\[
\begin{align*}
\text{H}_2\text{O} + \text{O}^{(1}\text{D}) & \rightarrow 2\text{OH} \quad (1.21) \\
\text{CH}_4 + \text{O}^{(1}\text{D}) & \rightarrow \text{OH} + \text{CH}_3 \quad (1.22)
\end{align*}
\]

in particular, 90% of OH comes from reaction (1.21) and 10% from reaction (1.22). HO\textsubscript{x} catalytic cycle has the same structure as the previous ones:

\[
\begin{align*}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \quad (1.23) \\
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \quad (1.24) \\
\text{or} \quad \text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + 2\text{O}_2 \quad (1.25)
\end{align*}
\]

The second and third reactions determine the efficiency of this cycle. The importance of these two reactions depends on altitude, i.e., on the concentration of O and O\textsubscript{3}: in the lower stratosphere, the second reaction dominates while in the upper stratosphere at about 50 km the first one is more important. We can estimate that this catalytic cycle is half as effective in destroying O\textsubscript{3} with respect to reaction (1.4) in the Chapman cycle at the VMR peak altitude (Seinfeld and Pandis, 2016). However, it is responsible for up to 80% of ozone loss below 20 km and above 50 km.

A crucial competing reaction that establishes the conversion time within the HO\textsubscript{x} family and provides an efficient holding cycle for this chemical family is the following:

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \quad (1.26)
\]

NO\textsubscript{2} may then be photolyzed and lead to the production of O, i.e., this reaction is a null cycle. As a consequence, any increase in stratospheric NO\textsubscript{x} would lead to a decrease in the effectiveness of the HO\textsubscript{x} catalytic cycle, damping the ozone destruction in the lower stratosphere; indeed, (1.26) removes HO\textsubscript{2}, whose reaction with O or O\textsubscript{3} determines the speed of the HO\textsubscript{x} cycle.

Moving to the ClO\textsubscript{x} family, the primary source of active chlorine in the stratosphere is either the oxidation of the naturally produced methyl chloride (CH\textsubscript{3}Cl) or the photodissociation of chlorofluorocarbons (CFCs):

\[
\begin{align*}
\text{CFCl}_3 + h\nu & \rightarrow \text{CFCl}_2 + \text{Cl} \quad (1.27) \\
\text{CF}_2\text{Cl}_2 + h\nu & \rightarrow \text{CF}_2\text{Cl} + \text{Cl} \quad (1.28)
\end{align*}
\]

These reactions typically occur in the 20-35 km altitude range, depending on the molecule, due to the absorption of solar radiation in the 185-210 nm spectral region.

Cl and ClO constitute the ClO\textsubscript{x} catalytic family, characterized by an extremely fast ozone-destroying cycle. This family has no holding cycles by itself. However, a relevant null-cycle
can take place in interaction with the NOx family:

\[
\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \quad (1.29)
\]

NO\textsubscript{2} is then photolyzed to produce atomic oxygen. Computing the importance of the catalytic chlorine cycle with respect to the Chapman cycle, we find that its effectiveness is highest around 40 km. At this altitude, it has an ozone removing efficiency similar to the Chapman cycle (Seinfeld and Pandis, 2016).

In the upper atmosphere, the reaction with CH\textsubscript{4} sequesters active chlorine into the reservoir species HCl, which stores about 70 % of the active chlorine:

\[
\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \quad (1.30)
\]

In the lower stratosphere, another important reaction that links the NO\textsubscript{x} and ClO\textsubscript{x} cycles is:

\[
\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \quad (1.31)
\]

Since HCl and ClONO\textsubscript{2} contain around 99 % of the active chlorine of the stratosphere, a small change in the abundance of these two species has a strong impact on the efficiency of the ClO\textsubscript{x} cycle.

The effect of increasing OH is opposite for ClO\textsubscript{x} and NO\textsubscript{x}: in the first case, a more abundant OH leads to faster conversion of HCl back to Cl and a more effective ClO\textsubscript{x} cycle. On the contrary, OH can react with NO\textsubscript{2} leading to the reservoir species HNO\textsubscript{3} (reaction 1.20).

Finally, BrO\textsubscript{x} cycles also play an important role. The reactions involving bromine compounds are very similar to the ones shown for the chlorine compounds with three main differences. Molecules like the halons CBrF\textsubscript{3} and the naturally produced CH\textsubscript{3}Br are photolyzed faster than analogous chlorine compounds, releasing active bromine as they enter the stratosphere. Second, the reaction:

\[
\text{Br} + \text{CH}_4 \rightarrow \text{HBr} + \text{CH}_3 \quad (1.32)
\]

is very slow. Besides, the reservoir species for bromine (HBr and BrONO\textsubscript{2}) are less stable than the chlorine counterparts. As a consequence, bromine compounds contribute to ozone depletion as efficiently as chlorine compounds even though their concentration is 150 times lower.

To this regard, a useful concept to assess the contribution of different ODS is the ozone-depleting potential (ODP). The efficiency of a species depends on the emission amount, its lifetime in the troposphere, the altitude of its photodissociation, and the stratospheric chemistry involved. The ODP is defined as the total steady-state ozone destruction, vertically integrated, that results per unit mass of species \(i\) emitted per year relative to that for a unit mass emission of CFCl\textsubscript{3} (CFC-11):

\[
\text{ODP}_i = \frac{\Delta O_3}{\Delta O_3_{\text{CFC-11}}} \quad (1.33)
\]

Values of the ozone depletion efficiency for the most important ozone-depleting species are reported in Table 1.1. As we see, bromine-containing compounds like CF\textsubscript{3}Br have an ODP several times higher than CFC\textsubscript{11}.
In addition to catalytic cycles, which involve mainly gas-phase reactions, heterogeneous chemistry plays an essential role in the stratosphere, mainly in the Antarctic ozone hole formation process and in the presence of stratospheric aerosol, related to volcanic eruptions, which are the topics of the next two sections.

1.2.3 Ozone hole

The first work identifying the extensive threat posed by CFC emissions to the stratospheric ozone was Molina and Rowland (1974). Ten years later, the first evidence of the presence of an Antarctic ozone hole was published in Nature by Farman et al. (1985): the authors detected a substantial ozone depletion between 10 and 25 km over the Antarctic region, using balloon-borne measurements. This finding was completely unexpected, since not predictable by the gas-phase reactions known at that time. The theory of the ozone hole in Antarctica was developed in the few following years, bringing a new insight into the role of heterogeneous chemistry in the stratosphere (Solomon, 1999).

To explain the phenomenon called ozone hole, two aspects of the polar meteorology, especially in the Southern Hemisphere, have to be highlighted. The first one is the presence of a stable polar vortex during winter months: a core of very cold air develops particularly over the Antarctic continent and persists till spring, sealing off the air within it from the subpolar circulation. In the Arctic, the polar vortex is more disturbed by the stronger tropospheric wave activity, and it usually dissipates during early spring. The second aspect concerns mainly Antarctica: due to the extremely low temperatures inside the polar vortex (below −80° C), polar stratospheric clouds (PSCs) can form. PSCs are classified as follows. Type I clouds are formed by HNO$_3$-rich particles of small diameter (less than 1 µm). Type II clouds are composed of larger particles consisting of ice and minor amounts of HNO$_3$ and H$_2$SO$_4$ as hydrates. Type II PSCs are formed at lower temperatures with respect to type I, but play a key role in the ozone hole phenomenon, as their larger particles settle at a higher speed in comparison to type I particles.

A chain of heterogeneous chemistry reactions occurs on PSC particle surfaces, involving chlorine reservoir species and leading to the formation of HNO$_3$. A central reaction of this process is the following:

\[
\text{ClONO}_2 + \text{HCl} (s) \rightarrow \text{Cl}_2 + \text{HNO}_3 (s) \tag{1.34}
\]

This requires the absorption of HCl on the surface of a PSC particle, which occurs at temperatures < 200 K. As a consequence of this reaction, two chlorine reservoirs are destroyed,
1.2. Stratospheric ozone chemistry

Molecular chlorine is released as a gas, and the HNO₃ reservoir is trapped into the PSC. Other heterogeneous reactions occur on the PSC particle surfaces, for example:

\[
\begin{align*}
\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3 \\
\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}
\end{align*}
\] (1.35)

As the particles forming PSCs undergo gravitational fall, the stratosphere gets dehydrated and denitrified.

When the solar light comes back to the polar region after the winter, the chlorine species produced through the previous reactions can be photolyzed, liberating Cl, which reacts with ozone:

\[
\begin{align*}
\text{Cl}_2 + \text{hv} \rightarrow 2 \text{Cl} \quad (1.37) \\
\text{HOCl} + \text{hv} \rightarrow \text{Cl} + \text{OH} \\
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 
\end{align*}
\] (1.38)

ClO rapidly accumulates in the stratosphere and a key gas phase reaction takes place, which was discovered by Molina and Molina (1987) and involves the ClO dimer (ClOOCl):

\[
\begin{align*}
\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \quad (1.40) \\
\text{Cl}_2\text{O}_2 + \text{hv} \rightarrow 2 \text{Cl} + \text{O}_2 \quad (1.41) \\
or \quad \text{Cl}_2\text{O}_2 + \text{hv} \rightarrow \text{Cl} + \text{ClOO} \quad (1.42) \\
\text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{ClO} \quad (1.43)
\end{align*}
\]

Together with [1.39], this set of reactions leads to a consistent ozone loss within a few weeks. In addition, the settling of PSCs has extensively removed NOₓ from the polar vortex region, so that reaction [1.31] cannot take place. Furthermore, in the lower stratosphere, the following cycle involving bromine and chlorine compounds is of great importance (accounting for the 40% of ozone destruction):

\[
\begin{align*}
\text{ClO} + \text{BrO} \rightarrow \text{BrCl} + \text{O}_2 \\
\text{BrCl} + \text{hv} \rightarrow \text{Br} + \text{Cl} \\
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \\
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\end{align*}
\] (1.44)

which does not require atomic oxygen.

Figure [1.3] shows the time development of the ozone hole in terms of concentration of several species in the upper panel, and temperatures inside the polar vortex in the lower panel. During the recovery period, it is interesting to note that ClONO₂ initially overshoots its average value: it takes time to re-establish a steady-state between chlorine reservoir species. The reaction forming HCl is slower than the one forming ClONO₂, leading to a slower increment of HCl during the late spring.
1.2.4 Stratospheric aerosols

A layer of sulfate aerosols is typically found in the stratosphere between 15 and 25 km. Aerosols in this layer are sub-micron sized particles, which were discovered by Junge et al. (1961) and are typically composed of a solution of sulfuric acid and water (Carslaw et al., 1997). Stratospheric aerosol has both natural and anthropogenic sources. The sulfuric acid comes from carbonyl sulfide (COS), sulfur dioxide (SO$_2$), and dimethyl sulfide (DMS), which enter the stratosphere mainly in the tropics via the upwelling BDC branch or by direct injection of SO$_2$ from explosive volcanic eruptions. Considering a spherical aerosol with a radius of 0.1 µm, it settles out of the stratosphere at a very slow rate (about 100 m y$^{-1}$). Because of this low settling speed, sulfate aerosols are mostly removed from the stratosphere via the descending branch of the BDC at the high latitudes.

Major volcanic eruptions, such as El Chichon in 1982 or Mount Pinatubo in 1991, can inject large quantities of material into the stratosphere and have an important impact on the lower stratosphere. Strong injections of sulfur compounds increase the stratospheric aerosol loading.
This leads to a change in the UV radiation available to create odd oxygen and modifies the temperature and the dynamics. A direct impact on the stratospheric chemistry was first observed and studied after the Pinatubo eruption in 1991 (McCormick et al., 1995). Heterogeneous chemistry plays here a central role: the reaction 1.19 does not have a temperature dependent sticking coefficient. Therefore, it can take place whenever aerosols are present in the stratosphere. In case of high aerosol loading, it changes the partitioning of nitrogen. In this way, more HNO$_3$, a reservoir compound, is formed, leaving less NO$_2$ available for the reaction 1.31. As a consequence, the partitioning of chlorine compounds is also affected, in favor of active chlorine. The HO$_x$ family is also affected for the same reason, showing the importance of NO$_x$ in regulating the other catalytic cycles. An ozone loss is then expected and it was observed in the tropical stratosphere up to 28 km a few months after the Pinatubo eruption (Schoeberl et al., 1993; Rodriguez et al., 1994).

1.3 Stratospheric dynamics

Stratospheric dynamics is dominated by the so-called BDC that is responsible for the transport of stratospheric air masses from the tropical UTLS to mid-latitudes and polar regions. The circulation concept was for the first time proposed by Brewer (1949) and Dobson (1956) to explain the distribution of ozone and other trace gas constituents in the stratosphere. In Fig. 1.4 a scheme of the circulation in the middle atmosphere is shown.

The upwelling branch of the BDC is located in the tropical regions: at the tropopause level polluted and dry air from the troposphere enters the stratosphere with a speed of 20-30 m per day. Then, the air is slowly transported towards the middle-upper stratosphere and towards high latitudes where it sinks. The descending motion towards polar regions starts around 30° latitude N and S. The BDC circulation affects the distribution of several trace gases, including ozone in the lower stratosphere, whose mean lifetime is of about 100 days at 20-25 km. As a consequence, although ozone production is more efficient in the tropics, its maxima in terms of number density are located in the lower polar stratosphere and occur at the beginning of spring, after it is transported and accumulates during the winter months.

The physical causes of the BDC are linked to the tropospheric wave activity at mid and polar latitudes (Holton et al., 1995). In particular, planetary-scale Rossby waves propagate upwards into the stratosphere, grow in amplitude as the air density decreases, and finally break in the so-called surf zone, as depicted in Fig. 1.4. Here they deposit westward momentum, decelerating the polar jet and allowing a poleward flow. The continuity of mass requires upwelling from the tropical regions and sinking at high latitudes. In addition, episodes of sudden stratospheric warming, which are characterized by a rapid temperature rise and a strong wind disturbance in the polar stratosphere, are followed by radiative cooling and sinking of air, which strengthen the stratospheric circulation (Tao et al., 2017). As a consequence, the BDC shows significant seasonal variations: during summertime, the circulation is much fainter with respect to wintertime, when the wave-breaking is more important. In addition, the circulation also shows
Chapter 1. Ozone chemistry and stratospheric dynamics overview

Figure 1.4: Schematic representation of the middle atmospheric circulation with blue arrows indicating the transport by BDC. The yellow arrow indicates the mesospheric pole-to-pole transport, where gravity waves (GWs) are the primary source of wave energy. Red arrows depict the year-round source of tropospheric wave energy propagating into the stratosphere. Vertical dotted lines indicate regions with restricted two-way transport ('mixing barriers'). The dashed thick blue line above the troposphere indicates the tropopause. From North et al. (2014)

hemispheric differences since the tropospheric wave activity is stronger in the Northern Hemisphere, due to the more extensive presence of mountains and land with respect to the Southern Hemisphere.

The BDC may be separated into two branches, as described by Birner and Bönisch (2011): a deep branch, more strongly associated with planetary wave breaking in the middle stratosphere, and a shallow branch, associated with synoptic and planetary scale wave breaking in the subtropical lower stratosphere. In the upper stratosphere and lower mesosphere, the circulation is driven by gravity wave breaking which leads to a single cell circulation from the summer to the winter hemisphere, as indicated by the yellow arrow in Fig. 1.4 and to strong pole-to-pole temperature gradients.

The QBO is a natural oscillation of the east-west direction of tropical stratospheric winds. This phenomenon is related to tropical wave activity and has a variable period of 22 to 34 months. The reversal of the wind pattern propagates from the upper stratosphere downward and it shapes the variability in the lower stratosphere, below 35 km. Associated to this oscillating wind patterns, the QBO signature has a significant influence on the temperature of the tropical
stratosphere and the extra-tropical circulation. Temperature anomalies affect the ozone chemistry directly but also impact stratospheric dynamics. Namely, through the thermal wind relationship, positive temperature anomalies are found in correspondence of a descending westerly QBO phase. This positive temperature anomalies result in a speeding up of the BDC upwelling (Baldwin et al., 2001). The opposite occurs in the case of descending easterly QBO phase. As a final result, a QBO induced meridional circulation takes place, which reinforces or dampens the BDC depending on the phase. This circulation also affects ozone distribution. Park et al. (2017) illustrated the effects of the QBO on ozone profiles as a function of altitude with two peaks of ozone variation found at 20-27 km and 30-38 km, showing opposite phase in the tropics and the same phase at mid-latitudes.

Another dynamical process influencing stratospheric ozone is the El Niño Southern Oscillation (ENSO). This is an ocean-atmosphere coupled oscillation occurring in the tropical eastern Pacific Ocean. The upper branch of the BDC is affected by this oscillation, which causes temperature anomalies in the tropical UTLS, also leading to a longitude-dependent modification of ozone in this region (Randel et al., 2009). Major ENSO warm events have been associated with observed decreases in ozone columns, whereas cold ENSO events have an opposite effect.

### 1.4 Solar influence on stratospheric ozone

The solar activity influences stratospheric chemistry at different time scales and periodicity. The most relevant modulations of the solar activity are the 11-year cycle, related to the sunspots activity, and the 27-days cycle, which is related to the sun rotation. These two oscillations are responsible for the variation of the incoming UV radiation, particularly in the extreme UV region, with a magnitude up to a factor of 2 between solar minimum and maximum (Wayne, 2006). These variations modify the overall amount of odd-oxygen in the stratosphere, as the photolysis rates of O\(_2\) and O\(_3\) are directly affected (J(O\(_2\)) and J(O\(_3\)) respectively). The effects on ozone in the upper stratosphere depend then on the relative importance of changes in J(O\(_2\)) and J(O\(_3\)). Because the variation in the incoming UV radiation occurs mostly at shorter wavelengths, the photolysis of O\(_2\) is mainly affected, with the effect that more production of O\(_3\) occurs than its photolysis. This leads to an in-phase and positive-correlated variation of upper stratospheric ozone concentrations with the UV flux, which has its maximum when the solar activity is at maximum. Besides, a temperature average difference of 1.5 K between solar minimum and maximum was identified by models and observations (Ramaswamy et al., 2001). Differences in the structure and magnitude of the solar-ozone response (SOR) were found between several satellite data sets and by comparing observations and models. Soukharev and Hood (2006) studied a 25-year period using independent satellite data and found statistically significant ozone variations between the maximum of the solar cycle and its minimum in the upper and in the lower stratosphere. The SOR associated with the 11-years solar cycle was found to occur mainly below 25 km.

Maycock et al. (2016) studied the SOR using SAGE II v7.0 data and Solar Backscatter Ultraviolet Radiometer (SBUV) time series. The authors found in SAGE II number density time series a three-peaked structure in the tropics and subtropics above 35 km with a magnitude of up to
Chapter 1. Ozone chemistry and stratospheric dynamics overview

3-4%, consistent with previous studies, e.g., Remsberg (2014). Non-significant SOR were identified in the middle tropical stratosphere, whereas below 25 km in the tropics and subtropics a positive response to solar activity was found, with a magnitude of 2%.

In the upper stratosphere, above 40 km, variations in ozone occur with the daily rising and setting of the sun. The main responsible for diurnal variations of ozone at these altitudes is the conversion of O into ozone after the sunset, followed by its reconversion to O at dawn. Sakazaki et al. (2013) used Superconducting Submillimeter-Wave Limb Emission Sounder (SMILES) observations and model simulations to study the amplitude of diurnal ozone variations globally throughout the stratosphere. Up to 30 km diurnal variations are negligible. Between 30 and 40 km, the minimum in ozone concentration is met at dawn with an increase in the afternoon and little changes during nighttime. These variations have an amplitude of about 2-3% and are thought to be caused by photochemistry and NO$_x$/HO$_x$ cycles. Between 40 and 50 km, the magnitude does not change, while the daily maximum shifts towards the evening. At these altitudes, the diurnal transport by tides plays a relevant role. Above 50 km, the diurnal variations increase consistently with height: ozone being depleted after the sunrise and being formed after the sunset. The amplitude of diurnal ozone variations in the upper stratosphere is also affected by the solar activity.

Solar proton events are short-period phenomena affecting the ozone in the upper atmosphere. They are addressed in Ch. 8.

1.5 Present and future of the ozone layer: Montreal protocol and model forecasts

During the last century, anthropogenic activities played an important role in determining the evolution of the stratospheric ozone layer. The main driver has been the emission of ODS whose effects have already been discussed in the previous sections. Already at the end of the 1980s, serious actions were undertaken to ban the production and reduce the emissions of CFCs worldwide: the Montreal Protocol was signed in 1987 and several amendments have been implemented in the following years. Thanks to these agreements, the concentration of compounds like CFC-11 and CFC-12 has been decreasing since the end of the 1990s. However, concerns have been recently raised about unexpected emissions of CFC-11 over the last years (Montzka et al., 2018).

A number of other drivers will play a significant role in the 21st century, when the expected ozone recovery will take place, following the decreasing concentration of ODS. The amount of N$_2$O and GHG emissions, the precise decrease rate of ODS and the evolution of the stratospheric circulation and temperature are the dominant factors.

Several studies, such as Waugh and Eyring (2008), Li et al. (2009), and Chipperfield et al. (2017), showed that, according to chemical-transport model (CTM) simulations, ODS-induced changes have been the dominant factor in ozone trends during the last decades everywhere in the stratosphere except for the lower tropical stratosphere. A useful metric to evaluate the impact of ODS on stratospheric ozone is the effective equivalent stratospheric chlorine (EESC), which gives an estimation of the reactive chlorine and bromine amount in the stratosphere. To compute it,
tropospheric ODS abundances are weighted to reflect their potential influence on ozone. Several model studies have been used to assess and forecast the date when EESC will get back to 1980 values, giving a time scale for the ozone recovery. SPARC has established the Chemistry-Climate Model Validation activity (CCMVal) in 2 phases, to improve the understanding of coupled chemistry-climate models (CCMs). A summary of the results for EESC is presented in the SPARC report CCMVal (2010), from which Fig. 1.5 is taken. The decrease in ODS concentration to values pre-1980 is much slower with respect to the rapid increase occurred until the end of the last century. Most probably, between 2040-2060 EESC values will be back to 1980 values, with some differences depending on latitude and altitude in the stratosphere.

**Figure 1.5:** Date of return to 1980 values for EESC concentration at 50 hPa at several latitudes according to two model studies: values are derived from individual model trends (colored symbols) and multi-model trends (large black triangles) for CCMVal-1 and CCMVal-2 (left and right respectively in each latitude band). From CCMVal (2010).

The increasing concentration of GHG in the troposphere is causing a cooling of the stratosphere through radiative transfer feedbacks (Groves et al., 1978; Goessling and Bathiany, 2016). This affects temperature dependent reactions, such as 1.2 and 1.4 in the Chapman cycle and 1.14 in the NOx catalytic cycle. In particular, the reaction rates of 1.14 and 1.4 steeply increase with temperature. As a consequence, the cooling leads to a decrease in the efficiency of the ozone destruction in the upper stratosphere, as discussed in several studies, e.g., WMO (2014) and Fleming et al. (2011). At the same time, the termolecular reaction 1.2 has a rate inversely proportional to temperature so that the cooling also accelerates the ozone production. Actual stratospheric temperature changes are the result of the interplay between the GHG cooling and the ozone recovery due to decreasing ODS. The net result of CO2 loading is an increase in global ozone both in terms of total column and in the upper stratosphere. Model studies suggested that ODS decreasing and GHG increasing contributed each to about half of the upper stratospheric ozone increase.

Footnote 1: In particular CO2.
Another consequence of the decreasing stratospheric temperature comes from the following reaction, which has high activation energy and is, therefore, temperature dependent:

\[ \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \] \hspace{1cm} (1.48)

A temperature decrease would lead to an increasing concentration of N atoms (relative to NO) and thus an increasing loss rate of NO via reaction:

\[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \] \hspace{1cm} (1.49)

which is the termination of NO catalytic cycles.

The future of the ozone layer is also influenced by the evolving concentration of N\textsubscript{2}O and CH\textsubscript{4}, which lead to the production of NO\textsubscript{x} and HO\textsubscript{x} in the stratosphere, as described in section 1.2.2. Catalytic cycles are indeed going to play a significant role in ozone loss especially in the upper stratosphere, already during the early 21st century. Ravishankara et al. (2009) pointed out the importance of the increasing N\textsubscript{2}O emissions concerning the ozone recovery date (to the level of 1980). Portmann et al. (2012) showed that N\textsubscript{2}O is becoming the most important anthropogenic ODS.

CH\textsubscript{4} related ozone chemistry is complex and it is difficult to isolate its contribution to the ozone layer. Increasing emissions of CH\textsubscript{4} at the surface result in increasing CH\textsubscript{4} in the stratosphere and thus also of HO\textsubscript{x}. The impact of increasing CH\textsubscript{4} is altitude dependent: the catalytic ozone depletion by HO\textsubscript{x} occurs in the upper stratosphere, whereas their catalytic ozone production is favored in the presence of NO\textsubscript{x} in the lower stratosphere (see reaction 1.26). In this respect Fleming et al. (2011) separated CH\textsubscript{4} effects into the following contributions:

- through its oxidation, it increases atmospheric H\textsubscript{2}O and HO\textsubscript{x} species which decreases ozone via the enhanced HO\textsubscript{x} catalytic cycles;
- the increased H\textsubscript{2}O cools down the middle stratosphere, reducing the ozone chemical loss rates, partially offsetting the enhanced HO\textsubscript{x}-ozone loss;
- it converts active to reservoir chlorine via the reaction 1.30, leading to more ozone;

The net result of CH\textsubscript{4} loading is an ozone decrease above 40-45 km and an increase below 40-45 km as well as in the total column.

In addition to this picture, changes in the BDC are expected in this century as a result of tropospheric warming (Garcia and Randel, 2008). Hardiman et al. (2014) pointed out in their model study a robust result concerning the strengthening of the tropical upwelling associated with climate changes. The strengthening of the BDC is predicted to be around 2 % per decade between 1960 and 2100, but it still has to be confirmed by observations. As a result of the enhanced upwelling in the tropics, it is expected that ozone in the tropical lower stratosphere will decrease in the long term. Evidence of this decline is still controversial, e.g., Ball et al. (2018) and Chipperfield et al. (2018).

Summing up all these contributions, Dhomse et al. (2018) recently presented an extensive model study, using 20 different CCMs about the expected ozone recovery date to pre-1980
values. They selected a representative concentration pathway (RCP) of 6.0; this means that the greenhouse gas concentrations are prescribed to follow the trajectory described in the 6.0 scenario by the 5th IPCC assessment report (IPCC, 2013). Consistently with other studies, the CCMs simulations predicted that the total ozone will return globally to 1980 levels in 2049 (with 1σ uncertainty of 2043–2055). The dates vary with latitudes, as a faster recovery is expected in the Northern Hemisphere due to its faster response to dynamical changes. All models showed in the long term a decline of the total column ozone in the tropics.
Chapter 2

Stratospheric ozone measurements

To understand and monitor the state of the atmosphere, observations have to be performed at different temporal and spatial scales, ranging from a few minutes to many decades and from under one kilometer to thousands of kilometers, respectively. To study various aspects and phenomena in the atmosphere, we need a set of instrumentations, which differ in terms of observation geometry, technique and resolution. Measurements can be distinguished depending on the location of the instrument, i.e., the platform: observations can be made from space, balloons, onboard aircraft and from the ground. Thus, we can speak about satellite platforms, balloon platforms, aircraft platforms (in this chapter these two are grouped together), and ground-based platforms. Each of them enables a unique set of measurements and each has its advantages and disadvantages, but all contribute to a better understanding of Earth’s atmosphere.

2.1 Ground-based observations

2.1.1 Total columns

Accurate information about the total atmospheric ozone content can be obtained using ground-based instruments, which exploit sun spectroscopy in the UV spectral range. The most important techniques are the Dobson spectrophotometer, the Brewer spectrophotometer and the Fourier transform spectrometer (FTIR).

A spectrophotometer is an instrument that measures the amount of incoming UV sunlight in a region where ozone absorption takes place, and therefore it infers the ozone column. In particular, the Dobson spectrometer measures the relative intensity of a selected pair of UV wavelengths, pointing towards the sun (or the moon) or observing the zenith-sky. A standard wavelength pair is 305.5 and 325.0 nm: the first one is highly absorbed by ozone while the second is relatively unaffected by ozone. In this way, measuring the relative intensity of solar light at specific wavelengths, it is possible to infer the ozone amount in a vertical column stretching from the instrument level to the top of the atmosphere (TOA).

The Brewer spectrometer was developed in the 1970s and uses a very similar approach to retrieve ozone columns, but with an improved and fully automated design compared to the Dobson instrument. Five wavelengths are usually combined in the spectral region between 306 and 320 nm, including a correction for SO₂. A well calibrated Brewer instrument has an estimated uncertainty of about 2%.
Chapter 2. Stratospheric ozone measurements

An FTIR is an instrument which acquires broadband near infrared (NIR) to far infrared (FIR) spectra, enabling the column amount of several trace gases, among which ozone, to be studied. FTIR retrieval products usually include distinct tropospheric and stratospheric abundances, in addition to standard total column amounts (Vigouroux et al., 2008). An advantage of this technique is that an absolute calibration is not needed, because the ozone absorption lines are self-calibrated using the surrounding continuum.

The Network for the Detection of Atmospheric Composition Change (NDACC) includes several stations around the world equipped with ground-based instruments, with about 20 locations providing regular observations from Brewer and Dobson spectrometers. The Infrared Working Group, which is also part of NDACC is a network of stations distributed on all continents deploying FTIR instruments.

2.1.2 Vertical profiles

The light detection and ranging (lidar) is a remote sensing instrument operating in the visible (Vis) spectral range, which uses light scattering to measure atmospheric properties. In order to measure the vertical ozone distribution, the differential absorption laser (DIAL) technique is used (McDermid et al., 1990). This technique requires the simultaneous emission of two laser beams at wavelengths with different ozone absorption cross-section. Typically, laser beams at 308 nm and 353 nm are emitted by a ground-based laser into the atmosphere. A telescope collects backscattered light. Observing the backscattered radiance in Rayleigh and Raman channels, it is possible to retrieve the ozone and temperature profiles from 15 to 60 km. Typical relative errors of the ozone profile range from 1-2 % near the peak and up to 10-30 % at the upper and lower altitudes.

For the validation of ozone profiles retrieved from OMPS-LP observations from 6 lidar stations are taken into consideration and listed in Table 2.1. These instruments are part of the NDACC network.

Table 2.1: List of the lidar stations used in this study, with their respective locations and the number of measurements available for each station during the OMPS operational period.

<table>
<thead>
<tr>
<th>Lidar station</th>
<th>latitude</th>
<th>longitude</th>
<th>number of profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hohenpeissenberg</td>
<td>47.80</td>
<td>11.00</td>
<td>100</td>
</tr>
<tr>
<td>OHP</td>
<td>44.00</td>
<td>6.00</td>
<td>100</td>
</tr>
<tr>
<td>Tablemountain</td>
<td>34.50</td>
<td>242.30</td>
<td>50</td>
</tr>
<tr>
<td>Lareunion</td>
<td>-21.10</td>
<td>55.40</td>
<td>40</td>
</tr>
<tr>
<td>Lauder</td>
<td>-45.00</td>
<td>169.70</td>
<td>50</td>
</tr>
</tbody>
</table>

Another ground-based remote sensing technique is the microwave radiometry, which studies the collision broadening of ozone emission lines. It enables to infer the altitude-resolved ozone profile from 20 to 70 km. Despite its low vertical resolution (8-12 km), it has the ability to study short-term variations of upper stratospheric and mesospheric ozone. Fernandez et al. (2015) presented an improved ground-based microwave radiometer called...
2.2. Balloon- and Airborne observations

Ozone Monitoring System for Campaigns (GROMOS)-C and the results of a measurements campaign, including a comparison with satellite data. All the instruments presented in this section may also be installed on balloon or aircraft platforms to study the vertical and regional distribution of trace gases. Several measurement campaigns have been set up to study regional ozone distributions in the troposphere and UTLS region. These campaigns provide a large amount of information; however, they offer only a limited view of ozone, as they are constrained in their regional coverage.

2.2 Balloon- and Airborne observations

2.2.1 Ozonesondes

Ozonesondes are balloon-borne instruments which are used to measure the ozone concentration from the surface up to approximately 35 km with a resolution of about 100 m. They are a reference for the validation of satellite measurements and represent a unique source of information about the vertical atmospheric profile especially in the UTLS where satellite measurements have large uncertainties. Ozonesondes are inexpensive, easily deployable and all-weather sounders. For the validation of ozone profiles from OMPS-LP ozonesonde observations were taken from two archives, the Southern Hemisphere ADDitional OZonesondes (SHADOZ) (Thompson et al., 2007) and the World Ozone and Ultraviolet Radiation Data Centre (WOUDC). The first one is a network involving several sonde stations in the tropics, whereas the second one collects measurements mostly in the extra-tropics and polar regions. Table 2.2 presents a list of all ozonesonde stations used for the validation of the OMPS-LP ozone profiles in this thesis, with corresponding latitude, longitude, number of used profiles and archive which they belong to.

<table>
<thead>
<tr>
<th>Ozonesonde station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>N of profiles</th>
<th>Data archive</th>
</tr>
</thead>
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<td>Neumayer</td>
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<td>351.73</td>
<td>280</td>
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</tr>
<tr>
<td>Syowa</td>
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<td>280</td>
<td>WOUDC</td>
</tr>
<tr>
<td>Davis</td>
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<td>77.97</td>
<td>160</td>
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</tr>
<tr>
<td>Marambio</td>
<td>-64.23</td>
<td>303.38</td>
<td>320</td>
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</tr>
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<td>Ushuaia</td>
<td>-54.85</td>
<td>291.69</td>
<td>80</td>
<td>WOUDC</td>
</tr>
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<td>Macquarie Island</td>
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<td>158.94</td>
<td>260</td>
<td>WOUDC</td>
</tr>
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<td>Lauder</td>
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<td>28.22</td>
<td>100</td>
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<tr>
<td>La Reunion Island</td>
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<td>55.48</td>
<td>190</td>
<td>SHADOZ</td>
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<table>
<thead>
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<th>Longitude</th>
<th>Station</th>
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</table>
2.3. **Satellite observations**

Figure 2.1 shows the locations of the considered sonde stations over the globe, where we visually see that the number of stations is largest at northern mid-latitudes. Hence, the validation results in this latitude region are the most reliable.

![Figure 2.1: Location of the ozonesonde stations used for the validation of the retrieval results.](image)

2.2.2 **Measurements from aircraft**

In addition to airborne observations during dedicated campaigns, commercial aircraft have been exploited to obtain a vertical sampling of the troposphere and lower stratosphere. Two projects are particularly relevant in this field: the Measurement of OZone and water vapour on Airbus In-service airCraft (MOZAIC) and the In-service Aircraft for a Global Observing System (IAGOS) (Petzold et al., 2015). IAGOS builds on the heritage of the former research projects like MOZAIC and the Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC). The system involves the regular collection of in-situ observations of reactive gases, greenhouse gases and aerosol concentrations in the UTLS at high spatial resolution. IAGOS is able to provide vertical profiles of these species over continental sites or regions, many of which are undersampled by conventional ground-based networks.

2.3 **Satellite observations**

Passive satellite remote sensing instruments provide continuous global coverage of the atmosphere; they can be classified in terms of their geometry of observation as nadir, occultation and limb-viewing sounders (Hassler et al., 2014).
2.3.1 Limb and occultation sounders

Both limb and occultation sounders have a line of sight (LOS) that intersects the atmospheric limb, tangentially to the Earth surface.

For occultation measurements, the geometry is fixed by the position of the celestial body selected as a source of radiation: the Sun, the Moon or stars. Radiance from the chosen source is collected after it is attenuated traveling a horizontal ray-path through the atmosphere. The schematic geometry of a solar occultation measurement is shown in Fig. 2.2, in the upper panel. The tangent point (TP), i.e., the lowest point of the LOS which the measurement refers to, and the tangent height (TH), i.e., the geometrical height of the TP above the ground, are indicated. Solar occultation instruments provide the best signal-to-noise ratio (SNR) due to the strength of the light source, enabling the detection of several trace gases without the need for averaging. However, sun/moon occultation measurements can be done only two times per orbit, in correspondence of the sun (or moon) rise and set. The stellar occultation technique provides better coverage compared with sun/moon occultation and since the stars are point source the instrument pointing is excellent.

The viewing geometry of a limb instrument is similar to the occultation one, but the LOS does not point directly toward the light source and its elevation angle is variable, making possible a vertical scan of the atmosphere. Limb-viewing instruments provide a dense sampling along each orbit, measuring hundreds to a few thousand profiles per day. Limb techniques are of two kinds, depending on the spectral region that they exploit: limb scattering and limb emission. In the first case, the sensor collects solar light scattered into the field of view (FOV) of the instrument. In the second case, radiance emitted by atmospheric compounds in the infrared (IR) and microwave spectral regions is collected, so that day and night observations are possible. The vertical resolution is similar for both techniques and the SNR is higher for limb emission instruments, but they are much more expensive, as they require a cooling system for the optics. For limb emission sensors a self-calibration is provided by black bodies onboard or by external targets, whereas for limb-scattering sensors either extraterrestrial solar radiation or a limb measurement at an upper TH are used for normalization. A schematic view of the solar scattering limb geometry is shown in the lower panel of Fig. 2.2. The sensitivity of limb measurements decreases in the lower stratosphere and troposphere, because of the saturation of the measured signal due to the increasing atmospheric optical thickness along the LOS.

The history of solar occultation measurements began in 1978 with the launch of the instrument Stratospheric Aerosol Measurement (SAM)-II, which was followed by SAGE I and II and the Russian occultation spectrophotometer SFM-2. SAGE I measured only for 33 months starting from February 1979, whereas SAGE II worked for 21 years, being launched in 1984. Another milestone in the exploration of the atmosphere from space is the Upper Atmosphere Research Satellite (UARS) launched in 1991, carrying the Halogen Occultation Experiment (HALOE). HALOE performed solar occultation measurements, focusing on several chlorine compounds, and its measurements were used to evaluate the effect of these chemical species on the upper stratospheric ozone. The SCIAMACHY instrument was launched in March 2002 (Burrows et al., 1995; Gottwald and Bovensmann, 2010) onboard Environmental satellite (Envisat). In addition to solar occultation observations, it was able to perform measurements in Nadir
2.3. Satellite observations

geometry (described below) and exploiting the limb-scattering technique. More recently, the Canadian satellite SCISAT was launched in February 2004. On board it carries two solar occultation instruments: the Atmospheric Chemistry Experiment - Fourier Transform Spectrometer (ACE-FTS) and the Measurement of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation (MAESTRO). In addition, the SAGE III instrument was launched in 2001 onboard Meteor-3M and recently installed on the international space station, performing occultation and limb measurements. Stellar occultation measurements were performed by Global Ozone Monitoring by Occultation of Stars (GOMOS), which was onboard Envisat and was able to perform also limb-scattering observations.

Atmospheric measurements using the infrared limb-emission technique started with the Limb Infrared Monitor of the Stratosphere (LIMS) launched in 1978. On board of the UARS platform also the MLS was launched, which performed microwave observations and pioneered the limb sounding of the stratosphere and mesosphere. The successor of this sounder was launched in 2004 onboard the Aura satellite and it is currently in operation (throughout the dissertation it is referred simply as MLS). This instrument is able to measure a variety of trace gases in the stratosphere and its stability made it a reference for later observations. Another limb-emission instrument is the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) onboard Envisat, which was able to collect high-resolution infrared emission spectra of a large number of atmospheric constituents. Another two currently operating instruments are the Sub-Millimeter Radiometer (SMR) onboard the Odin satellite and the Sounding of the Atmosphere using Broadband Emission Radiometry (SABER) on Thermosphere Ionosphere Mesosphere Energetics Dynamics (TIMED).
Chapter 2. Stratospheric ozone measurements

Focusing on the shortwave limb scatter technique, it was for the first time successfully exploited by the research mission Solar Mesospheric Explorer (SME), launched in 1983, which was preparatory for the NASA Limb Ozone Retrieval Experiment/Shuttle Ozone Limb Sounding Experiment (LORE/SOLSE) instrument launched in 1997. Two instruments followed at the beginning of the century: the Optical Spectrograph and Infra Red Imaging System (OSIRIS) launched in February 2001 (Llewellyn et al., 1997) and the SCIAMACHI instrument. At the end of 2011, a few months before the end of Envisat lifetime, the Ozone Mapping and Profiler Suite (OMPS) was launched and it is still operational (Flynn et al., 2014).

Stratospheric ozone profiles are currently monitored by limb sounders like the aging OSIRIS, MLS, SAGE III limb and OMPS-LP.

2.3.2 Nadir sounders

Nadir observations are characterized by a LOS which points towards the sub-satellite point. The vertical resolution, typically of about 6 km, is achieved exploiting the varying atmospheric optical depth as a function of wavelength or the pressure broadening of spectral lines. Their horizontal spatial resolution is the highest compared to limb sounders, providing full global coverage of the Earth daily (Harris et al., 2015). Besides, due to the shorter light path in comparison with limb sounders, they can observe lower into the troposphere.

The first measurement of atmospheric ozone from space was made in nadir geometry by the Soviet space program in the middle of the 1960s. In the early 1970s, NASA initiated its efforts to perform global measurements of atmospheric ozone with the Backscatter Ultraviolet Radiometer (BUV) instrument aboard the NASA Nimbus 4 satellite. This instrument was significantly enhanced and extended with the launch of the SBUV and the Total Ozone Mapping Spectrometer (TOMS) in 1978, which flew on NASA’s Nimbus 7 satellite. These measurements continued with other TOMS and SBUV/2 instruments onboard several National Oceanic and Atmospheric Administration (NOAA) satellites, leading to the longest available satellite-based ozone record, reaching the present day.

The ESA’s Global Ozone Monitoring Experiment (GOME) launched in 1995 was the first European satellite instrument measuring total ozone in the UV-Vis spectral range and complemented the American efforts. Follow-up satellite instruments of the GOME mission are SCIAMACHY (in nadir geometry) and the Ozone Monitoring Instrument (OMI) a Dutch–Finnish sensor on the NASA Aura satellite launched in 2004, which continued the TOMS total ozone column record. An interesting aspect of OMI is also its synergy with instruments onboard Envisat and with GOME missions. In 2006 the UV-Vis spectrometer GOME-2 was launched, first of a series of three operational MetOp missions, which are planned to monitor stratospheric ozone at least until 2020. In addition, since the beginning of 2012, the Nadir Mapper and the Nadir Profiler as part of the OMPS suite have been collecting observations (McPeters et al., 2019). Recently, the TROPOspheric Monitoring Instrument (TROPOMI) was launched in 2017 onboard Sentinel-5P as a successor of OMI. It is a spectrometer measuring in several spectral bands from UV to shortwave IR with unprecedented spatial resolution. It is part of a long-term ESA project which will see several satellite platforms flying in the next decades (Berger et al., 2012).
2.3. Satellite observations

2.3.3 Short description of relevant instruments

A short description of the four instruments used in this work follows: SAGE II, SCIAMACHY, MLS and OMPS. A detailed description of OMPS-LP follows in Ch. 3.

**SAGE II**

SAGE II was launched onboard the Earth Radiation Budget Satellite (ERBS) in October 1984 and operated until August 2005 (McCormick, 1987). The instrument was a sunphotometer collecting solar radiance attenuated by the atmosphere in seven spectral channels using the occultation geometry. As discussed above, observations of SAGE II are sparse in comparison to the other limb sounders, because measurements are possible only twice per orbit, resulting in 30 observations per day. Owed to the high SNR obtained using the solar occultation technique, SAGE II ozone profiles are retrieved with a vertical sampling of 0.5 km and a resolution of 1 km from cloud top to 60 km. In this study, version 7.0 of SAGE II level 2 (L2) data have been used (Damadeo et al., 2013).

**OMPS**

The OMPS instrument suite was launched on the Suomi National Polar-orbiting Partnership (SNPP) satellite platform in October 2011 and started to collect data in February 2012. The spacecraft is in a sun-synchronous orbit with a nominal equator crossing time at 13:30 in the ascending mode. The suite consists of three sensors: the Nadir Mapper, the Nadir Profiler and the Limb Profiler (LP). For a review of the whole suite refer to Flynn et al. (2014). In the following, only the Limb Profiler is discussed and referred to as OMPS-LP. The OMPS-LP sensor looks at the Earth limb in the opposite direction with respect to its flying direction as depicted in Fig. 2.3, showing the instrument geometry. Radiance is collected through three vertical slits. The central one is aligned with the ground track, while the other two are separated across-track by 4.25°, corresponding to 250 km distance between the TPs. Each slit covers a vertical range of about 100 km to include under all conditions the 10 - 65 km range of interest. The sensor performs 180 observations per orbit (around 160 with solar zenith angle less than 80°) and completes 14-15 orbits per day. The instrument measures limb scattered radiance in the spectral range between 280 and 1000 nm, with an instantaneous field of view of about 1.5 km and a sampling of 1 km. The spectral resolution varies from 1 nm in the UV to 40 nm in the NIR as described in the next chapter.

**SCIAMACHY**

The SCIAMACHY instrument was launched onboard the ESA Envisat satellite in March 2002, collecting observations from August 2002 to April 2012, when a platform-to-ground communication failure occurred. The satellite has a sun synchronous orbit with 10:00 equatorial crossing time. Its primary mission objective was to perform global measurements of trace gases in the troposphere and in the stratosphere in limb, nadir and occultation geometries (Burrows et al.,
Chapter 2. Stratospheric ozone measurements

In the limb mode, SCIAMACHY observed the atmosphere in the flight direction, scanning horizontally 960 km across-track, and vertically every 3.3 km. The instantaneous FOV was equal to 2.6 km. The instrument was able to measure radiance in 8 spectral channels, covering the 240-2380 nm range, with a spectral resolution varying from 0.22 to 1.48 nm depending on the channel.

### MLS

The MLS instrument onboard the Aura satellite has been performing measurements since July 2004, with a 13:45 local equator crossing time at the ascending node. It observes in limb geometry the thermal emission from atmospheric trace gases in the millimeter/sub-millimeter spectral range. MLS is equipped with heterodyne radiometers operating at ambient temperature in 5 spectral ranges (Waters et al., 2006). It scans the Earth limb 240 times per orbit enabling the retrieval of several gases including ozone during day- and night-time. The instrument has a broad latitude coverage, performing each orbit measurements within [82°S, 82°N]. Version 4.2 of MLS L2 data is considered in this work for validation of OMPS-LP ozone profiles and as a transfer function in the SCIAMACHY/OMPS-LP merging procedure. Quality flags and recommendations reported in Livesey et al. (2017) are taken into consideration throughout the study. A validation of MLS stratospheric ozone profiles can be found in Froidevaux et al. (2008).
Chapter 3

OMPS Limb Profiler

In this chapter, a more detailed description of the Limb Profiler instrument is provided. In particular, the next three sections introduce the radiance collection technique, the instrument pointing and stray light, which may affect the observations, and the measurement geometry of the sensor.

3.1 General features

To collect spectrally resolved radiance from the atmospheric limb, the OMPS-LP sensor employs a prism in the spectrometer unit. The prism dispersion provides a higher spectral resolution of about 1 nm in the UV region and a lower resolution of up to 40 nm in the near IR. This quite poor resolution prevents the retrieval of trace gases such as NO$_2$, but it is suitable for ozone spectroscopy and the retrieval of aerosol parameters (Jaross et al., 2014). The sensor images the whole Earth limb without the need of a scanning mirror. A 2-D charge-coupled device (CCD) is used to collect radiance so that the spectrally dispersed photons and their vertical distribution are simultaneously captured (Bhartia et al., 2013). On the other hand, the use of such a technique poses a challenge in terms of the SNR: in fact, the Earth limb scattered radiance decreases by at least five orders of magnitude over the altitude range, due to the decreasing particle density (Jaross et al., 2014). As a consequence, in order to cover the required dynamic range, four sensor ‘gains’ are used: the atmospheric scene is observed for 19 s collecting interleaved images at two integration times, which differ by a factor 30, and through a large and a small aperture (Rault and Loughman, 2013). Then, as the download rate is by far slower than the data collection rate, only a selected number of pixels from these 4 images are downloaded. The ground processing selects the unsaturated pixels and combines them into a single matrix. The reconstructed and combined image has a non-uniform wavelength and grid (spectral and vertical smiles), and it has to be re-sampled and mapped onto a regular grid, more useful for the final user, to get level 1 gridded (L1G) data. The gridding procedure employs a bi-linear interpolation. Pixel-to-pixel calibration errors linked to this consolidation procedure are estimated to be around 1%. Examples of radiance profiles, which also show the large dynamic range of the measured values, are displayed in Fig. 3.1 panel (a). As radiance measured at large and small aperture can differ by several percents, radiance profiles at a specific wavelength are derived from one aperture only. On the contrary, radiance collected at long and short integration times does not show statistically significant differences, so that a switch between the two
images is done in the middle stratosphere, depending on the wavelength (Jaross et al., 2014). These changes of the sampled image are clearly visible in the SNR displayed in panel (b) of Fig. 3.1 for example, the jump at 450 nm (fixed threshold) between large and small aperture.

**Figure 3.1:** Panel (a): example of OMPS-LP radiance profiles at some selected wavelengths; panel (b): OMPS-LP SNR at different THs.

### 3.2 Main issues: pointing and stray light

The pointing of the instrument has to meet strict requirements as it is one of the most critical issues affecting the quality of the limb scattering technique. To retrieve reliable ozone profiles, the TP altitude has to be known with high precision: for example, a 1 km uncertainty in the TP height translates into a 10-20 % error in the ozone profile (Loughman et al., 2005). The high pointing accuracy requirement cannot be directly met for OMPS-LP sensor, because the star-tracker on board the SNPP satellite is mounted on a distant position from the instrument. As a consequence, misalignments of the instrument focal plane and thermal effects play a relevant role.

To solve this problem, several pointing corrections are established in the L1G data processing, as described in Moy et al. (2017). First, static corrections were implemented independently for each slit, to account for a ground-to-space shift between star tracker and sensor. The values of these corrections are between 1 and 2 km, depending on the slit. The spacecraft bus is affected by a thermal flexure which causes seasonally and latitudinally dependent variations of the sensor pointing, as the relative position of the star tracker and the instrument changes. On top of this, as described by Jaross et al. (2014), the thermal sensitivity of the instrument itself causes additional vertical and spectral shifts in the data. The associated TH error in the pointing is estimated to reach values up to 500 m in the Northern Hemisphere. The optical path is indeed modified due to the warp of the instrument structure, depending on the solar heating. Additionally, using the Absolute Radiance Residual Method (ARRM) technique, Moy et al. (2017) detected two jumps in the pointing of the instrument of 100 m for all the slits on 25 April 2013 and 5 September 2014.
3.3 OMPS-LP observation geometry

The static corrections and the jumps in the pointing are accounted for in the current version 2.5 of L1G data. On the contrary, as a satisfactory explanation for the seasonally and latitudinally dependent variations still has to be found, this issue is currently accounted for during the L2 processing. Following NASA recommendations in (Kramarova et al., 2018), we implemented the TH corrections provided by the NASA team in the retrieval process. These corrections do not account for a possible long term drift, but vary seasonally and are provided as daily values as a function of the sequential observation number within the orbit. Their magnitude is about +300 m at the South Pole and up to -100 m at high northern latitudes.

The second important issue that affects the registration accuracy of the limb radiance is the so-called stray light. The general phenomenon of stray light describes photons that are registered by the detector at wavelengths or altitudes which they do not belong to. For example, as limb scattering is proportional to the air density, photons from lower altitudes can be scattered within the instrument to the detector areas associated with different altitudes or wavelengths. Furthermore, with multiple images on a single detector, photons from the IR part of one slit can be scattered into the UV part of the neighboring image. This problem is discussed in Jaross et al. (2014) and was reduced at the instrument level with the application of cutoff filters at the focal plane, and with a thorough study of the point spread function during pre-launch operations. The full detector response to several point sources was extensively studied during ground testing: a stray light matrix was created, providing the basis for subtracting the stray light contribution from the measured limb radiance. Stray light is an issue mainly at high altitudes, with levels that are usually less than 10% of the measured value and tend to increase with altitude for the same wavelength (Jaross et al., 2014).

The CCD used for OMPS-LP photons detection operates at −45° to minimize dark current and other noise sources. Dark current and non-linearity of the sensor are corrected accurately and introduce minor errors in the reported radiance. In addition, transient events can affect the instrument reliability: energetic charged particle can penetrate through the CCD shield and cause transients in pixel signals. Such events are particularly frequent in the so-called South Atlantic Anomaly (SAA). A related quality flag is reported in L1G data and used for the validation and merging.

3.3 OMPS-LP observation geometry

To describe the limb geometry within the radiative transfer model, several angular fields are necessary: satellite azimuth ($\phi_{sat}$), solar azimuth ($\phi_{sun}$) and zenith angles ($\psi$) at the TP. These three angles are reported in L1G OMPS-LP data at three THs: 25, 35 and 45 km. The solar zenith angle ($\psi$) is defined as the angle between the normal to the surface at the TP and the sun pointing vector. The azimuth angles ($\phi$) are the angles between the direction to the North Pole and the projection of the vector pointing to the sun (or to the satellite) on the plane orthogonal to the normal vector at the TP. By convention, positive angles are East of the North so that values are within the [-180, 180] range. Of our interest, is the relative azimuth angle between the vector

\[\text{i.e., the same for all orbits of the day.}\]
pointing to the sun and to the satellite, which is used by SCIATRAN to set the geometry:

\[ raa = \varphi_{Sat} - \varphi_{Sun} \]  

(3.1)

A depiction of the azimuth angle definitions is displayed in Fig. 3.2, where the cube represents the satellite and the star identifies the sun. The angles lie in a plane orthogonal to the normal vector at TP.

![Figure 3.2](image)

**Figure 3.2**: Example of azimuth angles and \( raa \) in a plane orthogonal to the normal vector at TP. The vector pointing the sun and the satellite are projected onto this plane.

An important quantity which defines the geometry of observation is the scattering angle, which combines zenith and azimuth angles as follows:

\[ \cos(\theta) = \sin(\psi) \cos(\varphi_{sat} - \varphi_{sun}) \]  

(3.2)

In Fig. 3.3 the values of scattering angles together with solar zenith angles (SZAs) are plotted as a function of latitude for three OMPS orbits in different seasons. SZAs are shown as solid lines, with symmetric values with respect to the equatorial region and shifting according to the seasons, whereas scattering angles are plotted as dashed lines, decreasing along the orbit. Only SZAs less than 80° are plotted and the ozone retrieval is run only for the corresponding states, usually 140 per orbit, to avoid high stray light levels.

Within the SCIATRAN model, the angles are recalculated to the sub-satellite point (SSP). An example of SZA and relative azimuth angle (RAA) at the TP, the TOA and the SSP are shown in Fig. 3.4, considering only SZA less than 80°.
3.3. OMPS-LP observation geometry

**Figure 3.3:** SZA (solid lines) and scattering angles (dashed lines) at the TP along three OMPS orbits on the following dates: 1 July 2016, 1 October 2016 and 1 January 2017.

**Figure 3.4:** SZA and RAA at TP, TOA and SSP for the 03 March 2015, orbit 22705.
Chapter 4

Retrieval of ozone profiles from OMPS-LP observations

4.1 Ozone profile retrieval algorithm

The algorithm used to retrieve ozone profiles from OMPS-LP measurements has been developed based on the SCIAMACHY v3.0 ozone retrieval (ozonesondes in Jia et al. (2015)). A direct application of the SCIAMACHY retrieval algorithm to OMPS-LP observations is not possible because of a very different spectral resolution of the two instruments. In addition, the measurements differ in terms of spectral channels, radiance collection technique, and atmospheric sampling. Even though the algorithm has been newly developed, the same radiative transfer model (SCIATRAN, Rozanov et al. (2014)) and a similar retrieval approach are used. Besides, the spectroscopic and atmospheric parameter databases are the same in order to minimize the systematic errors between the data sets.

4.1.1 Theoretical background

This section was partially published in Arosio et al. (2018).

The retrieval of ozone profiles from OMPS-LP observations is performed using the regularized inversion technique with the first order Tikhonov constraints (Tikhonov, 1963; Rodgers, 2000). An iterative approach is implemented to account for the non-linearity of the inverse problem. The forward modeling takes into account the atmospheric multiple scattering in the framework of the approximate spherical solver of the SCIATRAN radiative transfer model (Rozanov et al., 2014). In particular, SCIATRAN 4.0 was used for the final processing of the data. The radiative transfer equation is solved using the combined differential-integral (CDI) approach (Rozanov et al., 2001): first, the entire radiation field is calculated in the pseudo-spherical approximation for a set of solar zenith angles using the finite difference method. Pseudo-spherical approximation means that the direct solar beam is traced in a fully spherical geometry while a plane parallel atmosphere is assumed to calculate the scattered light. Then, the integration along the line-of-sight is carried out in spherical geometry, i.e., intersecting a spherical shell atmosphere, accounting also for the atmospheric refraction. At this point, the single scattering contribution is calculated fully-spherically whereas the multiple scattering contribution at each point along the line of sight is approximated by an angular integration of the pseudo-spherical radiative
field calculated at the first step (Rozanov et al., 2000). Weighting functions are calculated using the same method as for the radiance but considering only the single scattering contribution. Discussing inverse problems, it is common practice to introduce the notions of measurement vector $\vec{y}$, which contains the measured quantities, and of state vector $\vec{x}$, which describes the unknown atmospheric state. The relationship between the measurement vector and the state vector can be formally expressed as:

$$\vec{y} = F(\vec{x}) + \vec{\epsilon}$$

(4.1)

where $F$ is the forward model, which contains our understanding of the physics of the measurement, and $\vec{\epsilon}$ represents errors of any kind. Linearizing the forward model around an initial guess state $\vec{x}_0$, the general equation that has to be solved can be written as:

$$\vec{y} = \vec{y}_0 + K(\vec{x} - \vec{x}_0) + \vec{\epsilon}$$

(4.2)

where $\vec{y}_0$ is the simulated spectrum and $K$ is the linearized forward model operator represented by the weighting function matrix. Each element of $K$ is defined as:

$$K_{ij} = \frac{\partial F_i}{\partial x_j}$$

(4.3)

Following Rodgers (2000), the solution of Eq. 4.2 can be estimated iteratively. Taking into account that in our algorithm the retrieval is performed from a zero a priori profile, the iterative step $i + 1$ can be expressed as:

$$\vec{x}_{i+1} = \left( K^T S^{-1} \vec{\gamma} S_1 + S_0 + S_1^T \vec{\gamma} S_1 \right)^{-1} K^T S^{-1} \left( \vec{y} - \vec{y}_i + K_i \vec{x}_i \right)$$

(4.4)

Here, $S_\epsilon$ is the measurement noise covariance matrix. $S_0$ is the diagonal matrix optimized to constrain the solution within physically meaningful values and minimize a possible negative bias caused by the use of a zero a priori profile. The effect of the chosen matrix is significant only at low tropical altitudes and globally at high altitudes, where the ozone concentration is very small. Finally, $S_1$ is the first order derivative matrix ($S_1^T \vec{\gamma} S_1$ is the first order Tikhonov term). The diagonal matrix $\vec{\gamma}$ contains altitude dependent weights, used to constrain the smoothness of the retrieved profile. In the following, the sum $S_0 + S_1^T \vec{\gamma} S_1$ will be referred to as $S_r$.

### 4.1.2 Preliminary tests

To illustrate the different spectral resolutions of SCIAMACHY and OMPS-LP and how the smoothness of the ozone spectroscopic features changes, Fig. 4.1 shows the ozone cross section at 203 K at SCIAMACHY high resolution and convolved to OMPS resolution in two spectral regions. Spectral ranges characterized by strong ozone absorption are located both in the UV and Vis regions of the spectrum. In particular, three are the most important absorption regions (see e.g. Salby, 2012): the Hartley band from 200 to 310 nm, the Huggins band from 305 to 400 nm and the Chappuis band from 450 to 850 nm. The former two ranges are sensitive to the upper
stratospheric ozone, whereas the latter to the lower stratospheric region, where the peak of the number density occurs. Referring to OMPS-LP spectral ranges, we can exploit wavelengths starting from 290 nm in the UV, whereas the Chappuis band is restricted in our case to 500-670 nm, where the ozone absorption is strong.

Several preliminary tests have been performed to assess the influence of the parameters involved in the retrieval. For this purpose, the residual fits and the weighting functions are analyzed. In addition, a direct comparison with NASA ozone profiles, considered at this stage as a reference, is also carried out and shown in the next plots. This helps to draw the attention at altitudes where the discrepancies are particularly large, and guides the choice of some parameters. In the following plots, ozone profiles averaged over the tropical latitude band (that is within 20° S and N) are analyzed. Ozone profiles are plotted in terms of VMR as a function of altitude (and identified as IUP/OMPS in the captions) with the shaded areas indicating the standard deviations. The number of considered OMPS-LP profiles as a function of altitude is indicated on the right side of each plot.
Chapter 4. Retrieval of ozone profiles from OMPS-LP observations

In Fig. 4.2 ozone relative weighting functions are plotted at several wavelengths within three spectral ranges used in the retrieval. In panel (a) the Hartley band up to 302 nm is considered and we notice that the sensitivity to ozone above 55 km decreases even at 290 nm, so that we expect the retrieval above this altitude to be less reliable. In panel (b) the weighting functions in the Hartley/Huggings band up to 312 nm are shown: the peaks of the weighting functions move downwards as the wavelength increases, covering the range between 35 and 45 km. In the Chappuis band, panel (c), we notice that the sensitivity to ozone below 15 km drops quickly, indicating that the retrieval in the lowermost stratosphere is affected by the chosen regularization parameter and the first guess profile.

![Figure 4.2: Examples of ozone relative weighting functions in three spectral ranges and at several wavelengths within each range, for a measurement in the tropics.](image)

In Fig. 4.3 the sensitivity of the retrieval scheme to two important retrieval parameters is shown: in the left panel different polynomials are subtracted from the UV and Vis spectral ranges, keeping constant all the other settings. Substantial differences are visible, particularly at 30 km and at the higher altitudes, where the values change up to 20 % depending on the chosen order of the polynomial. We found that subtracting a first-order polynomial, i.e., considering the differential structure in the Chappuis band, helps in avoiding jumps at the junction between spectral ranges around 35 km. In the right panel three values for the Tikhonov regularization parameter are used, differing by one order of magnitude. As expected, with the decrease of this parameter, the profile gets less smooth, the standard deviation increases and the retrieved profile is more free to depart from the a priori profile. On the other hand, artificial oscillations appear at several altitudes, especially at 30-40 km, indicating that the retrieval is not enough constrained. Different values of this parameter are chosen as a function of altitude in the final algorithm, in order to avoid oscillations, especially at low and high altitudes where the retrieval sensitivity to ozone is the lowest, and to give enough freedom to depart from the a priori profile at the other altitudes.
4.1. Ozone profile retrieval algorithm

In Fig. 4.4 the consequences of the different usage of the spectral information from the Hartley-Huggins bands on the retrieval profiles are shown. In particular, the left panel illustrates the usage of the entire spectral range between 290 nm and 313 nm between 39 and 60 km in comparison to splitting this interval into the Hartley band up to 302 nm and the Huggins band between 305 and 313 nm. For the latter band, the normalization TH is lowered from 62 km to 52 km. As it can be seen comparing the two profiles with the NASA retrieval, the use of a single spectral range leads to higher values between 40 and 45 km, while a good agreement with NASA results is seen in the second case. In the right panel, the altitude range over which the Hartley band from 290 to 302 nm is used to retrieve ozone is shifted downwards. The vertical range over which the information from the Huggins band is used is accordingly adjusted so that the upper TH from the Huggins band corresponds to the lower TH from the Hartley band. Looking at the weighting function plot, Fig. 4.2, we infer that around 45 km there is enough sensitivity to retrieve ozone using wavelengths from the Huggins band for wavelengths longer than 305 nm so that the switch between the two bands in the final algorithm version occurs around 46-47 km.

Figure 4.5 shows the sensitivity of the retrieved profiles to the Chappuis and Huggins bands. In the left panel, the Huggins band is considered in three different ways: in one case information from two spectral segments (315-320 and 322-331 nm) is used at different altitudes, while in the other cases only one of these two ranges is used. These spectral ranges are exploited to retrieve ozone between 32 and 37 km. We notice that using both ranges or just the longer wavelengths gives very similar results, while omitting the 322-331 nm at these altitudes leads

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Profiles refer to the 01 June 2015, orbit 18612.
Chapter 4. Retrieval of ozone profiles from OMPS-LP observations

**Figure 4.4:** IUP-OMPS ozone profiles in terms of VMR averaged over the tropical region for different usages of the Hartley band in the left panel and the altitude ranges used for the Hartley band in the right panel. In black, the NASA profiles are reported for direct comparison.

To a substantial reduction at 35 km, especially in comparison with the NASA profile. As a consequence, only the 320-331 nm range is used in the final version of the retrieval. As it follows from Fig. 4.2, the retrieval sensitivity to ozone in the Chappuis band extends up to at least 35 km. In the right panel of Fig. 4.5 the upper altitude for the usage of the Chappuis band is shifted upwards, from 32 to 38 km and at the same time also the Huggins band is accordingly modified, i.e., the lower altitude is shifted upwards. This results in an ozone variation at these altitudes larger than 10%. The region around 35 km is particularly problematic in terms of vertical resolution as we will see in Sect. 4.1.4, discussing the algorithm characterization. A careful study of merging the information between Chappuis and Huggins bands was performed to get a reasonable vertical resolution and low residual fits.

In Fig. 4.6 fit residuals in the Chappuis band are displayed. This discussion guides the choice of the altitude range over which information from this spectral band should be used in the retrieval. As we notice, above 30 km the measured spectrum gets more noisy at these wavelengths and the residuals tend to increase in absolute values, suggesting the use of the Chappuis band below 30-32 km.

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2Profiles in the left panel refer to the 03 May 2016, orbit 23399, and in the right panel to the 01 June 2015, orbit 18612.
4.1. Ozone profile retrieval algorithm

4.1.3 Final algorithm setup

After the preliminary studies, the final version of the ozone retrieval for OMPS-LP observations was established. Four spectral segments are selected: three in the Hartley and Huggins bands and one in the visible spectral range. We have to take into account the presence of water vapor and O₂ absorption features in the Chappuis band so that wavelengths in the intervals 585.0-605.0 nm and 620.0-635.0 nm are rejected. The treatment of these absorption features requires line-by-line calculations, which are computationally expensive to be implemented for the whole time series. Considering the decreasing sensitivity above 55 km and the saturation of limb signal in the lower stratosphere, the retrieval of ozone profiles is performed over the altitude range between 12 and 60 km, with the lower boundary that can be higher in the presence

Profiles in the left panel refer to the 03 August 2016, orbit 24702, and in the right panel to the 01 June 2015, orbit 18612.
of a cloud, as described in Sect. 4.2. An evenly spaced vertical grid spans this vertical range with steps every 1 km.

The measurement vector $\vec{y}$ consists of the logarithms of the normalized limb radiances. In detail, OMPS-LP spectrum in the four spectral segments at each altitude is normalized by a limb measurement at an upper TH. This provides a self-calibration of the instrument, by removing the need for solar irradiance measurements, and reduces the effects of surface/cloud reflectance uncertainties (Flittner et al., 2000). Table 4.1 lists the details about spectral segments and the used normalization altitudes.

As given by Eq. 4.5, for each $j$-th TH a polynomial is subtracted from the logarithm of the normalized radiance to remove slowly variable spectral features, for example, related to Rayleigh or aerosol scattering (Rozanov et al., 2011). The last column of Table 4.1 provides information about the order of the polynomial subtracted: zeroth order or no polynomial in the UV region and first order for the Chappuis band.

$$\vec{y}_j = \log \left( \frac{I_{TH,j}}{I_{TH,norm}} \right) - \vec{P}_n$$

Table 4.1: List of the spectral segments considered for the ozone retrieval with corresponding TH ranges, altitudes used for the normalization and order of the subtracted polynomial ( - means that no polynomial is subtracted).

<table>
<thead>
<tr>
<th>TH range [km]</th>
<th>Spectral segment [nm]</th>
<th>Norm. TH [km]</th>
<th>Poly. order</th>
</tr>
</thead>
<tbody>
<tr>
<td>48-60</td>
<td>290-302</td>
<td>63.5</td>
<td>-</td>
</tr>
<tr>
<td>34-49</td>
<td>305-313</td>
<td>51.5</td>
<td>-</td>
</tr>
<tr>
<td>28-39</td>
<td>321-330</td>
<td>51.5</td>
<td>0</td>
</tr>
<tr>
<td>12-31</td>
<td>508-660 †</td>
<td>42.5</td>
<td>1</td>
</tr>
</tbody>
</table>

† 585.0-605.0 and 620.0-635.0 nm ranges are rejected.

As $O_3$, $NO_2$ and $O_4$ have relevant spectral signatures in the selected spectral ranges, the radiation field in the forward model is calculated, taking into account these three gases. The respective cross-sections are taken from Serdyuchenko et al. (2014), Bogumil et al. (2000) and Hermans (2011), and are beforehand convolved to the OMPS-LP spectral resolution. Ancillary information about the temperature and pressure profiles for each OMPS-LP observation is provided in L1G files, from the Global Modeling and Assimilation Office (GMAO). A climatology profile is adopted as first guess for ozone, using the McLinden climatology (C. McLinden, Meteorological Service of Canada, private communication).

Before the main retrieval, a spectral correction is applied in the Chappuis band to take into account issues related to the spectral calibration and a possible thermal expansion of the sensor. This correction consists in a shift and squeeze of the modeled spectrum relative to the measured one. This pre-processing procedure is applied independently for each observation at each TH between 12 and 31 km. The differential absorption structure in the Huggins band is mostly not resolved in OMPS-LP spectra, due to the relatively low spectral resolution of the sensor, as can

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4The cross section can be found at http://satellite.mpic.de/spectral_atlas/cross_sections/Oxygen/O4_Hermans (2011)_298K_335.59-666.63nm.txt
be seen in Fig. 4.1. As a consequence, the UV retrieval uses either normalized radiances or their slopes and the influence of a possible spectral misalignment is not expected to be significant; thus, the shift and squeeze algorithm is not applied.

Typical values of the spectral shift are inside the range $[+1, +4]$ nm for the first point of the interval and $[-2, +1]$ nm for the last spectral point. An example of the pre-processing results for the 15 March 2016 are reported in Fig. 4.7 which displays the values of the squeeze parameter, i.e., the difference between the shift parameter at the beginning and at the end of the Chappuis band, as a function of the state number for all the orbits in that day. We see a pretty constant behavior with values around zero at the beginning of the orbit, turning negative around the tropics and increasing towards northern mid-latitudes at the end of the orbits.

![Figure 4.7: Squeeze parameters obtained at the pre-processing step for all the orbits on the 15 March 2016.](image)

Similar behavior as a function of latitude was also found in September. During summer at the end of the orbit, strong negative values abruptly appear, while in winter months a substantial variability between consecutive OMPS-LP states was detected in the last part of the orbit.

For all spectral ranges, the $S_e$ matrix is obtained at this stage from the fit residuals, after all the relevant gases in the selected spectral windows have been fitted. The noise to signal ratio is taken as the root mean square of the fit residuals and fed into SCIATRAN. The inversion scheme is then implemented as described by Eq. 4.4. The state vector $\mathbf{x}_{i+1}$ contains the retrieved ozone vertical distribution at each $i$-th iteration expressed in terms of VMR. The smoothing weights, i.e., square roots of the diagonal elements of $\mathbf{\gamma}$, linearly increase with the height above 45 km, remain constant between 20 and 45 km, and increases again towards lower altitudes.

Surface albedo is retrieved simultaneously, by assuming a Lambertian surface and using the sun-normalized radiance from the L1G data set. For the albedo retrieval, we selected two spectral ranges at THs around 38 km: 350-365 nm and 445-455 nm, where ozone absorption is weak. Figure 4.8 shows the results of the Lambertian surface albedo retrieval for one orbit: 22705 on the 15 March 2016. A direct comparison with the NASA surface reflectance at 524 nm product for the same orbit is reported. Generally, the values are in good agreement, even though IUP-OMPS albedo happens to give very low values over some parts of the ocean.
Chapter 4. Retrieval of ozone profiles from OMPS-LP observations

**Figure 4.8:** Retrieved surface albedo values in the Vis spectral range in comparison with NASA surface reflectance at 524 nm, for the orbit 22705 on the 15 March 2016.

Additional TH corrections are applied accordingly to NASA recommendations as described in Ch. 1 and DeLand et al. (2017): the effect of these pointing corrections is illustrated in Fig. 4.9, where the relative differences between two versions of the IUP-OMPS data set averaged over the entire 2016 are shown as a function of latitude and altitude. The two retrieval versions differ only due to the applied TH corrections (and some settings which affect only the lower levels): focusing on the altitudes above 30 km, we can see that the differences are positive in the Southern Hemisphere and negative towards northern mid-latitudes, compensating the hemispheric asymmetry of the pointing.

**Figure 4.9:** Relative differences between IUP-OMPS retrieved profiles obtained including and excluding the additional TH corrections. The figure refers to the 2016 data set.
4.1.4 Retrieval characterization

This section was partially published in Arosio et al. (2018).

The information content of the measurements as well as the sensitivity of the retrieval can be analyzed using the averaging kernels \((A)\) and the retrieval noise covariance matrix \((S_m)\) obtained respectively as (Rodgers, 2000):

\[
A = \left( K^T S_e^{-1} K + S_r \right)^{-1} K^T S_e^{-1} K \\
S_m = \left( K^T S_e^{-1} K + S_r \right)^{-1} K^T S_e^{-1} K \left( K^T S_e^{-1} K + S_r \right)^{-1}
\]

The square root values of the diagonal elements of the matrix \(S_m\) will be referred to as the retrieval noise uncertainties\(^5\). The vertical resolution of the retrieved profile is computed as the inverse of the diagonal elements of the averaging kernel matrix, multiplied by the altitude layer width. Examples of averaging kernels, vertical resolution and retrieval noise uncertainty are plotted in Fig. 4.10.

\(^5\)Also referred to as theoretical precision of the retrieval.

\(^6\)AKs do not change significantly with time and latitude, so that this plot can be considered illustrative of the typical AKs.

\[\text{Figure 4.10: From left to right, examples of averaging kernels (plotted every 4 km for the sake of clarity), vertical resolution and noise uncertainties of the retrieval scheme. AKs are plotted for a measurement at 30° N, whereas vertical resolution and retrieval noise uncertainties are shown as a function of the latitude, i.e., solar zenith angle, for one day (15 September 2016).}\]

The left panel shows averaging kernels (AKs) for an example profile at 30° N\(^6\). For the sake of clarity, only each fourth AK is plotted. The middle and right panels show the latitudinal dependence of the vertical resolution and the retrieval noise uncertainty, respectively, for one day of OMPS-LP measurements (15 March 2016).

Below 30 km, the actual vertical resolution of the retrieval scheme is typically about 2.5-3 km getting worst around 33 km, where the transition between UV and Vis spectral ranges occurs. The best vertical resolution of the profiles is achieved around 45 km, whereas above 50 km it gets coarser, due to the increasing Tikhonov parameter. The retrieval noise uncertainty associated with the ozone profiles does not show any significant dependence on the solar zenith
angle (or latitude) above 25 km. It lies in the range of 1-4% up to 60 km and tends to increase at lower altitudes, particularly in the tropical UTLS; at these levels, the ozone concentration drops significantly and the retrieval sensitivity gets lower, with relative uncertainties up to 10-30%.

When averaging several profiles, the statistical (or random) component of the uncertainty is expected to be reduced. For example, if we considered 10000 profiles, each of them with a retrieval noise uncertainty of 30%, the resulting error on the averaged profile would be equal to 0.3%. Therefore, when the results of the validation of OMPS-LP profiles with other instruments are analyzed, the retrieval noise error is rather negligible, as we deal with thousands of measurements. On the contrary, the systematic component of the uncertainty is important, as it does not average out when considering a large number of profiles.

4.1.5 Parameter error estimation

Several synthetic simulations are performed in order to assess the impact of parameter uncertainties on the retrieved ozone profiles. This error component is associated with the assumed knowledge about the atmospheric state within the retrieval iterations, e.g., the temperature and pressure profiles assumed as fixed parameters. It can be both random and systematic, depending on the nature of the uncertainties on the parameters. We are going to assume random uncertainties on the parameters, so that parameter errors here reported are also random. However, by using synthetic retrievals, it is also possible to evaluate a component of the systematic retrieval uncertainty, as explained below.

The following parameters are taken into account: surface albedo, aerosol extinction profile, TH registration, pressure and temperature profiles. These parameters were also identified by Rahpoe et al. (2013) as relevant to assess the uncertainty of limb ozone retrievals. For each parameter, a reasonable value of its uncertainty is estimated and used to generate perturbed scenarios. Table 4.2 indicates the five considered parameters and the values of their respective estimated uncertainties.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albedo</td>
<td>±0.1</td>
</tr>
<tr>
<td>Temperature</td>
<td>±2 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>±2%</td>
</tr>
<tr>
<td>Aerosol</td>
<td>±40%</td>
</tr>
<tr>
<td>TH</td>
<td>±100 m</td>
</tr>
</tbody>
</table>

In order to study the parameter errors as a function of latitude, one OMPS-LP orbit (22705) on the 15 March 2016 is chosen. In particular, ten states are selected along the orbit every 20° latitude. In Table 4.3, the latitudes and scattering angles for the OMPS-LP states used for the sensitivity studies are reported.

<table>
<thead>
<tr>
<th>Latitude [°]</th>
<th>Scattering angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-75.1</td>
<td>157.8</td>
</tr>
<tr>
<td>-54.7</td>
<td>142.1</td>
</tr>
<tr>
<td>-32.9</td>
<td>122.3</td>
</tr>
<tr>
<td>-10.9</td>
<td>101.5</td>
</tr>
<tr>
<td>11.1</td>
<td>80.6</td>
</tr>
<tr>
<td>32.9</td>
<td>59.9</td>
</tr>
<tr>
<td>54.5</td>
<td>40.1</td>
</tr>
<tr>
<td>74.8</td>
<td>23.6</td>
</tr>
</tbody>
</table>
The procedure to assess parameter errors is the following. The SCIATRAN forward model is run for each state using the standard settings defined in Sect. 4.1.3 except for one of the parameters listed in Table 4.2, which is accordingly varied. In this way, a synthetic OMPS-LP spectrum is obtained for each chosen state (listed in Table 4.3). Since in the retrieval scheme the SNR of the measurements is estimated from the residual fit, a similar procedure is followed for the synthetic cases. First, the root mean square of the fit residuals at every altitude and for each spectral segment is computed using a standard retrieval run of the same orbit and states. Then, a Gaussian generator is implemented to randomly generate $N = 50$ noise sequences for each spectral range. The noise sequences are then added to the synthetic spectrum previously simulated. In this way, we obtained $N$ intensity matrices, i.e., synthetic OMPS-LP spectra, which are fed into the retrieval scheme to get ’perturbed’ ozone profiles, $O^\text{pert}_3(\text{param}, \phi, z)$, for each parameter and latitude. A set of 50 synthetic spectra and just as many retrieved profiles, $O^\text{ref}_3(\phi, z)$, are also generated without varying any parameter. Comparing then the results of these unperturbed retrievals with the ozone profiles obtained perturbing the single parameters in the forward model, we can estimate the effect of each parameter uncertainty on the retrieved ozone profile. To obtain a robust result, we averaged the 50 retrieved profiles, obtaining $O^\text{avg,ref}_3$ and $O^\text{avg,pert}_3$, for the perturbed and unperturbed scenarios, respectively. A side drawback of this approach is related to the fact that the fit residuals are wavelength dependent. This means that for a real OMPS-LP spectrum, the fit residuals may be large for a particular wavelength, which is constant with time, and smaller for the rest of the spectral range. On the contrary, the Gaussian generator may assign the large fit residual value of that single spectral point to other wavelengths within the same spectral segment. This is visible when comparing the retrieval noise uncertainty from the error propagation in SCIATRAN, as described in Sect. 4.1.4, and the standard deviation of the 50 synthetic retrievals: even though the order of magnitude is the same, at some altitudes the variability of the synthetic retrievals is higher than expected, for example in the lower stratosphere.

The mean unperturbed retrieved ozone profile $O^\text{avg,ref}_3$, the averaged perturbed ozone profile $O^\text{avg,pert}_3$, and the relative differences between them are defined for each parameter and latitude as follows:

$$O^\text{avg,ref}_3(\phi, z) = \frac{1}{N} \sum_{n=1}^{N} O^\text{ref}_3(\phi, z)$$

$$O^\text{avg,pert}_3(\text{param}, \phi, z) = \frac{1}{N} \sum_{n=1}^{N} O^\text{pert}_3(\text{param}, \phi, z)$$

$$\delta^\text{ref}(\phi, z) = \frac{O^\text{avg,ref}_3(\phi, z) - O^\text{true}_3(\phi, z)}{O^\text{avg,ref}_3(\phi, z) + O^\text{true}_3(\phi, z)} \times 200$$

$$\delta^\text{pert}(\text{param}, \phi, z) = \frac{O^\text{avg,pert}_3(\text{param}, \phi, z) - O^\text{avg,ref}_3(\phi, z)}{O^\text{avg,pert}_3(\text{param}, \phi, z) + O^\text{avg,ref}_3(\phi, z)} \times 200$$

where $O^\text{true}_3$ indicates the first guess ozone profile used in the SCIATRAN forward model, i.e., the ‘true profile’ for the sensitivity studies. First of all, the $O^\text{true}_3$ profile is compared with the unperturbed averaged retrieved ozone profiles. Figure 4.11 shows, in the left panel, all the
50 unperturbed retrieved profiles and their average $O_{3}^{\text{avg,ref}}$ in black, for the OMPS-LP state at 32.9° latitude. In the middle panel, both the first guess $O_{3}^{\text{true}}$ and the $O_{3}^{\text{avg,ref}}$ profiles are displayed. The shadow area around the first guess profile is the retrieval noise uncertainty associated to the retrieved profile from the OMPS-LP measurement at this latitude, while the standard deviation of 50 unperturbed profiles is drawn as shadow area around the second profile. The two values generally agree, even though the standard deviation of the 50 profiles is slightly larger. In the right panel, the relative differences $\delta_{re}f$ between the $O_{3}^{\text{avg,ref}}$ and the first guess profiles are plotted for all latitude bands.

![Graph](image)

Figure 4.11: In the left panel, all the 50 unperturbed retrieved profiles and their average are shown, for the OMPS-LP state at 32.9° latitude. In the middle panel $O_{3}^{\text{avg,ref}}$ and the ‘true’ profile (‘first guess’) are plotted; the shaded area around $O_{3}^{\text{avg,ref}}$ is the standard deviation of the 50 retrieved profiles, while the shaded area around the ‘first guess’ profile is the retrieval noise error associated to the single OMPS-LP retrieved profile. In the right panel, relative differences $\delta_{re}f$ between $O_{3}^{\text{avg,ref}}$ and the first guess profile are displayed for all latitudes in Table 4.3.

The relative discrepancies are significantly different from zero, contrary to what ideally expected, in particular around 30-35 km and above 50 km, where the discrepancy increases with altitude up to 10-15 %. These features are related to the fact that we chose as a priori the null profile and SCIATRAN computes at each iteration the difference between zero and the ozone profile. As a consequence, at altitudes where the sensitivity of the retrieval is low, the retrieved profile tends to underestimate the ‘true’ ozone. The large relative differences are also related to the very low ozone values at the upper altitudes. This feature is a component of the systematic uncertainty of the retrieved profiles and has to be taken into account when comparing IUP-OMPS with other reference instruments.

For the rest of the perturbed scenarios, the differences are computed relative to $O_{3}^{\text{avg,ref}}$ rather than to the first guess, in order to have an evaluation of the sensitivity of the retrieved ozone profile to the single parameters, not affected by the sensitivity of the retrieval itself. Below 20 km it is challenging to estimate the effect of each parameter because of a high variability found in the simulations, which leads to oscillating patterns in the central and right panels.
4.1. Ozone profile retrieval algorithm

(i.e., in the relative differences).

Regarding surface albedo, as reported in Table 4.2, it is varied by a $\Delta = \pm 0.1$, considered a realistic estimate of the error on the retrieved values. Figure 4.12 shows the effects of varying this parameter in the forward model. The deviation from the unperturbed case is evident only below 30 km and appears to be symmetric, in response to a decrease or an increase of the albedo. Even though the deviations are within few percents and the vertical structure below 20 km is strongly oscillating, we can assess that an overestimation of the albedo (i.e., adding $\Delta = +0.1$ in the forward model) leads to an underestimation of the retrieved profile in the lower stratosphere and vice versa. The UV retrieval is not affected by a change in albedo, as this spectral range is not sensitive to low atmospheric layers.

Figures 4.13 and 4.14 show similar plots when perturbing the temperature and pressure profiles, respectively. In particular, a reasonable estimation of the temperature uncertainty from reanalysis is $\pm 2$ K (Langland et al., 2008), whereas for pressure profiles it is about 2 %. These estimates were assessed, for example, by Nowlan et al. (2007), who studied the differences between MAESTRO and reanalysis from the National Centers for Environmental Prediction (NCEP) and the European Centre for Medium-range Weather Forecasts (ECMWF). As a consequence, the whole temperature and pressure profiles are perturbed by $\Delta = \pm 2$ K and $\Delta = \pm 2$ % respectively.

From Fig. 4.13 we notice that the effect of increasing the temperature profile by $\Delta = 2$ K leads to an underestimation of the retrieved ozone profile, with the largest effects in the lower and upper part of the stratosphere. However, the deviations are within 1-2 % at all altitudes above 20 km and no evident changes as a function of latitudes are detected. Regarding the pressure profile perturbation, the effect is more evident than for the temperature, leading to a deviation

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7 Albedo was retrieved as described in Sect. 4.1.3 also for the synthetic studies.
Chapter 4. Retrieval of ozone profiles from OMPS-LP observations

Figure 4.13: Same as in Fig. 4.12 but perturbing the temperature profile by ±2 K, at 11.1° latitude.

Figure 4.14: Same as in Fig. 4.12 but perturbing the pressure profile by ±2 %, at 11.1° latitude.

of 2-3 % of the entire ozone profile relative to the unperturbed case. Also, this deviation is found to be constant with the latitude.

An important parameter for ozone limb retrievals is the pointing knowledge of the instrument. According to Moy et al. (2017), the results from the Rayleigh Scattering Attitude Sensing (RSAS) and the ARRM methods indicate that OMPS-LP pointing has an accuracy of about ±100 m. As a consequence, forward model simulations with TH increased and decreased by a Δ = 100 m are performed, and the deviations of the resulting ozone retrievals are reported in Fig. 4.15. The vertical structure of the deviations has, in this case, a peculiar shape, as the retrieved profiles are shifted upwards or downwards with respect to the $O_3^{avg, ref}$. Perturbing the TH by adding Δ = +100 m leads to an underestimation of the ozone profile above its maximum. The discrepancy increases with altitude up to 5 % around 55 km. Differences are close to zero at 25-30 km and then change the sign in the lower stratosphere. The opposite happens when subtracting 100 m from the THs.
Finally, aerosol extinction profiles are assumed as known in the ozone retrieval and are a source of parameter errors. Looking at the precision of the retrieved aerosol extinction profiles (as described in Sect. 4.3), their uncertainties reach values up to 30-50% in the lower stratosphere (Rieger et al., 2018). As a consequence, aerosol profiles are perturbed by $\Delta = 40\%$; this is an upper boundary for aerosol errors, especially above 25 km where the typical precision of the retrieved aerosol extinction profile is within $\pm 5\%$. The results of the retrieved ozone profiles for the perturbed scenarios relative to $O_{\text{avg, ref}}^3$ are reported in Fig. 4.16.

The effects as a function of altitudes are relevant below 30 km and reach $\pm 5-7\%$ in the lower stratosphere, with an ozone underestimation for a positive perturbation of the aerosol extinction profile. Aside from the oscillating structures in the lower stratosphere, we find a significant latitudinal dependence, with the strongest deviation at high northern latitudes in the lower stratosphere. This is related to the sharp forward peak, which characterizes the aerosol scattering phase function. This means that as the scattering angle gets lower, i.e., the sun position gets closer to the LOS of the instrument, the contribution from aerosol scattering becomes more and more significant. As seen in Fig. 3.3, this condition occurs at northern mid and high latitudes.
Table 4.4 reports the estimated values of the parameter errors at several altitudes for the five chosen variables. Values in the last column indicate the retrieval noise uncertainties associated with a single profile, as discussed in Sect. 4.1.4.

<table>
<thead>
<tr>
<th>Altitude [km]</th>
<th>Albedo</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Aerosol</th>
<th>TH</th>
<th>Retrieval noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 km, pSH</td>
<td>-4 %</td>
<td>-2 %</td>
<td>+4 %</td>
<td>-3 %</td>
<td>+7 %</td>
<td>±5 %</td>
</tr>
<tr>
<td>15 km, mSH</td>
<td>-5 %</td>
<td>-3 %</td>
<td>+4 %</td>
<td>-2 %</td>
<td>+7 %</td>
<td>±10 %</td>
</tr>
<tr>
<td>15 km, TRO</td>
<td>-7 %</td>
<td>-5 %</td>
<td>+4 %</td>
<td>-2 %</td>
<td>+10 %</td>
<td>±25 %</td>
</tr>
<tr>
<td>15 km, mNH</td>
<td>-5 %</td>
<td>-3 %</td>
<td>+4 %</td>
<td>-2 %</td>
<td>+5 %</td>
<td>±10 %</td>
</tr>
<tr>
<td>15 km, pNH</td>
<td>-5 %</td>
<td>-2 %</td>
<td>+4 %</td>
<td>-5 %</td>
<td>+3 %</td>
<td>±5 %</td>
</tr>
<tr>
<td>25 km, pSH</td>
<td>-2 %</td>
<td>-2 %</td>
<td>+3 %</td>
<td>+2 %</td>
<td>±1 %</td>
<td>±5 %</td>
</tr>
<tr>
<td>25 km, mSH</td>
<td>-2 %</td>
<td>-2 %</td>
<td>+3 %</td>
<td>+2 %</td>
<td>±1 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>25 km, TRO</td>
<td>-2 %</td>
<td>-2 %</td>
<td>+3 %</td>
<td>-2 %</td>
<td>±2 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>25 km, mNH</td>
<td>-2 %</td>
<td>-2 %</td>
<td>+3 %</td>
<td>-2 %</td>
<td>±1 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>25 km, pNH</td>
<td>-2 %</td>
<td>-2 %</td>
<td>+3 %</td>
<td>-2 %</td>
<td>±1 %</td>
<td>±5 %</td>
</tr>
<tr>
<td>35 km, pSH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-2 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>35 km, mSH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-2 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>35 km, TRO</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-2 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>35 km, mNH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-2 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>35 km, pNH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-2 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>45 km, pSH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-3 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>45 km, mSH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-3 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>45 km, TRO</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-3 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>45 km, mNH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-3 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>45 km, pNH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-3 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>55 km, pSH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-5 %</td>
<td>±3 %</td>
</tr>
<tr>
<td>55 km, mSH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-5 %</td>
<td>±2 %</td>
</tr>
<tr>
<td>55 km, TRO</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>±1 %</td>
</tr>
<tr>
<td>55 km, mNH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-5 %</td>
<td>±1 %</td>
</tr>
<tr>
<td>55 km, pNH</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>+2 %</td>
<td>&lt; ±0.5 %</td>
<td>-1 %</td>
<td>±1 %</td>
</tr>
</tbody>
</table>

The most important sources of error from the previous analysis are: pointing errors, particularly in the lower and upper stratosphere, pressure uncertainties, aerosol extinction coefficient, and albedo only in the lower stratosphere.

In order to come up with an overall error estimation for the retrieved ozone profiles, we apply the following formula:

\[
\sigma_{\text{tot}}^2 = \sqrt{\sigma_{\text{albedo}}^2 + \sigma_{\text{temperature}}^2 + \sigma_{\text{pressure}}^2 + \sigma_{\text{temperature}}^2 + \sigma_{\text{aerosol}}^2 + \sigma_{\text{TH}}^2}
\] (4.12)

The overall parameter errors as a function of altitude and latitude are reported in Table 4.5 for three latitude bands in the lower, middle and upper stratosphere, in comparison with the retrieval noise uncertainty component.

---

8 for completeness, the parameter error related to the used ozone cross section is missing, but it was estimated as negligible by Rahpoe et al. [2013]
4.1. Ozone profile retrieval algorithm

<table>
<thead>
<tr>
<th>Lat. band</th>
<th>Low stratosphere</th>
<th>Middle stratosphere</th>
<th>Upper stratosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Hem.</td>
<td>11 %, 5-10 %</td>
<td>3 %, 3-5 %</td>
<td>5 %, 2 %</td>
</tr>
<tr>
<td>Tropics</td>
<td>14 %, 20-30 %</td>
<td>4 %, 2 %</td>
<td>6 %, 2 %</td>
</tr>
<tr>
<td>Northern Hem</td>
<td>9 %, 5-10 %</td>
<td>3 %, 3-5 %</td>
<td>5 %, 1 %</td>
</tr>
</tbody>
</table>

In addition to these estimates, we have to consider also the retrieval sensitivity to ozone, which changes as a function of altitude, as shown in Fig. 4.11: systematic deviations with values of 3-5 % are expected at 30-35 km, while above 50 km values may increase to up to 10-15 %, mostly independently from latitude.

Finally, the impact on the ozone retrieval of a perturbed first guess and a cirrus cloud in the instrument FOV are investigated. In the first case, we vary the first guess profile and then apply the standard retrieval algorithm. Then, the relative differences between the ozone profile retrieved using the unperturbed first guess and the profile using the perturbed one are calculated. Figure 4.17 shows the results when the entire first guess profile is scaled by values between -50 % and +100 %. We see that the retrieval scheme shows strong stability with respect to the profile chosen as first guess, being affected by less than 0.5% when it is doubled or halved.

![Figure 4.17: Relative differences as a function of altitude between the ozone profile retrieved assuming an unperturbed first guess and the ones retrieved assuming a first guess perturbed by the amounts reported in the legend.](image)

To estimate the effects on the retrieved ozone profile of a cirrus cloud present in the FOV of the instrument in the UTLS, two forward simulations are performed. In detail, two thin ice clouds consisting of fractal crystals with a radius of 50 µm and cloud optical depths (COD) equal to 0.1 and 0.05 are located in the forward model between 14.5 and 15.5 km. Then the standard
retrieval is run, assuming a clear atmosphere and a constant SNR for each spectral range. An unperturbed retrieval is also performed for the same OMPS-LP observation. The two perturbed ozone profiles and the relative difference with respect to the unperturbed retrieved profile (i.e., without the cirrus cloud in the forward model) are reported in Fig. 4.18.

![Figure 4.18](image)

**Figure 4.18:** Left panel: ozone profiles retrieved considering a cirrus cloud in the forward model and the unperturbed case in black. Right panel: the relative difference between the unperturbed ozone profile and the two cases with a cloud in the forward model. The horizontal blue band indicates the location of the cloud.

Even though the clouds are thin cirrus, the difference in the ozone profiles right above the cloud layer reaches values up to 10-15%. The relevant effect of a cloud in the FOV of the instrument on the retrieved ozone profile highlights the importance of an effective cloud screening. This can also be considered as a parameter error in the lower stratosphere and its nature can be systematic if the cloud filter is sub-optimal. This may help in explaining the bias of our results relative to ozonesondes and MLS observations described in Ch. 5.

### 4.2 Cloud flags

#### 4.2.1 The color index approach

The retrieval of atmospheric properties in limb geometry is strongly affected by the presence of tropospheric clouds in the field of view, as also seen in Fig. 4.18: namely, the optical depth of a thin cirrus is typically large enough for the limb transmission to approach zero. As a consequence, a cloud filter has to be designed and applied before the ozone retrieval, in order to reject THs at which a cloud is present in the field of view of the instrument. A typical cloud top height varies strongly as a function of latitude and follows the tropopause height, reaching up to 17-19 km in the tropics. In addition, PSCs have to be taken into account in the polar regions, as their optical thickness can be large enough to affect limb retrieval. These clouds are found during winter months at high latitudes, particularly over Antarctica inside the polar vortex at altitudes up to 25 km, as described in Ch. 1.
The applied algorithm to filter out THs affected by clouds is based on the color index ratio (CIR) concept, described and applied to SCIAMACHY measurements in Eichmann et al. (2016). This method combines two weak absorbing wavelengths: for OMPS-LP, radiances at 754 nm and 997 nm are chosen. For each OMPS-LP spectrum, i.e., at each TH, the color index (CI) is defined as the ratio between the radiance at these two wavelengths. The CI is sensitive to the presence of scattering particles along the LOS of the instrument. From the Rayleigh scattering theory we know, indeed, that the scattering on air molecules is strongly wavelength dependent, whereas scattering on aerosol and cloud particles, described by the Mie theory, is weaker wavelength dependent. To obtain the cloud flag, the CI is computed at all THs and then the CIR is calculated as:

\[
CIR(z_{TH}) = \frac{CI(z_{TH})}{CI(z_{TH} + \Delta z_{TH})}
\]  

(4.13)

where \(\Delta z_{TH}\) is the vertical grid step, which is equal to 1 km for OMPS-LP. A jump of the CIR at a certain altitude indicates the presence of Mie scatterers in the instrument FOV. Figure 4.19 shows an example of resulting CIR for several simulated clouds scenarios: cirrus clouds consisting of hexagonal crystals with an optical depth between 0.01 and 0.15 are taken into consideration.

The chosen threshold to flag a TH as cloudy is 1.15. The CIR is computed between 0 and 30 km to account for the presence of PSCs in the polar regions, where the threshold is lowered to 1.10. Since the ozone retrieval is run above 12 km, we are generally not interested in liquid water clouds. Besides, at the considered wavelengths is not possible to distinguish between water and ice clouds, as their scattering properties are similar. This approach is also not suitable to distinguish between high aerosol loads and cirrus clouds, even though over the last 15 years no major volcanic eruptions have been recorded. A dedicated aerosol retrieval is needed to assess
Figure 4.20 shows the average cloud top height detected using the presented CIR method, averaged over 2016. We can notice that the main climatological features are well captured: e.g., high tropical clouds especially over Southeast Asia mostly related to deep convection, low clouds in the polar regions and above oceans, for example on the west side of South America. The frequency of cloud detection from limb measurements is higher in comparison to nadir observations, due to the long LOS. In the tropics, up to 80-90% of the observations are flagged as cloudy, whereas the minimum frequency is reached at mid-latitudes over the eastern Pacific ocean where a low cloud is detected in less than half of the cases.

4.2.2 Filtering PMCs

The presence of polar mesospheric clouds (PMCs) in the instrument FOV has also to be taken into account, as their particles act as scatterers, changing the light path in the atmosphere. A PMC filter is implemented and a retrieval of these clouds following the approach applied to SCIAMACHY data is planned for the future.

The formation of PMCs (also called noctilucent clouds) is related to the extremely low temperatures reached in the polar mesopause during summertime. These clouds typically occur at altitudes of 82-85 km and mainly above 50° latitude. At these altitudes during summer months, the temperature drops down to 120-140 K and the air gets super-saturated with respect to the water vapor. This leads to the formation of ice clouds if the concentration of cloud condensation nuclei is high enough (Fogle and Haurwitz, 1966; Gadsden and Schröder, 1989). The presence of PMCs interferes with the ozone retrieval, as it affects limb radiance down to 40 km and leads to spurious high ozone concentrations in the upper atmosphere. PMC ice particles act as a layer of scatterers, so that photons may be deviated into the instrument FOV.
before reaching the ozone layer. The PMC flag is restricted to high latitudes above 50°, to avoid artifacts at lower latitudes. The radiance profile at 353 nm is used, as the ozone absorption at this wavelength is low. Several conditions on the radiance profile at this wavelength and on its gradient are implemented. In the absence of scatterers in the FOV, radiance is expected to decrease monotonically as a function of altitude above 40 km, as the amount of the scattered light decreases with air density. This is illustrated in panel (a) of Fig. 4.21. When a PMC is present in the FOV of the instrument, the radiance profile deviates from the exponential decrease, as shown in panel (b) of Fig. 4.21.

![Figure 4.21](image)

**Figure 4.21:** Panel (a): example of radiance profiles at 353 nm in the absence of PMCs, on the 15 September 2016. Panel (b): example of radiance profiles in the presence of PMCs, on the 15 July 2016.

The radiance profile between 40 km and 80 km is examined and the observation is flagged as affected by a PMC if the following simple conditions are met at least for two consecutive layers:

- the radiance increases with the altitude, or
- the gradient of the radiance increases more than 50% between consecutive altitudes.

Figure 4.22 shows the percentage of measurements affected by PMCs over 2016. It is remarkable that the chosen conditions lead to a rejection of up to 40% of the measurements in the uppermost latitude band, towards the North Pole. This is also the effect of OMPS-LP sampling, which covers these high-latitudes only during summer when the conditions for the formation of PMCs take place.

### 4.3 Retrieval of aerosol extinction profiles

The implementation of the aerosol extinction retrieval has been performed by Dr. E. Malinina and described in Malinina (2019). Stratospheric aerosols act as a source of scattered solar light and have to be taken into account in the ozone retrieval. Flittner et al. (2000) showed that neglecting aerosols in the ozone retrieval of limb observations leads to a relative error of up to 10% in the lower stratosphere. In
Chapter 4. Retrieval of ozone profiles from OMPS-LP observations

Figure 4.22: Percentage of measurements affected by the presence of PMCs as a function of latitude and longitude in 2016.

occasion of a major volcanic eruption, the aerosol load may be too high for a reliable retrieval of trace gases in the UTLS. For OMPS-LP measurements, accurate modeling of aerosol scattering is particularly relevant towards high northern latitudes, where the scattering angle is small (Fig. 3.3). This is related to a pronounced forward peak that characterizes the aerosol scattering phase function.

The aerosol extinction coefficient is retrieved independently from the ozone retrieval. A similar approach as the one used to retrieve stratospheric aerosol extinction profiles from SCIAMACHY data (Rieger et al., 2018) is implemented. The SCIAMACHY aerosol extinction retrieval could not be directly applied to OMPS-LP data, mainly because of its coarser spectral resolution, as the radiance measured at 750 nm is found to be affected by O$_2$ absorption. For this reason, radiance at 869 nm is chosen for the OMPS-LP aerosol extinction coefficient retrieval instead of 750 nm, as used for OSIRIS and SCIAMACHY.

OMPS-LP retrieval of stratospheric aerosol extinction profiles covers the altitude range from 10.5 km to 33.5 km, where the presence of the so-called Junge layer is expected. Aerosol particles in this layer are assumed to be sulfuric droplets, whose refractive indexes are taken from the Optical Properties of Aerosols and Clouds (OPAC) database (Hess et al., 1998). The stratospheric air is assumed to have 0 % relative humidity. Outside of this altitude range, the aerosol load is set to zero.

The retrieval approach is based on a first-order Tikhonov regularization scheme. At each altitude, radiance is normalized using the measurement at 34.5 km and surface reflectance is simultaneously retrieved exploiting the sun-normalized spectrum at 34.5 km. Mie theory is used to calculate the aerosol scattering phase function. Regarding the particle size distribution in the retrieval algorithm, a uni-modal log-normal distribution is assumed, with median radius ($r_g$) equal to 0.08 $\mu$m, and a width parameter ($\sigma$) equal to 1.6. The resulting probability distribution
function is then given by this equation:

\[
\frac{dn(r)}{dr} = \frac{N}{\sqrt{2\pi \ln(\sigma)r}} \exp \left( \frac{(\ln(r_g) - \ln(r))^2}{2\ln^2(\sigma)} \right)
\] (4.14)

The retrieved aerosol product is then used in the ozone retrievals. However, a cloud screening on these profiles has to be performed and the profile below the cloud is extrapolated by the scaled a priori. The respective scaling factor is calculated by averaging the values at three altitudes above the cloud.

The time series of the retrieved aerosol extinction profiles are shown in Fig. 4.23, zonally and monthly averaged in several latitude bands. The time of major volcanic eruptions and the Canadian wildfires occurred in 2017 are indicated with vertical lines in the plot.

\[\text{FIGURE 4.23: Zonally and monthly averaged retrieved aerosol extinction profiles in several latitude bands over OMPS-LP lifetime, with major volcanic eruptions superimposed.}\]
Chapter 5

Comparison and validation with independent data sets

5.1 Comparison with NASA retrieval algorithm

The NASA Environmental Data Record algorithm to retrieve ozone profiles from OMPS-LP measurements is based on the optimal estimation approach. Several versions of the retrieval algorithm were released starting from April 2012; here only the most recent version 2.5 is considered, which is described in (Kramarova et al., 2018). In this version, to improve the stability of the retrieval, a correlation radius of 5 km was introduced in the a priori covariance matrix instead of the previously employed Tikhonov parameter. To simulate limb radiance, the Gauss-Siedel radiative transfer model is used (Loughman et al., 2015) and the Bass and Paur ozone cross section selected (Bass and Paur, 1985). The algorithm is designed to retrieve ozone independently from two spectral ranges: the UV region between 28.5 and 52.5 km and the Chappuis band between 12.5 (or cloud top height) and 37.5 km. The doublet and triplet method, described in Flittner et al. (2000), is used to obtain the measurement vector, respectively, for the Hartley-Huggins and Chappuis bands. Wavelengths characterized by a strong ozone absorption are paired with weak absorbing ones. The selected spectral points are reported in Table 5.1. The normalization of the radiance is performed using an upper TH measurement: 55.5 km in the UV and 40.5 km in the Vis. An additional TH correction is applied by NASA on L1G data, as described in Ch. 4 and Kramarova et al. (2018). The scene reflectivity is retrieved at 675 nm; an additional TH correction is applied by NASA on L1G data, as described in Ch. 4 and Kramarova et al. (2018). As already mentioned, only the central slit of the instrument is considered and currently provided in L2 NASA product, because of the uncertainties in the pointing and stray light issues affecting the two side slits.

As a consequence of the described settings implemented in NASA’s v2.5 retrieval algorithm, independent profiles for Vis and UV are derived and reported in the L2 data. They are analyzed separately in the following discussion or overlapped in some plots. The quality flags related to SAA (Kahn and Kowitt, 2015) and PMCs are also used to filter out OMPS-LP states.
Chapter 5. Comparison and validation with independent data sets

Table 5.1: Wavelengths used in the v2.5 NASA algorithm to retrieve ozone from OMPS-LP observations, according to Kramarova et al. (2018).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Wavelengths [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength in UV</td>
<td>302, 312, 322 paired with 353</td>
</tr>
<tr>
<td>Wavelength in Vis</td>
<td>600 combined with 510 and 675</td>
</tr>
</tbody>
</table>

In the following description and figure captions, the profiles retrieved at the University of Bremen are called IUP-OMPS. Fig. 5.1 presents NASA and IUP-OMPS ozone profiles averaged over 2016 in terms of number density vs. altitude for the tropics, i.e. \([20^\circ S, 20^\circ N]\), and northern mid-latitudes, i.e. \([40^\circ S, 60^\circ N]\). Shaded areas indicate the standard deviation of the averaged profiles. Typical number density maxima around 27 km in the tropics and around 22 km at mid-latitude are displayed. We find that UV and Vis retrieved profiles from NASA do not always agree in the range 28-37 km where the two retrievals overlap: especially at northern mid-latitudes the discrepancy between the two reaches values up to 10%. The shape of NASA and IUP-OMPS profiles shows a good consistency but around 30 km we notice that IUP-OMPS profile is generally more smooth with respect to NASA’s and that the agreement with the UV retrieval in the middle stratosphere is generally better in comparison to the Vis profile.

\[ \text{Figure 5.1: IUP-OMPS and NASA-OMPS retrieved number density profiles averaged over 2016, in the tropical region in panel (a) and at northern mid-latitudes in panel (b).} \]

The analysis of the discrepancies as a function of altitude and latitude gives information regarding the main differences between the retrievals. Figure 5.2 shows profiles of relative differences between NASA-OMPS retrievals and our results, considering UV (panel a) and Vis retrievals (panel b) independently and yearly averaged over 2016. Five latitude bands are selected for this and the next comparisons: 60°N-90°N, 40°N-60°N, 20°S-20°N, 60°S-40°S and 90°S-60°S.
5.1. Comparison with NASA retrieval algorithm

Throughout this chapter, relative differences are computed as:

\[
\text{Rel diff} = \frac{2 \times (\text{IUP-OMPS - Reference data set})}{(\text{IUP-OMPS + Reference data set})} \times 100 \quad (5.1)
\]

In detail, the numerator of this fraction, i.e., the absolute difference, is firstly computed for each pair of profiles and averaged over the whole sample, to get \( \Delta_{\text{ABS}} \). At the same time, averaged NASA and IUP-OMPS ozone profiles are computed and used in the denominator. So that for each latitude and altitude, the relative difference is calculated in this case as:

\[
\text{Rel diff} = 2 \times \frac{\Delta_{\text{ABS}}}{(\text{IUP-OMPS}_{\text{Avg}} + \text{NASA-OMPS}_{\text{Avg}})} \times 100 \quad (5.2)
\]

**Figure 5.2:** The relative differences (Eq. 5.2) between IUP-OMPS and NASA’s UV and Vis retrievals, are respectively shown in panel (a) and (b) for five latitude bands (60°N-90°N, 40°N-60°N, 20°S-20°N, 60°S-40°S and 90°S-60°S), with corresponding standard deviations as shaded areas.

Panel (a) shows the differences with respect to NASA UV retrieval in the upper stratosphere. Discrepancies are similar for all latitude bands and display an agreement within ±5 % up to 42 km. Above 42 km, the relative difference increases up to 8-10 %. The most significant discrepancy is found in the tropics in the uppermost layers. This may be related to the different usage of UV spectral ranges or the TH normalization between IUP-OMPS and NASA.

In panel (b) the NASA Vis retrieval is compared with our results. Starting from the tropics, a very good agreement within 3-5 % is achieved above 20 km. In the Northern Hemisphere, the quality of the agreement gets worse: at mid-latitudes, positive differences within 5 % between 18 and 27 km and 5-11 % above 28 km are found. This bias further increases towards northern high-latitudes, with a peak around 29 km. In the Southern Hemisphere, the shape of the discrepancies as a function of altitude is similar to those in the Northern Hemisphere,
although their magnitude is reduced. The worst agreement is found in the southern polar regions, with values exceeding +10% above 32 km. The discrepancies above 28 km are possibly related to the merging of the spectral information from UV and Vis ranges at these altitudes in IUP retrievals, missing in the NASA profiles. Looking at the UTLS, we notice significant discrepancies between the two products, particularly in the tropical region, where ozone concentration quickly drops below 20 km. At these altitudes, as discussed in Ch. 4 using synthetic studies, the parameter error of the retrieved profiles gets large and specific settings of the two retrievals such as spectral ranges, a priori values, aerosol profiles, and cloud screening play a significant role.

Comparing panels (a) and (b), the discrepancy between Vis and UV retrievals is evident, especially at northern mid-latitudes. This jump is also documented by Kramarova et al. (2018): by validating their results with MLS, the authors found that at the overlapping altitudes (29.5-37.5 km) values retrieved from the Vis range are systematically lower at mid- and high-latitudes relative to UV results.

5.2 Validation against MLS observations

5.2.1 Collocation and data usage

MLS observations are chosen as independent data set to validate the retrieval results. Due to its high temporal and spatial sampling and the broad latitude coverage, a detailed comparison is possible. Version 4.2 of MLS L2 data is used, considering only MLS day-time profiles and taking into account quality flags and recommendations reported in Livesey et al. (2017).

To ensure that observations of a similar air mass are compared, measurements from the two instruments are spatially and temporally collocated. Due to the large number of available observations, it is possible to choose tight collocation criteria, so that a smaller spread of the differences is expected. Several values of the geographic distance between the centers of the two instrument footprints and of the time difference between measurements were initially tested. Table 5.2 reports the number of collocated MLS and OMPS-LP profile pairs per year for several combinations of the temporal and spatial collocation criteria. Changing the temporal window does not change the number of collocations significantly. Namely, increasing the interval from 3 to 6 h, the variation is on the order of a few thousand profiles, as the overpass time of the two instruments differs by only 30 minutes. As a consequence, 3 h is already enough to get a large number of collocated profiles. Even with a 24 h window, the number of collocations slightly increases at high latitudes, whereas the number of collocations in the tropics does not change, due to the geometry of the observations. Stronger variations occur when releasing the spatial constraints: multiplying by four the dimensions of the collocation area the number of profiles is more than doubled. The largest number of profiles in Table 5.2 occurs when considering a rectangular area 5° longitude wide.

Figure 5.3 shows the standard deviations of the IUP-OMPS profiles considered for the validation with MLS as a function of the collocation parameters. This is computed as the absolute standard deviation of all the collocations divided by the averaged profile. Changing the time
Table 5.2: Number of collocations with MLS during 2016 as a function of the chosen temporal and spatial constraints; both in terms of overall collocations and only in the tropics.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Overall collocations</th>
<th>Collocations in the tropics</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 h, 1° lat, 1° lon</td>
<td>69000</td>
<td>13000</td>
</tr>
<tr>
<td>6 h, 1° lat, 1° lon</td>
<td>72000</td>
<td>13000</td>
</tr>
<tr>
<td>12 h, 1° lat, 1° lon</td>
<td>75000</td>
<td>13000</td>
</tr>
<tr>
<td>6 h, 0.5° lat, 0.5° lon</td>
<td>22000</td>
<td>4000</td>
</tr>
<tr>
<td>6 h, 2° lat, 2° lon</td>
<td>170000</td>
<td>27000</td>
</tr>
<tr>
<td>6 h, 1° lat, 5° lon</td>
<td>290000</td>
<td>59000</td>
</tr>
</tbody>
</table>

Figure 5.3: Percentage variability of the ozone profiles in the tropics using different settings for the collocation of MLS with OMPS-LP profiles. In panel (a) varying the time window and keeping fixed the spatial grid; in panel (b) varying the latitude/longitude constraints and fixing a 6 h time frame.

A trade-off between tight collocation criteria, in order to have measurements of the same air mass, and a large number of observations, to have a significant sample to be averaged, was found using the following parameters: MLS observations are required to be within ±1° latitude and longitude and within a window of 12 h around OMPS-LP measurement (±6 h)). When multiple MLS measurements are collocated with the same OMPS-LP state, only the spatially closest profile is used. Besides, to ensure that both observations occurred either inside or outside the polar vortex, the difference of the potential vorticity at 20.5 km is required to be less than 5 PVU\(^1\)). Information about potential vorticity is taken from ERA-Interim.

As MLS observations are not affected by the cloud presence in the FOV, OMPS-LP flags are used to exclude from the validation all the altitudes below detected clouds.

\(^1\)Potential Vorticity Units
5.2.2 Converting MLS from VMR to number density profiles

MLS ozone profiles are originally provided in terms of VMR on a vertical pressure scale. To be consistent with NASA and sonde comparisons, MLS profiles are converted into number density vs. altitude using MLS retrieved temperature profiles and pressure information from ECMWF ERA-Interim. To check the impact of the MLS data transformation from VMR vs. pressure to number density vs. altitude, the Modern-Era Retrospective analysis for Research and Applications (MERRA)-2 database is also used as a source of pressure information (Gelaro et al., 2017). Fig. 5.4 reports the results of using different reanalysis: relative differences between MLS number density profiles converted using MERRA-2 and ECMWF are shown in panel (a). In detail, the following quantity is displayed:

$$\text{MLS}_{\text{Rel diff}}(\phi, z) = \frac{\text{MLS}_{\text{ecmwf}}(\phi, z) - \text{MLS}_{\text{merra}}(\phi, z)}{\text{MLS}_{\text{ecmwf}}(\phi, z) + \text{MLS}_{\text{merra}}(\phi, z)} \times 200$$ (5.3)

where $\phi$ and $z$ are, respectively, latitude and altitude; $\text{MLS}_{\text{ecmwf}}$ and $\text{MLS}_{\text{merra}}$ are the zonally averaged MLS ozone profiles converted into number density vs. altitude using ERA-Interim and MERRA-2, respectively. The differences are averaged over the entire 2016. The pattern is symmetric between the two hemispheres. Up to 40 km differences are negligible, whereas in the upper stratosphere discrepancies reach values of 2-3 % with peaks up to 5 % in the uppermost levels.

In panel (b) the linear change of the relative difference time series between MLS converted using the two reanalyses is shown. The linear change is expressed in terms of % per decade and computed over the 2005-2016 period. Also in this case, we notice that below 40 km the linear change is negligible; only above 50 km it exceeds 1 % per decade. In the following, MLS conversion is performed using ECMWF ERA-Interim. However, values reported in panel (b) give an estimate of the error related to the MLS conversion on the long-term ozone changes described in Ch. 7.

![Figure 5.4](image-url)  
**Figure 5.4:** Panel (a): relative differences between MLS ozone profiles zonally averaged over 2016 with the pressure information used for the conversion to number density vs. altitude taken from either ECMWF or MERRA-2 reanalyses. Panel (b): linear change of the differences between MLS converted using the two reanalysis, as a function of altitude and latitude, in terms of % per decade, computed over the period 2005-2016.
5.2. Validation against MLS observations

5.2.3 Results of the validation

For the comparison between averaged collocated profiles, the same five latitude bands are selected as for the comparison with NASA-OMPS. Each MLS number density profile is interpolated at the regular IUP-OMPS altitude grid (every 1 km) and then zonally averaged. Figure 5.5 shows the averaged ozone profiles over 2016 for tropics and northern mid-latitudes in terms of number density vs. altitude. The shapes are qualitatively in very good agreement, with MLS showing a less smooth profile at lower altitudes and IUP-OMPS characterized by a sharper decrease below 20 km at mid-latitudes. Standard deviations of the averaged profiles are reported in the plots as shaded areas: the variability is comparable between the two instruments, with larger values in mid-latitudes compared to the tropics.

Figure 5.5: Panel (a) and (b): collocated IUP-OMPS and MLS ozone profiles in the tropics and at northern mid-latitudes, respectively, averaged over 2016.

Figure 5.6 shows profiles of relative differences between IUP-OMPS and MLS in the five selected latitude bands. The number of collocations per band is $\sim 10000$ over 2016, as reported for the tropics in Table 5.2. The procedure to compute relative differences is the same as described for the NASA comparison (see Eq. 5.2). A good agreement found in Fig. 5.5 corresponds in Fig. 5.6 to relative differences mostly within $\pm 5\%$ between 20 and 56 km in all latitude bands. In more details, in the middle stratosphere at northern mid-latitudes, we find that the relative difference exceeds $\pm 3\%$ only at 45 km and around 28-30 km. The latter negative discrepancy becomes more evident towards polar regions. In the tropics, a positive bias of 1-5% is observed above 28 km. At southern mid-latitudes, IUP-OMPS shows the ozone peak shifted upwards with respect to MLS with about 5% higher number density around 25 km. Otherwise, an agreement within 3-4% is achieved. Below 20 km, the agreement with MLS degrades. Relative differences are generally negative and within 10%, except for the tropics where peaks exceeding 20% and strong oscillating structures are found, even though the absolute difference is rather small, as pointed out in Fig. 5.5. In the upper stratosphere, above 55 km, we notice a significant increasing negative bias of IUP-OMPS relative to MLS at all latitudes, less important
in the tropics. The variability of the averaged profiles increases as well, starting from 45 km. As discussed in Fig. 4.11, IUP-OMPS retrieval at upper altitudes tends to underestimate ozone values, due to the loss of sensitivity. In addition, stray light in L1G data above 55 km is still considered an issue (Kramarova et al., 2018). As a consequence, 57-58 km can be considered the uppermost altitude where IUP-OMPS profiles should be reliably considered.

Fig. 5.7 shows the relative differences between IUP-OMPS and MLS zonal means binned every 2.5° latitude as a function of altitude. Three periods are considered during 2016: the whole year in panel (a), summer months in panel (b) and winter months in panel (c). Considering the whole 2016, we can better characterize in this plot the very good agreement with MLS already described in the previous pictures between 20 and 56 km: relative differences being mostly within ±5% and never exceeding 10% at any latitude. Starting from the bottom of the three plots, we find in the tropical UTLS oscillating differences larger than 30%. This large discrepancy is related to high dynamic variability and low absolute values of ozone in this region, and the low retrieval sensitivity in the lowermost stratosphere. The presence of cirrus clouds not correctly filtered may also play an important role. In the Southern Hemisphere in the [40°S, 20°S] band, we notice a large negative difference below 20 km. A similar feature was also found by Kramarova et al. (2018), who compared NASA results with MLS. Around 28-33 km, we find that smaller IUP-OMPS ozone values towards northern high-latitudes are particularly evident during winter months (panel c). At the same altitudes in the tropics, higher values are visible: at these altitudes the overlap between the contributions from UV and Vis spectral windows occurs, and their merging can lead to some inconsistencies. In addition, a still not fully characterized residual thermal sensitivity of the instrument and stray light affecting the Vis spectral range may contribute to this bias. The IUP-OMPS higher values at 45 km within 0°N and 50°N, can be related to a non-ideal junction between the spectral ranges in the Hartley and Huggins...
5.2. Validation against MLS observations

The relative differences (Eq. 5.1) averaged over 2.5° latitude bins, plotted as a function of altitude. Panel (a) the whole year 2016, panel (b) June, July and August, panel (c) January, February and December.

bands, which occurs at 46 km. In panel (b) and (c), we notice in the upper stratosphere a fairly symmetric behavior of the discrepancies with larger values in the hemisphere experiencing the winter season. Stray light affecting the TH used for the normalization may explain these features.

Comparing panel (a) of this figure with the results presented in Kramarova et al. (2018), we notice that between 20 and 30 km the relative differences have a similar distribution, especially the negative anomalies towards high latitudes around 30 km and the positive anomaly around 25 km at southern mid-latitudes. These patterns are related by the authors to systematic errors in the L1G radiance, likely linked to issues in the pixel-to-pixel calibration in both the vertical and spectral dimensions. Above 40 km, NASA product gives extensively lower values in comparison to MLS. This feature is present in our data set only above 55 km, with relative differences within ±10 % up to 60 km in the tropics and 56 km towards polar regions.

5.2.4 Time series of the differences and OMPS drift

The time series of the monthly averaged relative differences between IUP-OMPS and MLS data records as a function of altitude for different latitude bands are shown in Fig. 5.8. The gap in December 2013 - January 2014 in all panels is related to a temporary modification of the downloaded pixels from the sensor which affected L1G radiance and led to a failure of the ozone retrievals.

In the northern polar regions, panel (a), discrepancies are within ±10 % not only in the middle but also in the lower stratosphere. On the contrary, above 45 km the differences tend to increase and outliers to be more frequently observed, especially towards the end of the time series. In the middle panel, we notice that IUP-OMPS ozone seasonal cycle in the averaged profile at mid-latitudes has a larger amplitude compared with MLS with a more pronounced number density maximum around 25 km in summer and lower values at 28-30 km in winter, as already identified in Fig. 5.7. In the lower panel, the bias in the tropical lower stratosphere remains constant with time and season, indicating that it is a systematic difference between the
Figure 5.8: Time series of the relative differences between OMPS-LP and MLS monthly and zonally averaged profiles: panel (a) at northern polar latitudes, panel (b) northern mid-latitudes and in panel (c) in the tropics.
two instruments, related most probably to the vertical resolution and sampling of each sensor. We notice here irregular patterns below 17 km, related to the large dynamical variability of the tropical UTLS and the negative bias between 19 and 21 km also visible at mid- and high-latitudes. Similar features are identified in the Southern Hemisphere as well (here not shown). Considering the whole time series, particularly in the tropics and at mid-latitudes, it is evident from these plots that a possible drift of OMPS-LP time series with respect to MLS is present: particularly above 30 km, the relative differences show indeed increasing values with time, a feature that becomes even more pronounced during 2018. In order to better study the presence of a drift with respect to MLS, we calculate the linear trends of the relative differences reported in Fig. 5.8 taking into account the presence of a seasonal cycle, i.e., including in the regression model harmonic terms with a period of 6 and 12 months. Fig. 5.9 shows the drift of OMPS-LP time series with respect to MLS as a function of altitude and latitude, computed over the 2012-2018 period. The drift is considered as significant if it exceeds the 95 % confidence level; significant values are displayed as non-dashed areas. Between 30 km and 45 km, the drift is significant at almost all latitudes and reaches a peak of 6-8 % per decade around 40 km in the tropics. This drift, also identified by the NASA team in Kramarova et al. (2018) relative to both MLS and OSIRIS, is larger than the expected instrument stability when the satellite was launched, which was required to be within 7 % per decade at all altitudes.

![Drift per decade](image)

**Figure 5.9**: Drift of OMPS-LP time series with respect to MLS between 2012 and June 2018, in terms of % per decade. Dashed areas indicate non-significant drifts.

Hubert et al. (2016) analyzed the stability of several satellite data sets and found that MLS time series within the 2004-2013 period has a bias within a few percents relative to ground-based data sets. As a consequence, if we assume that MLS has been keeping a similar good stability also after 2013, we deduce that OMPS-LP is drifting, either due to pointing issues or stray light. A drift in the pointing would indeed probably be more evident above the ozone peak, where the natural variability is less pronounced. Since the drift is significant only above 30 km, it is also possible that it can be caused by a degradation of the instrument detector or stray light affecting the UV part of the spectrum or the TH used to normalize the UV spectral range in the
retrieval. An analysis of the LIG data set using the RSAS methodology as in Moy et al. (2017) covering also the last two years is planned: this would help to clarify if a change or a drift in the pointing of the instrument happened during its lifetime. A comparison with OSIRIS time series may also be performed for a better characterization, even though the density of measurements and the latitude coverage of this sensor are much more reduced with respect to MLS. Besides, OSIRIS is also known to suffer from pointing issues, only recently accounted for in Bourassa et al. (2018).

5.3 Validation against ozonesondes

This section was partially published in Arosio et al. (2018).

5.3.1 Collocation and data usage

To provide an independent validation of IUP OMPS ozone profiles that, on the one hand, does not rely on remote sensing techniques and, on the other hand, focuses the attention on the lower stratosphere, we use ozonesonde measurements. Above 30 km, the pump efficiency deteriorates due to the low pressure (Johnson et al., 2002) and sonde measurements become less reliable. As described in Ch. 2 balloon-borne observations are retrieved from both WOUDC and SHADOZ (Thompson et al., 2007) archives. The 47 ozonesonde stations listed in Table 2.2 are considered, corresponding to over 1300 single collocated profiles over the period 2012-2017. Due to the pre-processing that SHADOZ stations have faced during the last years, as described in Thompson et al. (2018), we exclude profiles from Paramaribo station (which was not reprocessed) from the following analysis and include the other 12 SHADOZ stations listed in Table 2.2. Because of the sparseness of ozonesonde measurements, collocation criteria are looser in this case compared to those used for MLS validation. In detail, OMPS-LP measurements are required to be within a 5° latitude and 10° longitude box around the ozonesonde station and within ±12 h period centered at the sonde launch (i.e., a time window of 24 h). These criteria are the same ones used to validate SCIAMACHY by Jia et al. (2015), except for the larger time window chosen by the authors. Since more OMPS-LP profiles satisfy these criteria for each sonde profile, all collocated OMPS-LP observations are firstly averaged before the comparison. For the cloud screening, if an altitude is flagged in at least one of the averaged OMPS-LP profiles, the corresponding grid point and the ones below are excluded from all the profiles used for the comparison with the collocated sonde.

The typical vertical resolution of ozonesondes is in the range 10-100 m, much higher compared with the one from limb sounders. As a consequence, for the validation, ozonesonde measurements are degraded to the vertical resolution of OMPS-LP. For this task, a convolution with the AKs of the retrieval scheme is implemented. First, we calculate the linear interpolation matrix $L^*$ to map the low-resolution OMPS-LP profile onto the fine sonde grid. Then this matrix is inverted using the pseudo-inverse formulation (Rodgers, 2000), obtaining $L^*$ as:

$$L^* = (L^T L)^{-1} L^T$$

---

2018 could not be used because of the small number of available profiles.

3 i.e., ±2.5° altitude and ±5° longitude
5.3. Validation against ozonesondes

The ozonesonde high-resolution profile $\vec{x}_{\text{fine}}$ is then convolved as follows:

$$\vec{x}_{\text{coarse}} = \mathbf{A} \mathbf{L}^* \vec{x}_{\text{fine}}$$  \hspace{1cm} (5.5)

For the convolution of the sonde profile to be consistent at all altitudes, we have to ensure that the balloon measurement at each OMPS-LP altitude grid entirely covers the AK altitude range: the uppermost grid level taken into consideration is the last one where the corresponding AK altitude range is fully covered by the sonde data. An alternative approach to the AK convolution consists in a simple vertical average, using a 2.6 km (i.e., $\pm 1.3$ km) range around each grid point. This value corresponds to the average vertical resolution of the retrieved IUP-OMPS profiles below 30 km, as shown in Fig. 4.10 in Ch. 4. As a consequence, the altitude ranges available for the comparison differ depending on the chosen approach. Five latitude bands are defined in the same way as for the comparisons with NASA and MLS profiles.

5.3.2 Results of the validation and time series

Figure 5.10 shows averaged collocated profiles over the period 2012-2017 in the tropics and at northern mid-latitudes, with corresponding standard deviations. On the left side of these plots, the number of available collocations at each altitude is reported, which is about 1000 for the tropics and 3000 at northern mid-latitudes. At southern mid-latitudes, only 3-4 stations are available so that the comparison is less reliable. The overall agreement is very good in both cases, including the lower part of the plots; however, IUP-OMPS profiles in the tropics tend to be systematically higher than the ozone concentration measured by the sondes.

![Figure 5.10](image-url)

**Figure 5.10:** Comparison between collocated IUP-OMPS profiles and ozonesonde measurements in the latitude bands $20^\circ$ S-$20^\circ$ N in panel (a) and $40^\circ$ N-$60^\circ$ N in panel (b); standard deviations are shown as shaded areas. Profiles are averaged over 2012-2017.
Figure 5.11 shows the relative differences (refer to Eq. 5.1) in five latitude bands, in panel (a) using the AK convolution approach and in panel (b) the vertical averaging. The differences between the two panels of this figure show that the averaging procedure can be critical in the comparison between 15 and 20 km, where the gradient in the ozone profile is usually strong. Looking at the results as a function of latitude below 30 km, an excellent agreement is found at northern mid-latitudes, as also shown in Fig. 5.10 with relative differences mostly within ±3% between 12 and 30 km. Towards the northern polar regions, a negative bias becomes evident with values down to -7% at 18 km. At southern mid-latitudes, we notice a discrepancy that changes sign around 20 km, with values of +5% at 30 km and -7% at 15 km. A similar positive bias at southern mid-latitudes is also visible in Fig. 5.5, and the shape indicates that our retrieved profiles are vertically shifted upwards with respect to the reference data set, with higher values above the number density peak and lower values in the lower stratosphere. At southern polar latitudes, the agreement is within 0-5% between 14 and 30 km. Focusing on the tropical region, a positive bias between the two data sets is visible below 20 km, with values exceeding 10% below 15 km. This positive bias was not clearly found in the MLS comparison, where negative values were reported between 18 and 21 km. This shows the importance of ground-based measurements to validate satellite products, especially in atmospheric regions where the comparison with other satellite data sets is not reliable.

Looking at the panel (b) of Fig. 5.11, the same patterns are depicted, but stronger oscillations below 20 km are found, due to the smaller vertical range over which the sonde profiles are averaged. In the tropics, a positive bias of IUP-OMPS profiles relative to sondes is more constant with height, showing values around +2-7% between 16 and 30 km. Over the 20-30 km altitude range at almost all latitudes we notice a positive bias, with the best agreement at northern mid-latitudes. In any case, the discrepancies are generally within ±10% at all latitudes below
30 km. Above 30 km, we notice a consistent positive bias increasing with altitude; this, as mentioned above, is most probably related to a general decrease in the reliability of ozonesonde measurements due to the low pressure.

Considering several retrieval versions, we can assess how much the ozone retrieval in the lower tropical stratosphere has been improved by adjusting some retrieval parameters. Fig. 5.12 displays profiles of the relative difference between IUP OMPS and sondes averaged in the tropics in 2016, for four versions of the retrieval. The use of retrieved aerosol profiles was implemented in the so-called ‘Vers 1’. The exclusion from the Chappuis band of spectral points affected by the absorption of species like O_4, O_2 and H_2O was implemented between ‘Vers 1’ and ‘Vers 2’, and it is crucial to reduce the discrepancy around 16-20 km. The decrease of the cloud flag threshold, implemented in ‘Vers 3’, helps to exclude thin cirrus cloud cases and improves the agreement with sondes below 18 km. Tuning the Tikhonov parameter at the lower altitudes is also important to reduce the oscillations of the profile in a region where the sensitivity of limb measurements decreases.

The time series of the monthly averaged relative differences between OMPS-LP and sondes from 2012 to the end of 2017 as a function of altitude for different latitude bands are shown in Fig. 5.13.

Considering northern mid-latitudes (panel a), an agreement within 10 % is seen at all altitudes between 15 and 30 km for the whole time series with only a few outliers. We also recognize a hint of the negative discrepancies found during winter months around 28-30 km, which were discussed in the MLS comparison. In the tropical region (panel b), we see significantly higher values in the UTLS in contrast with the negative discrepancies identified around 18-21 km in the comparison with MLS. The discrepancy below 16 km tends to increase with time, reaching peaks above 30 %, particularly in some months of 2016 and 2017.
Chapter 5. Comparison and validation with independent data sets

**FIGURE 5.13:** Time series of the relative differences between OMPS-LP and MLS data sets monthly and zonally averaged over northern mid-latitudes in panel (a), tropics in panel (b) and southern mid-latitudes in panel (c).
In the lower panel of Fig. 5.13 the time series at southern mid-latitudes is displayed. We recognize here the positive discrepancy of +5-10 % generally above 25 km, which becomes more pronounced during the last two years. Below 20 km, strongly negative values are found, especially during the austral winter. A strong positive bias in the southern polar region (here not shown) was found in the lower stratosphere especially during winter months, which is probably related to the difficulties in catching strong horizontal gradient using a 1D retrieval scheme in the presence of the polar vortex.

5.4 Validation against lidar observations

Lidar stations used for the validation are listed in Ch. 2. Collocation criteria are the same as those used for sondes: 12 h, 5° latitude and 10° longitude. Lidar profiles have a typical vertical resolution of 300 m so that they need to be vertically smoothed before the comparison with OMPS-LP observations. In this case, a simple averaging is performed. Each lidar profile is averaged at each altitude level over a vertical range of ±1.3 km, similar to the what performed for sondes.

Figure 5.14 shows the results of the comparison for two stations: Observatoire de Haute-Provence (OHP) at 44.0° latitude and Table Mountain at 47.8° latitude, respectively in panel (a) and (b). These profiles are averaged over the 2012-2018 period, and the number of measurements used in both cases is reported on the left side of each plot. In both cases, we notice that the OMPS-LP profiles show slightly higher values around the ozone maximum and sharper decrease below.

![Figure 5.14: Lidar and OMPS-LP profiles for OHP and Table Mountain lidar stations, respectively in panel (a) and (b). Profiles are averaged over the 2012-2018 period. The figures on the left indicate the number of profiles used from each station.](image-url)
Figure 5.15 shows the relative differences between lidar and OMPS-LP for the five considered stations (according to Eq. 5.1). As we notice, between 20 and 40 km, the agreement between the profiles is within -3% and +6%, except for Lauder, where a positive discrepancy of about 7% is found. Below 20 km OMPS-LP shows smaller ozone concentrations compared with the lidar, particularly for the two stations in the Southern Hemisphere; otherwise, the differences are within ±10% down to 13 km. Above 40 km the quality of lidar data degrades, as the measurement uncertainty increases and the vertical resolution decreases (Leblanc et al., 2016). Both the discrepancies and the standard deviations increase for most of the stations above 37 km.

To have an insight from the lidar validation about the possible OMPS-LP drift, Fig. 5.16 shows the relative differences between OMPS-LP and the lidar profiles yearly resolved for three stations: Hohenpeissenberg, OHP, and Table Mountain. As we can see, between 30 and 40 km, the yearly averaged profiles tend to shift towards the right with time. At these altitudes, the largest values of the OMPS-LP drift with respect to MLS were found (see Fig. 5.9). It is difficult, however, to draw a definite conclusion from these plots, due to the large inter-annual variability. For example, the 2014 profile for Hohenpeissenberg overlaps with the 2017 curve. For Table Mountain, only three years of measurements are available and no significant indications of the drift are visible.
5.4. Validation against lidar observations

Figure 5.16: Relative differences between OMPS-LP and lidar ozone profiles for three lidar stations, according to the title of each panel, calculated for different years.
Chapter 6

Merging satellite data sets

6.1 Previous studies and general concepts

Single satellite missions are generally too short to investigate long-term changes in ozone profiles and to understand the impact of natural phenomena and anthropogenic activities on the stratospheric ozone distribution. The longest single-instrument records available are from \textit{SAGE II} and \textit{HALOE}, which were active from 1984 until 2005. The merging of several satellite data sets is then essential to obtain a time series covering the last decades, which can be used to study ozone trends. In the merging procedure, calibration discrepancies between the sensors, drifts and jumps in each time series, as well as differences in sampling between the instruments, have to be accounted for (Hubert et al., 2016).

Several methodologies to consistently merge satellite data sets have been developed in the last few years and multiple studies have addressed this task. In particular, the merging of instrument records can be performed using ozone absolute values or anomalies computed from the original time series. In the latter case, the seasonal cycle (SC) from each instrument is removed so that any non-physical difference in the intra-annual variability between the data sets is removed. The anomalies may then be adjusted to have the same mean values over a common period and merged. However, for the physical time series to be reconstructed after the merging, an SC should be added back to anomalies, and any long-term variation in the SC is lost. This disadvantage is not met using ozone absolute values; in this case, however, it is more difficult to take the different observation geometry and sampling pattern of the instruments into account.

Tummon et al. (2015) performed an intercomparison between 7 merged satellite ozone data sets over the period 1984-2011, presenting the methods and challenges involved in the merging of single-instrument time series. The authors stressed that it is still not feasible to eliminate all systematic biases from a vertically resolved time series so that measurements from one instrument have to be taken as a reference to correct the biases. The 7 compared data sets showed a good agreement in terms of interannual variability, SC and long-term trends in the lower and middle stratosphere at mid-latitudes, whereas in the tropical UTLS and in the upper stratosphere, a spread of $\pm 10\%$ around the mean was typically found. Among the various data sets considered by Tummon et al. (2015), we find the \textit{Stratospheric Water and OzOne Satellite Homogenized (SWOOSH)} (Davis et al., 2016) and \textit{Global OZone Chemistry And Related trace gas Data records for the Stratosphere (GOZCARDS)} (Froidevaux et al., 2015). Both studies
brought together satellite observations starting with the SAGE missions in the 1980s. SWOOSH provides monthly-mean water vapor and ozone mixing ratio profiles on pressure levels, using different binning settings (in terms of latitude and longitude) from 1980. GOZCARDS provides time series of zonal monthly mean values in terms of VMR vs. pressure, for several trace gases using NASA satellites. In both cases, the merging procedure considers SAGE II absolute values as a reference and removes the biases from the other time series with respect to SAGE II. For SWOOSH, a matching of SAGE II with the other satellite observations was first performed. Profiles were then interpolated to a common grid and the mean offset between the instruments was removed, homogenizing the data sets. Finally, each time series was spatially gridded and combined into a single product, with more weight to the instruments having the most frequent sampling. Tummon et al. (2015) also indicate that the choice of the instruments to be included in the merged product is more important than the choice of the method for merging. Kyrölä et al. (2013) merged SAGE II with GOMOS measurements, performing a bias correction independently for SAGE II sunrise and sunset observations with respect to GOMOS nighttime measurements.

Several authors merged satellite records using the anomaly time series, such as Bourassa et al. (2014) and Kramarova et al. (2017). Recently, Sofieva et al. (2017) merged measurements from SAGE II with the harmonized time series involved in the ESA Ozone-Climate Change Initiative (CCI) project and the OMPS-LP data set, using deseasonalized anomalies of zonal monthly mean time series to study trends over from 1980 to 2016. The period 2002-2015 was used to remove the bias between SAGE II and Ozone-CCI mean anomalies. In addition, OMPS-LP anomalies were offset to Ozone-CCI anomalies using the period 2012-2016. The merged data set consists of monthly zonal mean ozone profiles every 10° latitude. Bourassa et al. (2018) merged SAGE II with OSIRIS time series corrected for a tangent altitude drift. The authors calculated deseasonalized anomalies from the two time series and merged them after the subtraction of the offset over the overlapping period.

Ball et al. (2017) presented a novel approach to account for artifacts in ozone composites that are related to jumps when the instrument source changes or due to drifts in single-instrument time series. The authors built an ozone composite, by implementing a Bayesian methodology, called BAyesian Integrated and Consolidate (BASIC), which accounts for artifacts and drifts. In this chapter, the merging of the OMPS-LP data set with SCIAMACHY and SAGE II time series is described. The subsequent chapter deals with the study of ozone trends using these merged data sets.

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1from the University of Saskatoon.
6.2 Merging SCIAMACHY and OMPS-LP time series

6.2.1 Data sets gridding

To evaluate and remove biases between two satellite records, the overlapping period is generally exploited, as discussed while describing previous studies. As it was already stated in the introduction, SCIAMACHY and OMPS missions share only 2.5 months of observations, before a platform-to-ground failure interrupted the data transmission from Envisat. This overlapping period is not long enough to derive a statistically significant bias estimate. As a consequence, a reference satellite instrument is required as an external transfer function. MLS shares an extensive measurement period with both instruments and was chosen for this purpose as it satisfies several requirements: stability and reliability of observations (Hubert et al., 2016), dense spatial and temporal sampling, and broad latitude coverage (similar to SCIAMACHY and OMPS-LP) (Waters et al., 2006).

In detail, the following three time series have been considered:

- **SCIAMACHY** data from January 2003 to March 2012: we exclude the first five months of measurements because some studies reported anomalous values with respect to other satellite observations at the beginning of the mission, see for example (Sofieva et al., 2017). April 2012 is also excluded because data are only available for the first eight days;

- **OMPS-LP** data from March 2012 until December 2018: February 2012 is excluded because the satellite was only partially operative;

- 13 whole years of **MLS** as a transfer function, from January 2005 until December 2017: only MLS observations within the latitude range daily spanned by OMPS-LP are used to avoid inconsistencies between day- and nighttime measurements in the polar regions.

Ozone profiles are expressed in terms of number density [molec cm$^{-3}$] on a geometric altitude grid. As a consequence, MLS L2 VMR ozone profiles on a pressure grid have to be converted to geometric altitude vs. number density using the temperature profiles retrieved by MLS and the pressure information from ECMWF ERA-Interim, as it was done for the validation in Ch. 5. The typical SCIAMACHY vertical grid is adopted for the merged data set. It spans the altitude range between 8.6 km to 64.2 km, with evenly spaced steps every 3.3 km. MLS and OMPS-LP profiles, characterized by a higher vertical sampling (1 km), are linearly interpolated to the common grid. The presence of the SAA is taken into account for each data set, using the SAA flag in MLS and OMPS-LP L2 data and applying a rectangular mask covering the $[-70^\circ, -20^\circ]$ latitude and $[270^\circ, 360^\circ]$ longitude range for SCIAMACHY.

Similar to the collocation criteria, the parameters used to create level 3 (L3) data, i.e., bin the observations into a regular spatial and temporal grid, have to take into account the wish for a highly resolved time series and at the same time the need for a representative number of measurements in each bin to be averaged. Several ways to obtain L3 data for each satellite are studied to find a good trade-off between these two requests. Table 6.1 reports four possible combinations of latitude vs. longitude vs. time values, showing the average number of measurements in each bin for SCIAMACHY and OMPS-LP.
Table 6.1: Number of SCIAMACHY and OMPS-LP observations in each bin, choosing different settings to create L3 data in terms of latitude, longitude and time.

<table>
<thead>
<tr>
<th></th>
<th>5° lat x 20° lon x 30 days</th>
<th>10° lat x 10° lon x 10 days</th>
<th>5° lat x 5° lon x 30 days</th>
<th>2.5° lat x 30 days (zonal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCIAMACHY</td>
<td>40-75</td>
<td>10-35</td>
<td>10-25</td>
<td>80-250</td>
</tr>
<tr>
<td>OMPS-LP</td>
<td>75-120</td>
<td>20-50</td>
<td>15-35</td>
<td>180-320</td>
</tr>
</tbody>
</table>

Two optimal sets of values are identified, corresponding respectively to column 1 and 4 of Table 6.1:

1. A longitudinally resolved data set, with monthly mean values averaged every 5° latitude and 20° longitude grid;
2. A zonal product with a temporal resolution of 10 days and 2.5°-wide latitude bins.

In both cases, we find a number of measurements in each bin in the order of magnitude of 100 for both instruments. Between these two products, we choose the first one, which gives insight beyond the traditionally used zonal mean values, enabling the study of longitudinally-dependent long-term ozone variations. In the following, several plots display zonal averaged results: in these cases the L3 data sets is zonally averaged before further analysis.

To give an idea of the temporal sampling of the two instruments using the chosen settings, Fig. 6.1 shows the number of available profiles from SCIAMACHY and OMPS-LP in each latitude bin on a monthly basis. The values in the figures have to be divided by the number of longitudinal bins (18), to get the number of profiles contributing to each longitudinally resolved monthly mean value. At the beginning of 2012, the density increases, due to OMPS’ higher sampling per orbit, even though only one slit of OMPS-LP is considered. As mentioned above, the gap in the measurement time series at the end of 2013 (precisely from 26 November 2013 till 24 January 2014) is related to a change in the downloaded pixels from the CCD of the instrument which caused a failure of the retrieval algorithm.

![Figure 6.1: Number of SCIAMACHY and OMPS-LP retrieved profiles on a monthly basis as a function of latitude (every 5°), summed up over the longitudes.](image)

2 Without considering changes as a function of the altitude.
6.2. Merging SCIAMACHY and OMPS-LP time series

6.2.2 Studying the seasonal cycles

The study of the seasonal cycle (SC) of the instruments is an important preliminary step to assess how well they agree as a function of altitude and latitude and whether they need to be subtracted before the merging. The SC and its uncertainty, $\sigma_{SC}(t_m)$, for each month $m$, latitude, longitude and altitude are defined as:

$$SC_m(\phi, \theta, z) = \frac{1}{N_m} \sum_{j=1}^{N_m} O_3(\phi, \theta, z, t_j)$$ (6.1)

$$\sigma^2_{SC_m}(\phi, \theta, z) = \frac{1}{N_m} \sum_{j=1}^{N_m} \sigma^2_{O_3}(\phi, \theta, z, t_j)$$ (6.2)

for the three instruments, where $N_m$ is the number of available monthly mean values $O_3(t)$ for the month of the year $m$ in each time series, and $\sigma_{O_3}(t)$ is the standard error of the mean for each monthly value, related to the spread of the averaged profiles. Figure 6.2 shows the SCs of SCIAMACHY and OMPS-LP ozone profiles in number density at several altitudes and latitudes, together with MLS SC calculated over the periods 2005-2012 (overlap with SCIAMACHY) and 2012-2017 (overlap with OMPS), separately. In this way, the temporal evolution of the SC can be evaluated.

**Figure 6.2:** SCs for the three instruments as a function of latitude and altitude. MLS SC is plotted for the overlapping period with SCIAMACHY (2005-2012) and with OMPS-LP (2012-2016) separately.
From this plot, the general annual ozone variations related to photolysis, chemistry, temperature changes, and transport can be good described, as a function of altitude and latitude. We first notice that, in general, the SC gets stronger towards polar latitudes, while in the tropics it reaches its minimum: this is because around the equator the seasonal changes in both sunlight intensity and transport are the smallest. An overall symmetry can be observed between panels on the left and right sides of the plot, as expected, with a phase shift of six months; however, the SCs in the Southern and Northern Hemisphere may consistently differ, particularly in the lower stratosphere. In this region, the more intense tropospheric wave activity occurring in the Northern Hemisphere causes a stronger circulation and higher ozone concentration towards the North Pole in comparison to the Southern Hemisphere. At these altitudes, corresponding to the last row of the plot, outside the tropics the amount of ozone is regulated by the transport and photolysis: the shallow branch of the BDC carries ozone-rich air from the tropics towards the polar regions, mainly during the winter semester in each hemisphere. Here it accumulates during the winter months when the ozone lifetime is on the order of months, and the annual maximum is reached in the late winter. When the sun comes back in spring, photolysis of ozone takes places and a minimum in the concentration is reached at the end of the summer.

At southern high-latitudes, we notice that the ozone peak occurs in July-August and it is generally located around 70° S at the edge of the strong polar vortex, where ozone accumulates before it breaks down (Grandpré et al., 2000). The relative minimum in September is related to the ozone depletion inside the polar vortex, which interests latitudes down to 60°. Looking at the tropics below 30 km, the ozone concentration depends on the production of odd-oxygen by photolysis: as a consequence, the ozone maxima take place around the equinoxes, when the sun reaches the highest point over the equator, and the minima correspond to the time around solstices. In this way, a semi-annual SC develops. At altitudes around 30 km at mid-latitudes, we notice an annual SC because the main driver is the odd-oxygen production as in the equator. However, right above 30 km, another factor becomes important: the temperature dependence of the ozone destruction rates. The concentration of ozone is found to be inversely proportional to the temperature, with increasing ozone loss as the temperature increases. The ozone maximum is pretty broad, from late spring till the beginning of the fall, which indicates that the increasing ozone production in spring is offset by the increasing rate of destruction as the temperature increases (Perliski et al., 1989). The same inverse proportionality between ozone and temperature is visible in the tropics around 35-40 km: here the ozone number density maxima are out of phase with the sun forcing (shifted by a quarter of a year), in comparison with lower altitudes. Indeed, at the equinoxes, when the sun is at zenith at the equator, the temperature has also a maximum which offsets the maximum in the ozone photolysis production. In the upper stratosphere above 45 km, ozone is under chemical control: it is only produced by the photodissociation of molecular oxygen, whereas ozone destruction processes include the reaction with oxygen atoms and the catalytic cycles. The differences between the two hemispheres are pretty significant, due to asymmetries in the transport and distributions of NOx, ClOx and HOx. We notice at mid-latitudes a maximum in the late summer, with a slow ozone build up and a faster decrease. In the Southern Hemisphere, an approximated semi-annual SC builds up related to temperature effects, transport and photochemistry. In a similar plot but in terms of
ozone VMR we would see a different picture above 40 km, with a minimum in summer, related to the inverse proportionality between ozone concentration and temperature, as described by Perliski et al. (1989).

Comparing the SCs from the three instruments, we notice a generally good agreement; however, discrepancies are visible in terms of the offsets (additive bias), the amplitude of the SC (multiplicative bias) and its shape. Three examples of these types of discrepancies are visible in Fig. 6.2:

1. \([-40^\circ, -20^\circ]\) at 34.8 km: the shape and amplitude of the three instrument SCs are similar, but the curves are shifted in terms of absolute values, displaying a typical additive bias;

2. \([-40^\circ, -20^\circ]\) at 28.3 km: SCIAMACHY SC has a similar shape but a smaller amplitude with respect to MLS and OMPS-LP (multiplicative bias).

3. \([-10^\circ, 10^\circ]\) at 28.3 km: the three SCs have a similar amplitude but a different shape, with SCIAMACHY displaying an annual SC and the other two showing semi-annual variation.

Additive biases are removed in the merging procedure when the mean offsets between the data sets are subtracted. The multiplicative biases and the discrepancies in the SC shape are taken into account when calculating the anomalies. Discrepancies in the SC between MLS/OMPS-LP and SCIAMACHY can be related to their different vertical resolutions and by the used interpolation to the common grid. In addition, the natural atmospheric variability leads to an evolving SC with time. For example, at 34.8 km in the tropics, a vertical shift of up to 5-7% between MLS SCs computed over the two periods is found. Another region where strong discrepancies are visible between the three satellites and the two periods is the lower tropical stratosphere. At higher latitudes, the discrepancies may also be related to the slightly different latitude sampling between SCIAMACHY and OMPS-LP.

### 6.2.3 First approach: plain debiasing

The subtraction of the SC before merging is a common practice to account for sampling issues related to the instrument geometry and the different overpass time. In our case, SCIAMACHY and OMPS-LP have a similar geometry of observation: even though SCIAMACHY flew from North to South and OMPS-LP towards the North, they also observe the atmosphere in opposite directions, resulting in comparable scattering angles along the orbits. Besides, the difference between their ascending node times is around 3 h: SCIAMACHY at 10:00 and OMPS at 13:30. These are also similar to MLS equatorial crossing time at 13:45. As a consequence, considering a generally good agreement of the SCs of the three instruments, except for few latitudes and altitudes, and the similar geometry of observation, the first approach for merging SCIAMACHY and OMPS-LP time series consists in a plain-debiasing of the two data sets with respect to MLS. The bias is defined for each latitude, longitude and altitude as follows:

\[
BIAS_{SCIA}(\phi, \theta, z) = SCIA_{2005-2012}(\phi, \theta, z) - MLS_{2005-2012}(\phi, \theta, z) \tag{6.3}
\]

\[
BIAS_{OMPS}(\phi, \theta, z) = OMPS_{2012-2016}(\phi, \theta, z) - MLS_{2012-2016}(\phi, \theta, z) \tag{6.4}
\]
Fig. 6.3 shows the zonally averaged $BIAS_{SCIA}$ and $BIAS_{OMPS}$ as a function of latitude and altitude, expressed in term of % values, i.e., divided by each respective averaged ozone time series and multiplied by 100. The relative offset $OMPS-LP$ vs. $MLS$ is very similar to that shown in Fig. 5.6 panel (a), but in this case computed from monthly values averaged over the whole time series and on a coarser vertical grid. Comparing $OMPS-LP$ with $SCIAMACHY$ bias (right panel), we notice in both cases that the largest values are found in the lowermost stratosphere, but with opposite values in the tropics. Between 20 and 30 km, the pattern is similar for both the instruments and values are within $\pm 7\%$. Between 30 and 40 km a negative $SCIAMACHY$ bias locally exceeding $-5\%$ is detected, not present in $OMPS$ plot. Between 40 and 50 km, $SCIAMACHY$ shows a positive offset, locally above $7\%$, whereas above 50 km both instruments show lower ozone concentrations in comparison to $MLS$.

These biases in terms of absolute values (ozone number density) are equal to $\pm 4 \times 10^{12}$ molec cm$^{-3}$ below 30 km, $\pm 1 \times 10^{12}$ molec cm$^{-3}$ between 20 and 40 km for both $SCIAMACHY$ and $OMPS$.

Fig. 6.4 shows the distribution of the relative bias between $OMPS-LP$ and $MLS$ in % at several altitudes and longitudinally resolved. We can estimate here that the longitudinal variability is mostly within $\pm 2\%$ above 30 km. In the tropical stratosphere between 20 and 25 km, the mostly neutral values found in the zonal plot (Fig. 6.3) are the results of oscillating values with longitude between $-3$ and $+7\%$. Below 20 km the longitudinal variability increases and reaches its largest values, especially within $\pm 30^\circ$ latitude.

These biases are then applied to the $OMPS-LP$ time series in a way to keep the $SCIAMACHY$ mean level as the absolute reference conventionally. In this way, additive offsets between $SCIAMACHY$ and $OMPS-LP$ are removed with the help of $MLS$ as transfer standard as follows:

$$OMPS_{deb}(\phi, \theta, z) = OMPS(\phi, \theta, z) - BIAS_{OMPS}(\phi, \theta, z) + BIAS_{SCIAMACHY}(\phi, \theta, z)$$ (6.5)

At every altitude, latitude and longitude, the merging of the two time series is then achieved by concatenating the data sets. Only for March 2012 when the two missions overlap, the average
ozone value is computed. For each bin, it is checked whether the number of averaged profiles is higher than 20 and whether data from both instruments are present over the entire time series. The bins that do not meet these two conditions are filtered out. The standard deviation of the merged data set in each bin is computed, according to (Froidevaux et al., 2015), as:

$$
\sigma_{\text{merged}}^2(t) = \frac{1}{(N_{\text{merged}} - 1)} \sum_{k=1}^{2} (N_k - 1) \sigma_{O_3,k}^2(t)
$$

where $N_{\text{merged}}$ is the overall number of merged observations in each month and spatial bin, $N_k$ is the number of observations in each month and spatial bin for the instrument $k$, and $\sigma_{O_3,k}$ the respective monthly standard deviation of the ozone profiles. This expression corresponds, except for March 2012, to the standard deviation of the monthly profiles from the two instruments respectively.

MLS is not included in the merged data set, to avoid possible jumps at the beginning when the instrument started the observations and potentially at the end of its lifetime. In addition, it can be used as a comparison reference, as it was exploited only to remove the average bias.

Figure 6.5 shows in panel (a) the altitude-resolved merged plain-debiased time series zonally averaged in the inner tropics, i.e. $[-5^\circ, 5^\circ]$. In the lower panel, the respective standard deviation of the monthly mean, $\sigma_{\text{merged}}(t)$, is displayed in % values. The missing data at the beginning of 2005 correspond to a low sampling period of SCIAMACHY (particularly February 2005) with less than 20 measurements per longitude bin. From the standard deviation plot, we recognize OMPS higher variability below 20 km with respect to SCIAMACHY, but also lower values after 2012 in the middle-upper stratosphere.
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Figure 6.5: Merged plain-debiased time series in the tropics and respective standard deviation.

Figure 6.6 shows the SCIAMACHY and OMPS-LP relative offsets with respect to MLS before the bias correction as a function of latitude for several altitudes. The most significant discrepancies between the first (SCIAMACHY) and the second (OMPS-LP) parts of the subplots are found below 20 km, at 30-35 km in the Northern Hemisphere, and at 40-45 km overall. In the lower panel of this figure, the relative differences between the merged data set and MLS time series are displayed in the same way.

Relative differences after the debiasing are found to be within ±10% between 20 and 50 km and within 50° S and 50° N. Beyond 50° latitude, relative differences increase, particularly above 40 km and below 25 km. We notice that over the SCIAMACHY measurement period, an SC signature is observed, especially at 30-35 km at mid-latitudes and at 40-45 km at higher latitudes; these discrepancies are directly related to those found in Fig. 6.2. Over OMPS lifetime, less pronounced SC residuals are visible, with a particularly smooth distribution between 35 and 45 km. Below 20 km, the differences increase rapidly, showing strong seasonal patterns.

Above 50 km, a variation of the relative differences is visible within the measurement time of each of the two instruments, suggesting the presence of drifts of each instrument with respect to MLS. For example, the technical change in the L1G processing of OMPS-LP UV radiance at the end of 2013 affects the OMPS-LP UV retrieval and leads to a jump above 48 km between the 2012-2013 period and the last four years of observations. Caution is therefore required in interpreting the computed trends above 48 km. Furthermore, at these altitudes, diurnal variations of ozone play a relevant role and have to be accounted for, as described by Sakazaki et al. (2013). This was not done in this study, as the difference between the ascending nodes of the
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**Figure 6.6:** Upper group of panels: relative differences of SCIAMACHY and OMPS-LP data sets with respect to MLS before the removal of the biases, as a function of latitude for several altitudes. Lower group of panels, relative differences of the plain-debiased merged time series with respect to MLS. The vertical dashed lines indicate the transition between SCIAMACHY and OMPS-LP data sets in March 2012.

Two satellites is of 3.5 h, and the estimated ozone difference is around 1-2 %. In addition, such a bias is considered to be systematic and, if constant, it is removed by debiasing the time series.
6.2.4 Second approach: deseasonalized anomalies

As introduced at the beginning of this chapter, an alternative approach to the merging involves the computation of deseasonalized anomalies, e.g., Sofieva et al. (2017). In this case, SCIAMACHY and OMPS-LP time series are deseasonalized, subtracting the SC computed over their respective measurement time. Then the anomalies are debiased with the help of MLS data set. The relative anomalies, \( \Delta \), and their uncertainties, \( \sigma_{\Delta} \), in each bin (latitude, longitude and altitude) are defined as:

\[
\Delta(\phi, \theta, z, t) = \frac{O_3(\phi, \theta, z, t) - SC(\phi, \theta, z, t_m)}{SC(\phi, \theta, z, t_m)}
\]

(6.7)

\[
\sigma_{\Delta}(\phi, \theta, z, t) = \frac{1}{SC(\phi, \theta, z, t_m)} \sqrt{\sigma_{O_3}^2(\phi, \theta, z, t) + \sigma_{SC}^2(\phi, \theta, z, t_m)}
\]

(6.8)

for SCIAMACHY, OMPS-LP and MLS, where \( \sigma_{O_3} \) is the standard error of the mean for each monthly value and \( \sigma_{SC} \) was defined in Eq. 6.2. The anomalies \( \Delta(t) \) of SCIAMACHY and OMPS-LP are debiased using MLS anomalies as a transfer function as described by Eqs. 6.3 and 6.5. The merging is performed in the same way as done for the plain-debiasing approach, i.e., by concatenation of the time series and averaging March 2012 values. Generally, the estimated uncertainty of the merged anomalies has the following general formulation:

\[
\sigma_{\Delta,\text{merged}}(t) = \min \left( \sigma_{\Delta,\text{mean}}(t), \sqrt{\frac{1}{N} \sum_{k=1}^{2} \sigma_{\Delta, k}^2(t) + \frac{1}{N^2} \sum_{k=1}^{2} (\Delta_k(t) - \Delta_{\text{merged}}(t))^2} \right)
\]

(6.9)

where the index \( k \) indicates the considered instrument, \( \sigma_{\Delta,\text{mean}} \) corresponds to the uncertainty of the instrument closest to the value of the merged time series, and \( N \) is the number of the averaged instruments (two in this case). In our case, this formula holds only for March 2012, when the two time series overlap. For all other months, \( (\Delta_k(t) - \Delta_{\text{merged}}(t)) \) is equal to zero, as \( \Delta_{\text{merged}}(t) \) comes either from SCIAMACHY or from OMPS-LP and \( \sigma_{\Delta,\text{mean}}(t) \) is equal to \( \sigma_{\Delta, k}(t) \) so that the formula is just Eq. 6.8 for the single instruments.

Figure 6.7 shows in panel (a) the merged anomalies time series in the inner tropics \([-5^\circ, 5^\circ]\) with the respective uncertainties, \( \sigma_{\Delta,\text{merged}} \), in panel (b), according to Eq. 6.9. In the first panel, the QBO structure is strongly pronounced, which will be described in more details in Ch. 8. In the UTLS region, the pattern becomes more irregular. Uncertainties tend to decrease in the middle-upper stratosphere during OMPS period, as more observations are available from this instrument. Values are in any case within 0.5 and 1.5 %. On the contrary, in the lower stratosphere, OMPS-LP variability is stronger compared with SCIAMACHY as also seen in Fig. 6.5.
6.2. Merging SCIAMACHY and OMPS-LP time series

Figure 6.7: In panel (a) time series of the merged SCIAMACHY and OMPS-LP anomalies in the tropics [−5°, 5°]. In panel (b) the corresponding uncertainties are shown.

Figure 6.8 shows the differences of the merged anomalies relative to MLS anomaly time series as a function of latitude for several altitudes. In comparison to Fig. 6.6 (lower panel), the differences are generally smaller, within ±5% between 20 and 50 km for both SCIAMACHY and OMPS-LP. Also towards the polar regions up to 70° latitude, the discrepancies are within ±10% with only a few outliers. Above 50 km, the presence of a drift within the single data sets is again observed, e.g., the negative values in the second part of SCIAMACHY lifetime. Below 20 km, we find a strongly irregular pattern with oscillating differences mainly in the tropics. In this plot, we see that by using the anomaly approach, the seasonal residuals found in Fig. 6.6, particularly for SCIAMACHY, are largely reduced.

A similar computation is performed, by taking into consideration different periods to obtain MLS SC with the aim to study the impact of the debiasing procedure on the trend values. In particular, we considered:

- a reduced MLS data set, from 2009 to 2015, in order to deseasonalize MLS by computing the SC over a period centered around the junction of the other two instruments;
- two separate time spans: MLS anomalies are computed independently over the 2005-2012 to debias SCIAMACHY time series and over the 2012-2017 period to debias OMPS-LP.

In the second case, an additional bias, resulting from the difference between MLS anomalies over the two periods, has to be removed before performing the merging.
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Fig. 6.8: Absolute differences of the merged relative anomaly time series with respect to MLS anomalies as a function of latitude at selected altitudes. The vertical dashed lines indicate the transition between SCIAMACHY and OMPS-LP data sets in March 2012.

Fig. 6.9 shows an example of the results of these different procedures, focusing the attention to the tropical middle stratosphere, in particular at 35 km. The first three plots show SCIAMACHY and OMPS-LP anomalies obtained subtracting their respective SCs, which are computed over the corresponding whole time series, together with MLS anomalies, which are computed in three different ways in each panel: in panel (a) using the whole 2005-2017 MLS data set (‘full’); in panel (b) considering the shorter 2009-2015 period (‘reduced’); in panel (c) subtracting two independent SCs over SCIAMACHY and OMPS-LP time series (‘partial’).

The different approaches result in a merged time series where the SCIAMACHY and OMPS-LP contributions are slightly vertically shifted with respect to each other: this can affect the resulting ozone long-term changes. The estimated effect at this latitude and altitude on ozone trends is of about 1 % per decade.

Comparing these plots with the anomalies computed from the plain-debiased merged data set, we found a better consistency with the first approach, i.e., computing MLS SC using its whole time series. For example, in panel (d) of Fig. 6.9 three anomalies time series are plotted together in the tropics at 35 km: the one computed from MLS data set, the merged SCIAMACHY/OMPS-LP anomalies (subtracting for MLS the SC computed over its whole period) and the one obtained from the plain-debiased merged data set (subtracting an SC computed over 2003-2018). We notice a very good agreement of the two time series from the merged SCIAMACHY/OMPS-LP products and also with respect to MLS anomalies. We also notice some periods where MLS anomalies show higher values in comparison to the merged data set, in particular in the second half of 2010 and 2013.
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![Graphs showing merged anomaly data sets with SCIAMACHY and OMPS-LP anomalies at 35 km in the tropics, together with MLS anomalies obtained using three approaches to compute its SC. In panel (a) the whole MLS time series is used, in panel (b) only the 2009-2015 period and in panel (c) two different SCs are computed over 2005-2012 and 2012-2017. In black, the resulting merged anomaly is reported. Panel (d) shows anomalies from MLS time series (computed as in case (a)), from the merged plain-debiased and the merged anomaly data sets.](image)

**Figure 6.9**: Panels (a)-(c): SCIAMACHY and OMPS-LP anomalies at 35 km in the tropics, together with MLS anomalies obtained using three approaches to compute its SC. In panel (a) the whole MLS time series is used, in panel (b) only the 2009-2015 period and in panel (c) two different SCs are computed over 2005-2012 and 2012-2017. In black, the resulting merged anomaly is reported. Panel (d) shows anomalies from MLS time series (computed as in case (a)), from the merged plain-debiased and the merged anomaly data sets.
Therefore, we refer in the rest of the dissertation to anomalies computed using the respective entire time series for each instrument.

### 6.2.5 Comparison with MLS

As the MLS time series has been used as a transfer function and not included in the merged time series, it can still be used as an independent source of data to compare the merged data set. In particular, the correlation coefficient and the drift are computed with respect to MLS for each latitude and altitude. As discussed in the previous two sections, above 50 km, below 20 km and towards polar regions, significant discrepancies and issues have been found in the merged data set. As a consequence, the following analysis and the study of long-term ozone changes focus on the 20-50 km vertical range and within ±70° latitude. Both plain-debiased and anomalies merged data sets are considered together with MLS time series over the 2005-2017 period. The differences between the merged time series and MLS data are used to compute the drift, which is defined as the linear trend in the time series of the differences. A seasonal term (sum of harmonic terms with periods of 6 and 12 months) is also considered in the fit for the plain-debiased data set case.

![Figure 6.10](image)

**Figure 6.10:** Panel (a) and (c): Pearson correlation coefficient of the merged data set with respect to MLS time series over 2005-2017, following the plain debiasing and the anomalies approach respectively. Panel (b) and (d): drift of the merged time series with respect to MLS following the plain debiasing and the anomalies approach respectively; dashed areas identify regions where the drift is not statistically significant.
In panel (a) of Fig. 6.10 the Pearson correlation coefficient as a function of altitude and latitude is shown for the zonally averaged plain-debiased merged data set with respect to MLS. The values of the correlation coefficient are typically above 0.8 in this altitude range and within ±70° latitude, except for few outliers in the lower stratosphere. A very similar result, shown in panel (c), is found computing the correlation between deseasonalized anomalies; in this case, values are on average lower. This because the strong SC which contributes largely to the correlation, was removed. The drift between the plain-debiased merged and MLS data sets is shown as a function of altitude and latitude in panel (b) of Fig. 6.10; dashed areas in this and the following figures indicate non-significant values. Positive drift values are mainly found in the tropical UTLS and towards high latitudes in the upper stratosphere, whereas negative values are visible above 48 km. However, the drift is widely non-significant between 20 and 50 km: this means that the merged SCIAMACHY/OMPS-LP data set is consistent with MLS over the 11 years considered for comparison. As a consequence, we can use with confidence the merged data set to study long-term ozone changes. This consideration is valid only if considering the whole time series: when sub-periods of the merged data set are selected the OMPS-LP drift with respect to MLS has to be taken into account. Very similar values for the drift are obtained using the anomalies times series, as shown in panel (d).

**Figure 6.11:** Longitudinally resolved drifts of the merged time series with respect to MLS over 2005-2016 as a function of latitude and altitude. Dashed areas indicate non-significant trends. The title of each sub-plot indicates the longitude bands over which the profiles are averaged.
Fig. 6.11 shows the longitudinally resolved drift for the plain-debiased data set, i.e., the drift for each of the 18 longitude bins. Significant values are found only in a few cases, mostly above 40 km. Looking at the variations as a function of longitude we notice an asymmetry in the values above 30 km: negative values, although generally non-significant, are found in the [0°, 80°] longitude band, whereas positive trends, yet mostly non-significant, are detected in the [80°, 240°] longitude sector and close to zero values elsewhere. The drift with respect to MLS and its longitudinal distribution has to be taken into account in Ch. 7 when trends from the merged data set are discussed.

6.3 Merging with SAGE II

To study the long-term variations of stratospheric ozone, the SCIAMACHY and OMPS-LP data records are merged with SAGE II occultation measurements, going back to 1984. Because SAGE II observations are sparser in comparison with limb sounders, it is not possible to investigate longitudinally resolved variations, nor to use a 5° latitude grid. The data sets are monthly and zonally averaged, and gridded every 10° latitude to ensure a significant number of SAGE II profiles to be averaged. To give an idea of the different sampling of the instruments, Fig. 6.12 shows the number of SAGE II measurements available zonally in each monthly bin. As we see comparing this plot with Fig. 6.1, there is an order of magnitude between the number of observations from SAGE II and the other two limb sounders, with a further decrease of SAGE II sampling from 2002 with respect to the beginning of the mission.

![Figure 6.12: Number of SAGE II available profiles as a function of time and latitude in each monthly zonal bin.](image)

To take into account the different sampling and observation geometry, the approach to merge the three data sets is based on relative anomalies. From SAGE II data set, anomalies are obtained subtracting its SC calculated using its entire time series. The offset between SAGE II and the previously merged SCIAMACHY/OMPS-LP anomalies is then removed (conventionally keeping fixed the SCIAMACHY level) using the overlapping period of the two missions between August 2002 and August 2005. Before the merging, bins, where less than 10 measurements are available, are rejected, as not statistically significant for a reliable average value.

\[ without considering changes as a function of altitude. \]
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Besides, the distribution of SAGE II latitudes inside the bin may not be representative for the latitude range. A bin of SAGE II L3 data is rejected if the mean latitude of the measurements in the bin and its standard deviation do not cover the latitude center of the respective bin. The merging is performed concatenating the debiased anomalies and averaging the values from SAGE II and SCIAMACHY over 2002-2005.

A slightly different approach to compute monthly mean for SAGE II was also studied: instead of referring each averaged SAGE II observations to the center of each latitude bin, we can assign the average ozone profile to the mean SAGE II latitude (computed over all the measurements falling in that bin) and then interpolate on the usual regular spatial grid. This procedure does not provide significantly different or improved results in terms of ozone trends with respect to the more simple approach, which is then chosen.

Figure 6.13 shows the altitude-resolved time series of the merged anomalies in the tropics $[-10^\circ, 10^\circ]$ and at northern mid-latitudes $[40^\circ, 60^\circ]$, in the upper and in the lower panel respectively. Before plotting the merged series, the mean values of the merged anomalies have been set to zero at each altitude independently. We can notice the poor spatial coverage of SAGE II data set in the tropics, particularly towards the end of its lifetime.

![Figure 6.13: Time series of the merged anomaly data set from SAGE II, SCIAMACHY and OMPS-LP as a function of altitude; in panel (a) for tropics and panel (b) for northern mid-latitudes.](image-url)
Chapter 7

Long-term ozone changes

7.1 Trend studies from merged satellite measurements

Several studies dealing with the merging of satellite time series, like those introduced in the previous chapter, also analyzed the long-term ozone variations using the respective composites. The multi-linear regression (MLR) is a standard methodology applied to derive trends. Many studies used either a piece-wise linear term (PWLT) or EESC proxy in their MLR models to describe the changing trend in ODS in the stratosphere occurred at the end of the 1990s. Another way is to compute unlinked linear trends before and after this turnaround point. The detection of a stratospheric ozone recovery has seen many efforts over the last decade, using several different data sets and methods. WMO (2014) concluded for the first time that a statistically significant ozone increase was identified in the upper stratosphere. Harris et al. (2015), used the merged data sets described in Tummon et al. (2015). The authors applied both a model including two unlinked linear trends and a PWLT model over the period 1979-2012, taking 1997 as inflection point, which corresponds to the ODS peak concentration. The authors first computed trends from the various data sets, highlighting the different features found in the composites, and then a best estimate of the trends, combining the single results. In agreement with previous studies, before 1997, they found negative trends in the upper stratosphere in the range from -5 % to -10 % per decade. In the second half of the record, a positive trend was detected in the same regions, with values of about 2 % per decade at mid-latitudes and 3 % per decade in the tropics. The authors remarked about the difficulty of establishing the significance of the ozone recovery found in the post-1997 period. Measurement records spanning a longer period, better consistency of single-instrument time series and more accurate merging including uncertainty estimates are thought to be necessary elements to assess ozone variations over the last two decades. Steinbrecht et al. (2017) used several existing ozone composites (e.g., SWOOSHELGOCARDS SBUV) and ozonesondes data sets to analyze 2000-2016 trends, updating Harris et al. (2015) study. Thanks to four additional years of observations and improved single instrument data sets, the authors detected a significant increase of upper stratospheric ozone, corresponding to a recovery of 2-2.5 % per decade at mid-latitudes and 1.5 % in the tropics. The merging performed by Sofieva et al. (2017) was described in Ch. 6. The authors applied an MLR model with a PWLT and confirmed the strong negative trends before 1997 with values between -4 % and -8 % per decade in the upper stratosphere. After 1997, they found statistically significant positive values at mid-latitudes above 35 km, reaching
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up to 2-3 % per decade.

Ball et al. (2018) applied to their composite data set the dynamical linear modeling (DLM) methodology, which does not depend on a fixed ozone turnaround point. Ozone trends calculated using the lower stratospheric column showed for the first time evidence of significant negative values in the lower stratosphere, within 60° latitude. According to the authors, the decrease in the lower stratosphere offsets the recovery in the upper stratosphere, leading to an overall decline of the stratospheric ozone column. This analysis has recently been challenged by Chipperfield et al. (2018), who attributed the negative trends in the lower stratosphere to the strong inter-annual variability. Bourassa et al. (2018) also identified negative trends in the lower stratosphere at all latitudes, but with significant values generally below 20 km.

All presented studies investigated zonally averaged ozone trends and only SWOOSH data set reported longitude-resolved ozone time series. However, pronounced zonal asymmetries in the distribution of trace gases in the stratosphere have been found, particularly at northern mid-latitudes in winter. Gabriel et al. (2011) and Bari et al. (2013) investigated the zonal anomalies in ozone and water vapor distribution using a long-term mean from models, reanalysis and satellite measurements. They described the wave-one pattern which develops during winter months in the Northern Hemisphere, with an amplitude of 10-20 % of the zonal mean values. This pattern is characterized by a pronounced maximum over eastern Russia/North Pacific related to the Aleutian low and a minimum over North Atlantic/Northern Europe. Vertically, a double peak structure was identified, with maxima in the lower and in the upper stratosphere. A similar but weaker pattern was also identified in the Southern Hemisphere. In general, in the lower stratosphere, the asymmetries are directly dynamically driven, via advection by geostrophically balanced winds, whereas in the upper stratosphere they are related to temperature anomalies, which influence ozone photochemistry. Newchurch et al. (2001) found a wave-one pattern also in the lower tropical stratosphere using TOMS data. Kozubek et al. (2015) recently performed a study of zonally resolved stratospheric dynamics and its long-term changes. The authors used reanalysis data to analyze the structure of the BDC as a function of longitude and its impact on the ozone distribution. At northern mid-latitudes at 10 hPa, they identified a two-core structure of opposite meridional winds: one centered over the Canadian and the other over the Asian sector, corresponding to the wave-one pattern already described. By investigating the meridional wind at these heights, they found significant trends, showing a weakening of the two-core structure after the ODS turnaround point in 1997. These changes in the dynamics of the stratosphere affect the ozone distribution in this region as well. The discussion above illustrates the limitations of the zonal mean approach to describe stratospheric dynamics and related ozone trends.

Longitudinally resolved ozone trends have been investigated mainly in the 1990s using total column measurements from TOMS focusing at northern high-latitudes during the winter. In particular, Hood and Zaff (1995) studied the ozone total column distribution and trends over the 1980s during winter months. The authors first identified the typical asymmetric ozone distribution related to quasi-stationary planetary waves. In addition, a distinct longitude dependence of the mid-latitude ozone trends over this period was highlighted: the largest negative trends (-40 DU) occurred over Russia and western Pacific (where the climatological ozone has
its maximum), whereas positive trends were found over the northern Atlantic sector. By applying an ozone transport model, the authors concluded that the tropospheric decadal climate variability plays a major role in the total ozone trends, governing the planetary wave activity and influencing the transport to the lower stratosphere. Similar longitudinally dependent trends were already identified in the study of Stolarski et al. (1992), which analyzed total ozone measurements from TOMS.

### 7.2 Multi-linear regression model

This section was partially published in Arosio et al. (2019).

To study long-term ozone variations as a function of altitude, latitude and longitude, we follow a standard approach: an unweighted MLR model is applied to the merged time series, accounting for several factors affecting ozone variability in the stratosphere, called fit proxies. The following terms are considered in the MLR, similar to the ones applied to the SCIAMACHY time series by Gebhardt et al. (2014):

\[
O_3(t) = c_0 + c_1 t + \sum_{j=1}^{2} \left( c_{2j}\sin\left(\frac{2\pi j t}{12}\right) + c_{2j+1}\cos\left(\frac{2\pi j t}{12}\right) \right) + QBO(t) + Solar(t) + ENSO(t) + N(t)
\]

or

\[
\hat{O}_3 = X\hat{\beta} + \hat{N}
\]

where \(t\) is the time in months and \(c_i\) are the regression coefficients, which are contained in the \(\hat{\beta}\) vector. The \(c_0 + c_1 t\) is the linear part of the model: \(c_1\) is the slope per month, so that \(c_1 \times 120\) gives the trend at a given altitude, latitude and longitude, per decade. All trends shown in the next pictures are expressed in % per decade: in case the ozone change is computed in terms of number density, the respective value is divided by the average of the time series. The other terms of the equation before \(N\) are periodic variations that are described in the next subsection.

The \(t\)-th row of the \(X\) matrix contains the values of the fit terms for the selected month \(t\). \(N\) is the noise, i.e., the residuals of the fit, which corresponds to the variability in the time series not captured by the fit proxies.

The least square estimator \(\hat{\beta}\) is computed as follows:

\[
\hat{\beta} = (X^T X)^{-1} X^T \hat{Y}
\]

and the covariance matrix of the regression coefficients as:

\[
Cov(\hat{\beta}) = \frac{\hat{\sigma}^2}{N} (X^T X)^{-1}
\]

The square root of the diagonal elements of this matrix are the 1σ uncertainties of each \(\beta_i\) component. Throughout this chapter, trends are referred to as significant (at the 95 % significance level), if the following condition is fulfilled:

\[
\left| \frac{c_1}{\sigma_{c_1}} \right| \geq 2
\]
This ordinary least squares technique is applied twice to the time series in an iterative fashion: the first time to estimate the autocorrelation of the noise and the second time to compute the trends. As described by Weatherhead et al. (1998) and Tiao et al. (1990), it is a common practice to account for the autocorrelation of the data set with 1-month lag when dealing with geophysical time series. In mathematical terms, the noise $N$ is assumed to be an autoregressive process of the first order, i.e., its value at time $t$ depends on its value at the $t - 1$ time step, as described by the following formula:

$$N(t) = \phi N(t - 1) + \epsilon(t)$$

(7.6)

where $\phi$ is the autocorrelation factor and $\epsilon$ a randomly distributed noise sequence with zero mean (white noise). Inverting this equation, the white noise $\tilde{\epsilon}$ can be obtained. This corresponds to the so-called Cochrane-Orcutt transformation (Cochrane and Orcutt, 1949), which in matrix notation corresponds to:

$$\tilde{\epsilon} = P \tilde{N}$$

(7.7)

where $P$ is a function of $\phi$ (for details see Weatherhead et al., 1998). The second iteration of the MLR model is then applied to the following transformed time series $\tilde{Y}^*$, which is associated with a white noise vector, as required by the least square technique:

$$\tilde{Y}^* = X^* \tilde{\beta} + \tilde{\epsilon}, \quad \tilde{Y}^* = P \tilde{Y}, \quad X^* = PX$$

(7.8)

A weighting of the time series using the reciprocal of the monthly variance, i.e., $\sigma^2(t_m)$ in Eqs. 6.6 and 6.8 is also considered and tested: in this way, months with a smaller variability of the averaged profiles receive a stronger weight with respect to monthly values where the observations show a high variability around the mean values. Since no significant changes are found between the approaches in terms of trend values, we consider here the simple unweighted MLR.

### 7.2.1 Used proxies

In Eq. 7.1 several terms are present, which are related to phenomena significantly affecting the stratospheric ozone distribution and generally considered to compute trends (Zerefos et al., 2018).

The term after the linear one corresponds to the sum of harmonics with a period of 6 and 12 months. These are considered only for the plain-debiased merged data set to approximate annual and semiannual oscillations related to the seasonality. For the 50-60° N latitude band, the seasonal variability of ozone below 25 km has a particularly large amplitude, which is sub-optimally approximated by using simple harmonics. This variability in the Northern Hemisphere is directly related to the wave activity, which is strongest at high-latitudes during the late winter and influences the amount of ozone in the lower stratosphere. The cumulative eddy heat flux is commonly used as a proxy for the strength of the BDC (Weber et al., 2011), which is directly related to the wave activity intensity. As a consequence, the harmonic terms at these latitudes are replaced by the two-months lagged eddy heat flux at 50 hPa from ERA-Interim, integrated over each year starting from October (Gebhardt et al., 2014).
The influence of QBO is accounted for by considering as a fit proxy the monthly average of the zonal wind components measured at 10 and 30 hPa by sondes launched at the Singapore station (available at [http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo/index.html](http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo/index.html)). At these altitudes, the QBO phase is shifted by approximately a quarter and the superposition of these two components are expected to fit any QBO phase. This combination of tropical zonal winds is used at all altitudes and latitudes as follows:

$$QBO(t) = c_{4a}QBO_{10hPa}(t) + c_{4b}QBO_{30hPa}(t)$$  \quad (7.9)

As described in Ch. 1, solar activity has a noticeable impact on ozone, especially in the upper stratosphere. The period 1985-2018 covers exactly three full solar cycles, starting from the minimum between cycle 21 and 22 until the minimum after cycle 24. As a proxy for the solar activity, we consider the Mg II index, which is the core-to-wing ratio derived from the Mg II doublet that is known to be highly correlated to the solar irradiance variability in the UV and extreme-UV (Snow et al., 2014). The composite Mg II data set we use was derived at the University of Bremen from GOME, SCIAMACHY, GOME-2A and GOME-2B data (available at [http://www.iup.uni-bremen.de/UVSAT/Datasets/mgii](http://www.iup.uni-bremen.de/UVSAT/Datasets/mgii)). The solar proxy is then given by:

$$Solar(t) = c_5MgII(t)$$  \quad (7.10)

Finally, we include the El Niño 3.4 index (Trenberth and Stepaniak, 2001) as a fit proxy for ozone variations in the lower tropical stratosphere between 20° S and 20° N and up to 25 km. In the considered period, two strong El Niño events occurred, a minor one in 2009-2010 and a major one in 2015-2016, classified as one of the strongest ever recorded. Two La Nina strong phases were also recorded, in 2007-2008 and 2010-2011. The proxy used is based on sea surface temperature anomalies averaged from 5°S - 5°N and 170°-120°W. In detail, in order to account for the time lag between the ENSO proxy and its signature in the ozone time series at different latitude and altitudes, we consider a proxy comprising El Niño 3.4 index anomaly and its derivative as follows:

$$ENSO(t) = c_6[N_{34}(t) + \frac{dN_{34}(t)}{dt}\delta(t)]$$  \quad (7.11)

where δ indicates the time lag in months. An iterative procedure is used to assess δ. Starting from a time lag of 2 months, the MLR is repeated, updating the time lag at each iteration until it approaches a fraction of a month. The final time lag is allowed to vary between 0 and 12 months. If it does not converge within 10 iterations or it exceeds this range, the ENSO proxy is not used in the regression.
7.3 Zonal trends from 1985 until the present

As we assume no PWLT in the MLR formulation, the model in Eq. 7.1 without harmonic terms is applied to the merged zonal SAGE II/SCIAMACHY/OMPS-LP time series in terms of anomalies over two periods: 1985-1997 and 1998-2018. We assume 1997 as the turn around point for ODS. The aim is to confirm the ozone depletion over the first period and to analyze the expected recovery over the second period in the upper stratosphere as a consequence of decreasing ODS and increasing GHG emissions.

The resulting ozone trends for the two periods are shown in Fig. 7.1 in panel (a) over the period 1985-1997 and in panel (b) between 1998 and 2018. Trends are reported over the 20-48 km altitude range and within 60° latitude; non-dashed areas indicate significant trends, in this and the following figures. The defined altitude-latitude range is similar to the validity domain of the SCIAMACHY/OMPS-LP merged data set, after the discussion of the comparison with MLS time series in Sect. 6.2.5.

Before 1997 we find extensive negative trends above 30 km with values in the upper stratosphere of about -4 % in the tropics and exceeding -6 % within [20°, 60°] and [-60°, -20°] latitude, with larger absolute values in the Northern Hemisphere. Trends below 30 km are extensively negative but generally non-significant. After 1998, positive values are extensively detected, which are significant mainly at mid-latitudes above 35 km. We notice a hemispheric asymmetry with positive values up to +4 % in the Northern Hemisphere in comparison with +2 % reached at southern mid-latitudes. In the tropics, trends are positive and barely significant around 38-40 km, close to zero (or slightly negative at 25 km) and not significant below 38 km. Overall, in the lower stratosphere, we do not detect significant values.

Comparing these plots with the results found in previous studies such as Sofieva et al. (2017), Steinbrecht et al. (2017) and Bourassa et al. (2018), we notice a generally good agreement for both periods. More specifically, for the first period our values are well comparable with other studies considering SAGE II data or merging them with few other satellites. Only in the tropics,
positive values cover a reduced area in comparison with, for example, Kyrölä et al. (2013). In the second period, the ozone recovery in the upper stratosphere is reported with different distribution in many studies. Sofieva et al. (2017) 1997-2016 trends show higher values in the Southern Hemisphere around $-40^\circ$ to $-20^\circ$ latitude; Bourassa et al. (2014) 1997-2014 trends also show stronger values in the Southern Hemisphere and significant positive values up to 50 km, whereas above 45 km we found non-significant values, becoming negative in the tropics. In the middle tropical stratosphere at 30-35 km, we do not see negative values, which were found in previous studies, but positive non-significant trends. This is related to the inclusion of the last two years of observations: applying the MLR to the time series until 2015 or 2016, we find a significant negative trend of about -2% in this region. The increasing trends towards polar latitudes in the upper stratosphere in panel (b), especially in the Northern Hemisphere, is probably an artifact of the merged data set.

### 7.4 Long-term changes over the period 2003-2018

#### 7.4.1 Zonal trends using the two merging approaches

To investigate long-term ozone variations over the last 15 years, the model in Eq. 7.1 was applied to the period between January 2003 and December 2018 using the SCIAMACHY/OMPS-LP merged time series, which consists of 192 months. Over this time, one and a half seasonal cycles are covered: the second half of cycle 23 and all of cycle 24. Five more years of observations are required to cover two full cycles and have better robustness of the results. Figure 7.2 shows the resulting long-term zonal ozone changes. Their distribution is displayed as a function of latitude and altitude applying the MLR model to the two merged data set, in terms of both anomalies and ozone number density, as described in Sect. 6.2.4 and 6.2.3, respectively. In panel (a) the merged data set in terms of anomalies is considered, while panel (b) refers to the plain-debiasing approach.

![Figure 7.2](image.png)
The overall pattern shown in the two panels is similar; however, trend values in panel (a) are
slightly smaller in absolute values with respect to those in panel (b). Similarly to what we
discussed for Fig. 7.1, long-term changes are found to be statistically significant mostly be-
tween 35 and 45 km at mid-latitudes, with positive values of about 3-4 % per decade. The
ozone recovery is unevenly distributed in the two hemispheres, as also found in other stud-
ies, e.g., Bourassa et al. (2018): larger positive values exceeding +5 % are found at northern
high-latitudes. Above 48 km within [−30°, 30°] negative trends are observed, which become
significant at the uppermost altitude. As discussed in Ch. 6 these values have to be taken
with caution as the single-instrument data sets showed significant discrepancies with respect
to MLS at these altitudes. The robustness of the trends was tested, changing the beginning of
the merged time series. When the MLR model is applied starting from mid-2003 or 2004, the
negative values above 45 km are strongly reduced and are not significant anymore, whereas
the positive trends at mid-latitudes increase by ∼ 1 %. This indicates that the negative trends in
the upper stratosphere are either related to some issues at the beginning of the SCIAMACHY
measurement period or influenced by the inter-annual ozone variability. Looking at the mid-
dle and lower stratosphere, positive values of 1-3 % are visible at mid-latitudes but not always
significant, particularly for the anomaly data set. In the tropics long-term variations are close
to zero between 25 and 32 km, as also seen in Fig. 7.1. The significant negative trends in the
lower stratosphere reported by Ball et al. (2018) are not confirmed using the merged SCIA-
MACHY/OMPS-LP data set. Below 25 km in the [−30°, 30°] latitude range, negative trends are
identified, but they are generally non-significant. As described in the next section in Fig. 7.5
only below 20 km we find a statistically significant ozone decrease in some latitude bins.

7.4.2 Changes over SCIAMACHY and OMPS periods

The following discussion has been partially published in Arosio et al. (2019).
It is interesting to compare the previous results with the ozone changes computed over shorter
periods, in particular over SCIAMACHY and OMPS lifetimes. In this way, it is possible to in-
vestigate short-term stratospheric variability and understand its importance for the long-term
trends. When considering shorter periods, we have to take into account that slowly varying
proxies (as the solar activity) may affect the computed ozone variations, so that short-term
trends are less robust and have to be taken with more caution.

We refer in particular to the study of Gebhardt et al. (2014), who applied a similar MLR anal-
ysis to an older version of SCIAMACHY data. The authors found positive trends over the
SCIAMACHY lifetime in the upper stratosphere in the tropics and at mid-latitudes. However,
strong negative values, reaching -10 to -15 % per decade were detected in the tropics between
30 and 35 km. A similar pattern, although less pronounced, was reported by other studies. For
example, Kyrölä et al. (2013) pointed out negative ozone trends of -2 to -4 % over the period
1997-2011, analyzing merged SAGE II and GOMOS data. Two other studies came to similar
results: Eckert et al. (2014) found a comparable decrease in MIPAS observations from 2002 to
2012 and Nedoluha et al. (2015) presented a change of -0.006 ppmv y⁻¹ using HALOE and MLS
measurement time series.
In the two panels of Fig. 7.3, the focus is directly put to the SCIAMACHY and OMPS observation times. In particular, panels (a) and (b) refer, respectively, to the periods January 2004-June 2012 and January 2012-June 2018, covering approximately an integer number of QBO cycles in both cases. The merged data set in terms of ozone anomalies is used. Results in panel (a) can be compared with the trends reported in Gebhardt et al. (2014) and Galytska et al. (2019). Consistent with these previous studies, we notice strong negative trends in the tropical middle stratosphere and two areas of significant positive trends: one in the Southern Hemisphere in the lower stratosphere and the other in the upper stratosphere at northern mid-latitudes. Short-term changes in panel (b) over the period 2012-2018 show, to a certain extent, an opposite picture with respect to panel (a) in the middle and lower stratosphere: positive changes are found in the tropics around 35 km and negative changes in the \([-40^\circ, 10^\circ]\) band at lower altitudes. Above 35 km significant positive changes are found at all latitudes. The discussion of trends over this short period in the upper stratosphere has to take into account the positive OMPS-LP drift with respect to MLS, shown in Fig. 5.9. As a consequence, the actual positive values are expected to be smaller, particularly around 40 km in the Northern Hemisphere. In addition to the drift, it has to be noted that in this region MLS SC, as shown in Fig. 6.2, has a particularly pronounced natural variation between SCIAMACHY and OMPS periods: as a consequence, we find a sensitivity of the merging procedure to the period chosen to compute MLS SC which leads to an uncertainty in the long-term ozone changes estimated to be about 1% per decade in this region.

This figure shows that the long-term changes computed over the last 15 years are the result of complex changes in stratospheric dynamics, which occurred over shorter time scales. This discussion also stresses the difficulty to separate the atmospheric variability from long-term tendencies when short periods are considered.

**Figure 7.3:** Zonal mean linear short-term ozone changes over two periods considering anomaly data sets: in panel (a) over the SCIAMACHY time and in panel (b) over the OMPS period. Dashed areas indicate non-significant trends.
Galytska et al. (2019) recently focused the attention on the middle tropical stratosphere, studying ozone trends from SCIAMACHY observations and comparing them with simulations from the TOMCAT CTM. Model simulations are in agreement with the measurement data in the period 2004-2012. The authors explained the observed negative ozone trends found at these altitudes. Anti-correlated changes in ozone and NO\(_2\) were found in both SCIAMACHY observations and CTM simulations. They showed that seasonal variations of the stratospheric dynamics control these chemical changes. The CTM showed a slow-down of the vertical transport during autumn months (positive changes of the age of air) followed by a speed-up during winter months (negative changes of the age of air), which causes changes in the residence time of N\(_2\)O and as a consequence in NO\(_2\) and ozone profiles. When averaged over the whole year, age of air changes of different sign cancel out, resulting in no significant annual mean change, whereas the responses of N\(_2\)O and, as a consequence, NO\(_2\) and ozone remain, due to a non-linear relation between chemistry and transport (Galytska et al., 2019).

To check if the pattern identified in the tropical middle stratosphere is potentially affected by the switch between the two instruments, we analyzed a simulation run from the CTM TOMCAT (for details about the model refer to Chipperfield, 2006; Galytska et al., 2019). This run covers the period 2003-2017 and was constrained for SCIAMACHY observations, i.e., the output of the model is at SCIAMACHY equatorial crossing time, at 10:00. In Fig. 7.4, the top panel shows the time series of ozone at 31.5 km over the period 2003-2018, considering the anomaly merged data set. In the bottom panel, the time series simulated by the TOMCAT CTM is displayed. In both cases, the QBO fit term is subtracted from the time series to remove the oscillations at this altitude and to better visualize the linear changes. Besides, the linear fit terms are superimposed in the plots, considering three periods: the whole time series, 2003-2011 and 2011-2018 (or 2017 for TOMCAT). The trend values with the respective uncertainties from the MLR are reported in terms of % per decade on the bottom of each panel.

The results are very similar to what found in Fig. 7.3. At 31.5 km we notice a decline in ozone until 2010-2012 (with values close to -10% per decade), whereas after 2011-2012 the ozone amount in this region leveled up to values recorded in mid-2000, resulting in nearly no overall change in ozone. This fact is enhanced by the anomalous QBO event that occurred in 2015-2016 (Newman et al., 2016), which led to higher ozone in the tropical region during 2016 (Tweedy et al., 2017), as discussed at the end of Ch. 8.

In the lower tropical stratosphere (here not shown), the trend over 2003-2018 is also close to zero. However, looking at the period before and after 2011, we notice that over the SCIAMACHY time a positive trend is present (7% per decade), which was already described by Gebhardt et al. (2014). Over the OMPS period, the tendency becomes flat or slightly negative, reducing the overall value of the trend.

Going back to the period before 2002, no such oscillation has been found so far over the SAGE II period. We expect this short-term changes to be dynamically driven and a dedicated study with the help of TOMCAT simulations is planned.
7.4. Long-term changes over the period 2003-2018

7.4.3 Investigating the longitudinal variability

Exploiting the high spatial resolution of the SCIAMACHY/OMPS-LP data set, it is possible to investigate the longitude variations of the trends, over the period 2003-2018. Fig. 7.5 shows the linear ozone changes computed using the plain-debiased merged data set in each longitudinal bin. Missing data at mid-latitudes in the Southern Hemisphere are related to the presence of the SAA.

With respect to the zonal picture, the hemispheric asymmetry is more evident in this case, particularly around 40 km. In some longitude bands, the positive trends are strongly enhanced in the Northern Hemisphere, whereas at southern mid-latitudes the values happens to be non-significant. Looking at the lower stratosphere, we notice that the non-significant negative trends detected in the zonal mean values, become significant in some longitude bins mainly at altitudes below 20 km. The longitudinally resolved drifts between the merged data set and MLS time series, identified in Fig. 6.11, are too small (generally within ± 1 %) to explain the longitudinal differences in the ozone trends, which have values of about 2-4 %.

To better visualize the longitudinal variability of the ozone trends, Fig. 7.6 illustrates the latitudinal and longitudinal distribution of the long-term ozone changes at 41.3 km, where positive values have been detected in the zonal picture. The plain-debiased data set has been used, but very similar results are obtained using the anomaly approach. The longitudinal variability is evident, especially in the extra-tropical regions. The most relevant pattern in this plot is observed at northern mid and high latitudes, where ozone changes reach values above 5 % per decade over Canada and the North Atlantic, whereas they are non-significant and close to zero over Siberia. Above Antarctica, the trend is also positive, but a dedicated study focusing on
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Ozone distribution during Antarctic spring is required to assess the ongoing ozone recovery in this region.

Panel (b) of Fig. 7.6 shows the longitudinally resolved ozone field at 21.7 km. At this altitude, and even more pronounced at 18 km (not shown here), we notice the negative trends in the tropics and positive trends at mid-latitudes, even if in both cases they are mostly non-significant due to the large inter-annual variability. This pattern is a possible indication of the speed-up of the BDC, which transports ozone more efficiently towards higher latitudes, as its lifetime is long enough. At the same time, in the tropical region, ozone-poor tropospheric air is faster transported into the lower stratosphere.

Figure 7.7 shows the cross-section of the trends at 60° N and S to assess the consistency of the longitudinal pattern found in the previous plots. As we can see, the vertical structure of the positive trends in the upper stratosphere between 160° W and 20° W is homogeneous over three grid levels, from 38 to 44 km. At eastern longitudes, i.e., over the Siberian sector, values are consistently non-significant over the whole vertical range. In the Southern Hemisphere, the vertical consistency is similar to that found in panel (a), but the longitudinal variability is reduced.
7.4. Long-term changes over the period 2003-2018

Concluding this chapter, three are the main findings of this trend investigation:

- The ozone recovery post-1997 has been found, with values up to +4 to +5 % in the upper stratosphere at mid-latitudes. These values are extensively statistically significant and confirm the results discussed in previous recent studies;

- The unexpected significant zonal asymmetries in the long-term changes have shown a coherent vertical structure, especially at northern mid-latitudes, pointing out the need for further investigations to understand the driving mechanisms of these patterns;

- The change of sign in the tropical middle stratosphere during the last 15 years is an interesting example of short-term variability whose robustness has been proven by comparing the merged data set with a TOMCAT simulation.
Regarding the lower stratosphere, despite negative values have been detected using the merged SCIAMACHY/OMPS-LP merged time series, the large inter-annual variability prevents to draw reliable conclusions about the expected decrease of the ozone concentration in this region.
Chapter 8

Geophysical studies

8.1 The solar event in September 2017

On short time scales, solar proton events (SPEs) are responsible for substantial ozone reductions within a few days in the polar regions. SPEs are strong emissions of protons and heavier ions from the sun in the occasion of a so-called coronal mass ejection. These events are recorded during phases of intense solar activity, in the proximity of a solar maximum. When the Earth happens to be in the trajectory of such a strong proton emission, charged solar particles are guided by the Earth’s magnetic field towards the polar regions where they enter the atmosphere and interact with molecules in the mesosphere and stratosphere. During these interactions, odd oxygen and odd nitrogen are formed, through the dissociation of $\text{O}_2$ and $\text{N}_2$, so that $\text{HO}_x$ and $\text{NO}_x$ catalytic cycles are activated. $\text{HO}_x$ catalytic cycles dominate above 50 km, $\text{NO}_x$ ones below this altitude. If the event happens during the polar night, $\text{NO}_x$ have a long lifetime and can also be transported outside the polar regions. As a consequence, large ozone depletion has been predicted by models and observed on many occasions. One of the most famous events occurred in October 1989: according to balloon-borne measurements, the interaction of the incoming charged particles with the atmosphere led to ozone depletion over the southern polar cap up to 20 % at 40 km (Reid et al., 1991). The effects of this strong event were shown to interfere with chlorine and bromine loss cycles during the next 2-3 years (Jackman et al., 2000). A significant event also occurred between October and November 2003 and was studied using SCIAMACHY data by Rohen et al. (2005).

September 2017 witnessed the strongest solar activity of the 24th solar cycle, with two events that impacted on the Earth’s atmosphere. A large solar X-ray flare, class X9.3\footnote{1} took place on 6 September 2017. This eruption was accompanied by a fast expulsion of coronal plasma whose trajectory met the Earth. Another strong X8.2 solar flare followed the first event on Sunday 10 September, which resulted in an even stronger high-energy SPE.

Figure 8.1 shows the proton flux measured by the detectors on board the Geostationary Operational Environmental Satellite (GOES) using three thresholds for the energy of the incoming protons: 1 MeV, 10 MeV and 100 MeV. In the left panel, the event of the 10 September 2017 is shown, whereas on the right panel the event of end-October 2003 is presented. As we can see
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comparing the two panels, the 2003 event was one order of magnitude stronger than the event recorded in 2017, particularly in terms of the most energetic proton flux.

**Figure 8.1:** Proton flux as measured by the GOES satellite for the SPE recorded in September 2017 (left panel) and October/November 2003 (right panel).

The impact of the September 2012 event on the middle stratosphere was evident with a strong ozone depletion visible from OMPS-LP profiles. The signature of the ozone depletion is particularly clear above 48 km. **Fig. 8.2** shows the time series of ozone number density at 54 km during the first 20 days of September 2017: as we can see a dip of 10 % in the time series is observed on the 11th, followed by a recovery within the 15th of the month.

**Figure 8.2:** Ozone time series at 54 km covering the first 20 days of September 2017.

To have a closer look at the ozone loss during the SPE we consider the relative difference between the ozone distribution averaged over the first four days of the month and over four days around the event (11-14 September). **Panel (a)** of **Fig. 8.3** shows the results: ozone losses up to 25-30 % with respect to the beginning of the month have been recorded, especially above 70°N latitude. We have to take into account a seasonal decrease in ozone that overlaps with the SPE signature, which explains the mostly negative values, as also seen in **Fig. 8.2**. The data
density is not enough to obtain a complete coverage of the hemisphere. Panel (b) reports the relative differences computed between the ozone measured on the 11-14 September 2017 and in the same days in 2016. We notice that outside the polar vortex the ozone concentration was higher in mid-September 2017 in comparison with 2016. On the contrary, inside the polar vortex the relative differences show values of -10 to -20 %, particularly over the Canadian sector.

![Figure 8.3: Relative differences in the ozone concentration at 54 km over the Arctic region: in panel (a) between the beginning of September 2017 and the days around the SPE event, in panel (b) between the same days (11-14 September) in 2017 and 2016.](image)

Comparing these values with Rohen et al. (2005), we find that, as expected, the effects of the September 2017 SPE on the middle atmosphere were less strong that in 2003, when the ozone loss locally reached values of up to 60-80 % around 50 km.

### 8.2 Arctic and Antarctic ozone hole

The stratospheric phenomenon called ozone hole has already been discussed in Ch. Several studies focused on the time series of Antarctic ozone holes to find a possible recovery after the end of the 20th century. Although the strong inter-annual variability complicates the identification of trends in the time series of spring polar ozone concentration, some hints of healing have been recently found. For example, Solomon et al. (2016) pointed out that the fingerprints of an ozone recovery can be identified in both the increase of its column amount and in the decrease of the areal extent of the ozone hole, which have been observed each September starting from 2000. Recently, October 2015 witnessed a remarkably large ozone hole, reaching the historical record of daily size: it was attributed by Ivy et al. (2017) to a very cold and stable polar vortex but also to the enhanced aerosol concentration after the Calbuco volcanic eruption, which occurred in April 2015. The presence of aerosol particles increases the surface where heterogeneous chemical reactions involved in the ozone destruction can take place.

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2 We firstly binned OMPS-LP observation in 2.5° latitude and 5° longitude.
In Fig. 8.4, an example of ozone distributions in different years over the Arctic and the Antarctic are shown, in terms of stratospheric column, from monthly averaged OMPS-LP observations. In the first row, a comparison is performed between a usual ozone distribution at northern high-latitudes recorded in March 2010 and the low ozone amounts observed in March 2011. As studied for example by Manney et al. (2011), the exceptionally cold and stable conditions of the stratosphere during the late 2011 winter led to the largest ozone loss ever observed over the Arctic regions. An extensive presence of PSCs was recorded: through the heterogeneous chemistry on their surfaces, Manney et al. (2011) estimated that up to 80% of the ozone present in January was chemically destroyed by the end of March at altitudes around 18-20 km.

In the lower row of Fig. 8.4, a comparison of the ozone distribution is done between October 2014 and October 2015. In the first case, a slightly below average depletion was observed, whereas in 2015 the already mentioned large ozone hole was recorded, partly attributed to the presence of the additional aerosol particles from the Calbuco volcanic eruption. We can notice in the last two maps the substantial increase in ozone concentration just outside the polar vortex, where it accumulates before the vortex breaks up.
8.3. The QBO disruption in 2015-2016

During the northern hemispheric winter 2015-2016, a disruption of the QBO regularly propagating structure was recorded, which is the only event of this kind observed since 1953 (Newman et al., 2016), when the records started. This anomaly consisted in a rapid change of the QBO phase: in particular, an upward displacement of the westerly phase was observed in late 2015, which cut off the downward-propagating easterly phase. At the same time, anomalous easterlies developed in the lower stratosphere, whose origin has not been identified. By the second half of 2016, this anomaly appeared to be attenuated, with a normal downward propagation of the QBO phase. The anomalous pattern can be directly observed plotting, for example, the zonal wind measured at the Singapore ozonesonde station as a function of altitude. Figure 8.6, from Newman et al. (2016), shows the Singapore monthly mean zonal wind time series from 1980 to the present, with the indication of westerly and easterly phases superimposed. As can be seen, the regular QBO pattern was broken at the end of 2015, with two consecutive westerly phases.
As explained in Ch. 1, the QBO has a large impact on stratospheric ozone distribution, especially in the tropics but also in the extratropics. As a consequence, the signature of the described disruption can be directly identified also looking at ozone anomalies. Figure 8.7 depicts the ozone anomaly time series as a function of altitude averaged over the inner tropics [5°S, 5°N] from SCIAMACHY and OMPS-LP merged data set over the last 10 years. QBO phases are visible looking at the ozone field: negative ozone anomalies correspond to easterly QBO phases and vice versa. As we can see, the 2015-2016 disruption of the pretty regular descending pattern is visible, with the downward-propagating positive ozone anomalies in mid-2015 around 25 km that are displaced upwards. This displacement is indicated by the green arrow. Another positive anomaly appears in mid-2016, and it regularly propagates downwards. To the ozone anomalies recorded in that period, the warm El Niño event partially contributed. In particular, Diallo et al. (2018) pointed out that the decrease in ozone concentration in the lower tropical stratosphere is also related to El Niño, which aligned with the QBO anomaly. At the same time, extratropical total column ozone reached the minimum concentration over the last 40 years during spring-summer 2016 (here not shown).
8.3. The QBO disruption in 2015-2016

**Figure 8.7:** Cross section of ozone anomalies in the inner tropics [5°S, 5°N]; westerly and easterly QBO phases are recognized from ozone anomalies. The green arrow indicates the displacement of the downward-propagating westerly QBO phase.
Conclusions

Satellite observations in limb geometry have proved to be an essential tool to monitor and understand the stratosphere in the last decades, providing highly spatially and temporally resolved measurements of the distribution of trace gases. The onset of a recovery in the stratospheric ozone concentration has been predicted and detected during the last two decades after the substantial depletion observed at the end of the 21st century (WMO, 2018). This recovery is expected to have a complex spatial structure, as a function of altitude and latitude, as it depends on the interplay between dynamical forcings in a changing climate and ozone chemistry, which is affected by anthropogenic emissions of ODS.

The research activity during this Ph.D. project has been divided into three main steps. Firstly, the ozone profile retrieval scheme for OMPS-LP observations was developed. Then, the retrieval characterization, including the error budget, the validation of the profiles, and the comparison with independent data sets was performed to determine the quality of the derived product. Finally, the last step involved the merging of the OMPS-LP data set with SCIAMACHY and SAGE II time series, to study long-term ozone changes in the stratosphere. The new aspect that this project sheds light on, regarding the merging of the data sets, is the study of longitudinally resolved ozone trends, which goes beyond the commonly used zonally averaged approach.

The starting point of this study is the development of the ozone retrieval algorithm to be applied to OMPS-LP observations. Considering the final goal to merge the time series with SCIAMACHY limb measurements, the OMPS-LP ozone retrieval was adapted from the algorithm implemented for SCIAMACHY. The same spectroscopic databases and climatology were used, and a similar retrieval approach was implemented, based on the fit of spectral ranges and a Tikhonov regularization scheme. However, differences in the two instruments related to the atmospheric sampling, the spectral resolution, and the radiance collection method, required an extensive adjustment of the settings.

The retrieval characterization and the error budget were discussed in Ch. 4. In particular, the single ozone retrieved profiles are characterized by a vertical resolution of 2.5-3 km and are affected by a random uncertainty that decreases from 10-20 % in the lowermost stratosphere to 2-4 % above 20 km at all latitudes. The parameter error was found to be larger in the tropical lower stratosphere, and generally about 3-5 % in the middle and upper stratosphere at all latitudes. A cloud screening and the aerosol extinction coefficient retrieval were described and showed the most significant effects on the ozone profiles in the lower stratosphere. The processing of several versions of the retrieval scheme to improve and obtain a complete time series starting from the beginning of the mission was possible by exploiting the large calculation power available at the HLRN (Norddeutsche Verbund für Hoch- und Höchstleistungsrechnen).
The retrieved ozone data set was firstly compared with NASA profiles, finding discrepancies mostly within 10% above 20 km at all latitudes and generally higher ozone values in comparison with NASA. An extensive validation against independent measurements was then performed, in particular using MLS time series, ozonesondes and lidar observations. The results were presented in Ch. 5. A very good agreement within ±7% was found with MLS at most of the latitudes and altitudes between 20 and 50 km. Below 20 km, larger discrepancies were observed, especially in the tropics, related to the low ozone concentration, remaining issues in the cloud screening and the lower sensitivity of limb measurements at these altitudes. With respect to ozonesondes and lidars, a good agreement was also found below 30 km, particularly at northern mid-latitudes. These results with the description of the algorithm were partially published in Arosio et al. (2018). Besides, the stability of OMPS-LP ozone time series was checked in comparison with MLS and ozonesondes. In this context, a significant trend in OMPS-LP time series was identified with respect to MLS above 30 km.

Once the quality of the data set as a function of altitude, latitude and time had been assessed, the merging of OMPS-LP time series with SCIAMACHY and SAGE II observations was performed. As SCIAMACHY and OMPS overlap for only a short period, MLS was used as an external transfer function to remove the bias between the two time series. In detail, two approaches to merge SCIAMACHY and OMPS-LP data were discussed in Ch. 6: a plain-debiasing of the data sets and deseasonalized anomalies. In the first case, the merging was performed directly in terms of ozone number density, whereas in the second case the SC of each instrument was subtracted, to take into consideration the different sampling and geometry of the two sensors. In our case, however, SCIAMACHY and OMPS-LP have a very similar geometry of observation (in terms of scattering angle) and latitude coverage. The advantage of the first approach is that the merged time series can be directly used for model assimilation and geophysical studies, whereas in the second case a reconstructed SC has to be added, losing its temporal evolution. Due to the high spatial resolution of limb sounder observations, a longitudinally resolved data set was created, gridded every 5° latitude, 20° longitude and 3.3 km altitude. When comparing the merged time series with MLS high correlation values and no significant drifts over the period 2005-2017 were detected. Finally, the merging with SAGE II monthly averaged profiles was described. As SAGE II has a much sparser spatial sampling with respect to limb sounders and a different geometry of observations, the merging was performed using the anomalies approach and zonal mean values, binned every 10° latitude.

Afterward, an MLR model was applied to the merged time series, as described in Ch. 7, to study long-term ozone variations within the 20-50 km altitude range, excluding the polar regions. Going back to the 1985-1997 period, a substantial depletion was detected especially above 35 km, in agreement with previous studies (e.g., Harris et al., 2015; Sofieva et al., 2017). After 1997, an increase in upper stratospheric ozone was found, with the most significant values at mid-latitudes. The analysis was then focused on the period 2003-2018 to study ozone variations at higher spatial resolution. The previously identified recovery was confirmed, with values up to 4-5% per decade at northern mid and high latitudes. In the lower stratosphere, negative but non-significant values were detected. In the tropical middle stratosphere, a change of the trend sign was identified, occurring around 2011. A comparison with the TOMCAT CTM was
performed, showing a very good agreement between the model simulation and the merged time series at 32 km. The reasons behind this change are under investigation, but most probably of dynamic origin. In addition, it was possible to study longitudinally resolved patterns in the ozone changes. Large variability was identified not only in the lower stratosphere but also around 40 km. For example, at northern mid-latitudes, a strong recovery was found over the Canadian sector, whereas over Siberia values are close to zero and mostly non-significant. The vertical structure of these patterns has proven to be consistent.

Finally, geophysical studies were briefly presented in Ch. 8 focusing on the ozone-depleting effects of SPEs in the polar upper stratosphere, the ozone hole occurrence over the Antarctic and Arctic, and the anomalous QBO event that happened in 2015-2016.

8.4 Outlook

The research activities presented in this thesis can be further developed in mainly three directions: the improvement of the ozone profile retrieval and its error budget characterization, the analysis and validation of the consistency of the longitudinally resolved patterns found in ozone trends, and the investigation of the atmospheric processes driving the long-term ozone changes.

The error budget of OMPS-LP ozone profiles should be extensively assessed in order to better characterize the error in the trends computed from the merged data set. Further activities are needed to improve the ozone retrieval in particular concerning two aspects. The first one is the implementation of a PMC retrieval as done for SCIAMACHY affecting profiles at high latitudes during the summer, where a high percentage of the profiles are currently rejected because of the presence of a PMC in the instrument FOV. The second aspect is related to the drift identified in OMPS-LP time series with respect to MLS. It would be important to investigate the origin of this issue, implement a methodology to study the temporal evolution of the instrument pointing, and eventually mitigate the drift. In addition, in the lower stratosphere, a better validation of the product should also be performed, and eventually, an additional tuning of the retrieval settings should be done to improve the quality of the retrieved profiles.

The longitudinally resolved trends described in Ch. 7 are planned to be further investigated. Other independent data can be used to study whether similar patterns are also found. In particular, a validation of the merged data set as a function of longitude using ozonesondes and other ground-based observations would give an insight into the consistency of the described patterns. This kind of validation is in the framework of the discussion related to the discrepancies of ozone trends using measurements from different instruments and platforms. Besides, TOMCAT simulations may support the assessment of the robustness of the derived trends. CTM simulations are an essential tool to investigate the driving processes of the long-term ozone variations. An extensive comparison between TOMCAT simulations and the merged data set has to be performed to highlight the discrepancies and try to mitigate them. Afterward, it will be possible to investigate the atmospheric processes governing the discovered ozone trends. In particular, the origin of the sign change in the middle stratospheric trends still has to be investigated and it is most probably related to changes in the atmospheric dynamics.
Two other atmospheric regions of interest are the lower tropical stratosphere and the northern high-latitudes. In the first case, there is a need for longer time series and apposite methodologies to separate the high inter-annual variability characterizing this region and the long-term trend. Concerning the polar regions, the limited sampling of the sensors makes the assessment of trends challenging.
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