Master Thesis

Sensitivity studies related to tropospheric ozone satellite retrieval using the cloud slicing method

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Declaration

I, Nelson Igbinehi, hereby declare that all the contents of this work is written on my own and only with the means as indicated. I also give authorization for this work to be made available on the webpage at Postgraduate Program ENVIRONMENTAL PHYSICS (PEP) research archive.

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Abstract

Tropospheric ozone is produced by photochemical oxidation of carbon-monoxide (CO) and hydrocarbons (volatile organic compounds, VOCs) in the presence of nitrogen oxides, NO_x (NO + NO₂), and by downward transport from the stratosphere. It plays significant roles in atmospheric chemistry and climate change. Remote sensing application is necessary in order to determine the amount and distribution of tropospheric ozone around the globe and to assess its impact on climate and air pollution.

Tropospheric ozone can be retrieved using the cloud slicing method (CS). The CS retrieval utilizes the opaque nature of optically dense cloud to retrieve upper tropospheric ozone volume mixing ratio. A prerequisite is that the stratospheric ozone has to be invariant. Using the cloud slicing approach, tropospheric ozone information are derived by combining pairs of measurements of cloud top pressure and above cloud column ozone. In this study, an investigation was carried out to check the sensitivity of the cloud slicing retrieval technique to different cloud conditions. The influence of cloud types (ice and water) and cloud parameters such as cloud top pressure (CTP), cloud top height (CTH), cloud optical thickness (COT) on the retrieval technique were studied using simulated radiances. The radiative transfer model SCIATRAN and the weighting function differential optical absorption spectroscopy (WFDOAS) ozone retrieval algorithm were used to simulate the CS method under various conditions. The analysis carried out shows that the retrieved tropospheric ozone volume mixing ratio (VMR) increases with cloud optical thickness. Best agreement with truth is achieved at moderate cloud optical thicknesses. Retrieved ozone VMR are underestimated for optical thin clouds ($\tau < 3$). Ice and water clouds show similarity in the retrieved tropospheric ozone volume mixing ratio. The retrieved ozone VMR obtained at solar zenith angles 10° and 30° are similar. Solar zenith angle has no influence on the retrieved ozone VMR comparison with the truth.

1 Introduction

1.1 Motivation

The composition of the Earth's atmosphere comprises of trace gases including ozone. It became imperatively important to study and understand ozone in the atmosphere because of its role in the stratosphere and troposphere. Stratospheric ozone acts as a shield which protects life on Earth from the direct impact of ultraviolet radiation. Tropospheric ozone is an air pollutant that significantly impacts human health and the ecosystems, and also a greenhouse gas responsible for direct radiation forcing of $0.35 - 0.37 \text{ wm}^{-2}$ on the climate system [Ainsworth et al., 2012]. Tropospheric ozone is injected into the troposphere by downward transport from the stratosphere and produced by photochemical reactions of carbon monoxide (CO), hydrocarbons (volatile organic compounds, VOCs) and nitrogen oxides (NO_x = NO + NO₂) [Stevenson et al., 2006]. Furthermore, knowledge of the amount and distribution of tropospheric ozone around the globe is necessary in order to assess the impact on climate and air pollution.

Over the years, satellite remote sensing have been useful in providing consistent global coverage information of tropospheric ozone. Tropospheric ozone retrieval from space was first performed using the residual method. The residual method obtained tropospheric column ozone (TCO) by subtracting the integrated amount of ozone above the tropopause (stratosphere) derived from the Stratosphere Aerosol and Gas Experimental (SAGE) ozone profiles from collocated total ozone observed from the Total Ozone Mapping Spectrometer (TOMS) aboard the Nimbus 7 satellite [Fishman et al., 1990]. Another approach used to retrieve tropospheric ozone is the limb-nadir matching method (LNM). The limb-nadir matching method utilizes the feature of the scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument being able to observe the same atmospheric volume, first in limb and then in nadir viewing geometry within 7 min interval. The limb-nadir matching method derives tropospheric ozone columns by subtracting the stratospheric columns, which are retrieved from the limb viewing measurements, from the total column obtained from the nadir observations [Ebojie et al., 2014]. Tropospheric ozone has also been retrieved using the convective

cloud differential (CCD) method. The CCD method obtains total ozone from satellite measurements of region with high reflectivity of high tropopause level clouds which is often associated with strong convection and cloud tops near the tropopause Ziemke et al., 1998]. Tropospheric column ozone (TCO) is then derived by subtracting the stratospheric column ozone (SCO) from high reflecting scenes (R > 0.9) from total column ozone from low reflecting scenes (R < 0.2). This work is focused on the cloud slicing (CS) retrieval technique of upper tropospheric ozone introduced by Ziemke et al. [2001]. The cloud slicing principle is based on three assumptions: (1) the opaque nature of dense cloud (optically thick) (2) stratospheric column ozone is invariant over the grid box (region) where the cloud top pressure and above cloud column ozone regression is carried out. Which implies that, all above cloud column ozone variability over this region is tropospheric in origin and (3) assumes ozone volume mixing ratio is constant between the lowest and the highest clouds used in the retrieval. The cloud slicing uses the inability of ultraviolet wavelength radiation to penetrate into optically opaque clouds to permits the retrieval of upper tropospheric ozone. The cloud slicing technique was first applied using combined collocated measurements of temperature humidity infrared radiometer (THIR) cloud pressure data with total ozone mapping spectrometer (TOMS) above-cloud column ozone, onboard the Nimbus-7 satellite [Ziemke et al., 2001]. Ozone profile information is obtained from the cloud slicing method by combining collocated measurements of above cloud column ozone and cloud top pressure at heights between the lowest and highest cloud tops.

The need to carry out an investigation on the uncertainties associated with the cloud slicing retrieval technique of the upper tropospheric ozone, using radiation transfer simulation became necessary in order to check the ozone volume mixing ratio, and to validate the assumptions made. In carrying out this task, the influence of different cloud types (water and ice) and cloud parameters such as cloud optical thickness (COT), cloud top pressure (CTP), cloud top height (CTH) will be checked on the retrieval technique. This will be achieved via simulating radiances using SCIATRAN, a radiative transfer model. The WFDOAS (Weighting Function Differential Optical Absorption Spectroscopy) total ozone retrieval algorithm will then be used to retrieve total column ozone from the simulated spectra.

1.2 Outline of the thesis work

The thesis work commences with the scientific background giving the description of the Earth's atmosphere structure and composition, including the various regions of the atmosphere: troposphere, stratosphere, mesosphere and thermosphere (Chapter 2). A further explanation of atmospheric ozone, the solar radiation and ozone absorption is given is given here as well. In Chapter 3, ozone satellite measurement instruments, Global Ozone Monitoring Experiment (GOME, GOME-2A, and 2B), Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), and Ozone Monitoring Instrument (OMI) are described for which the Weighting Function Differential Optical Absorption Spectroscopy (WFDOAS) ozone retrieval applies. An overview of the total ozone retrieval with WFDOAS algorithm is also given here. Various tropospheric ozone retrieval techniques such as the residual method, limb-nadir matching method, convective cloud differential method, and the cloud slicing method (the last which is of main interest in this thesis work) are discussed. Also a brief discussion on the role of cloud on the cloud slicing technique is presented here. In Chapter 4, an overview of the motivation and goals of the study is given. Chapter 5 begins with the description of the radiative transfer tool SCIATRAN and the simulation of spectra. In Chapter 6, the analysis and the discussion of results are provided. Finally in chapter 7 a conclusion and summary of the thesis work and an outlook are presented.

2 Scientific background

2.1 Structure of the Earth's atmosphere and its composition

The Earth's atmosphere is one of the major components of the climate system. It is a tiny and fragile envelope of air surrounding the Earth. It is held around the Earth by gravitational attraction. The atmosphere plays an essential role because it serves as a protector for life on Earth by shielding the direct blasts of heat and radiation emanating from the sun, thereby regulating the Earth temperature and redistributing heat around the globe. The present day atmosphere consists of water and ice particles, aerosols, and a gas mixture (78% nitrogen, 21% oxygen, carbon dioxide, argon, water vapor, ozone, and other gases). The reactive trace gases have a large influence on the dynamics and thermodynamics of the atmosphere. Although these gases amount to less than 1% of the atmosphere composition they determine absorption, transmission, and reflection of solar and terrestrial infrared emission, and therefore, control the energy balance of our planet. In recent time (industrial era), human activities have altered the atmosphere composition through the burning of fossil fuels, and other activities which lead to the release of greenhouse gases such as carbon dioxide (CO_2) , methane (CH_4) , nitrous oxide (N_2O) and the halo-carbons (a group of gases containing fluorine, chlorine, and bromine). These greenhouse gases trap the out going infrared (thermal) radiation emanating from the surface of the Earth, thus causing temperature increases around the globe, termed global warming. Table 1 below shows the gaseous constituents of the atmosphere up to an altitude of 105 km.

Constituents	Molecular weight	Fractional concentration by volume
Nitrogen (N_2)	28.013	78.08%
Oxygen (O_2)	32.000	20.95%
Argon (Ar)	39.95	0.93%
water vapor (H_2O)	18.02	0-5%
Carbon dioxide (CO_2)	44.01	380 ppm
Neon (Ne)	20.18	18 ppm
Helium (He)	4.00	5 ppm
Methane (CH_4)	16.04	1.75 ppm
Kryton (Kr)	83.80	1 ppm
Hydrogen (H_2)	2.02	0.5 ppm
Nitrogen oxide (N_2O)	56.03	0.3 ppm
Ozone (O_3)	48.00	0-0.1 ppm

Table 1: Fractional concentrations (by volume) of constituents in Earth's atmosphere [Wallace and Hobbs, 2006].

The atmosphere from the surface to about 120 km is structured into four different layers according to their temperature variability and gas composition as shown in Fig. 1. They are the troposphere, stratosphere, mesosphere, and thermosphere. These various layers of the atmosphere will be discussed below.

Troposphere: The troposphere is the lowest layer of the Earth where weather phenomena and cloud formation take place. It extends from about 0 to 12 km above the Earth's surface as shown in Fig. 1. There is a decrease in temperature with altitude in the troposphere due to adiabatic expansion of air (air cools as it rises up), with an average lapse rate of about 6.5° C km⁻¹. It makes up to 80% of the mass of the atmosphere, which makes its denser than the layers above it [Wallace and Hobbs, 2006]. The troposphere is warmed up from beneath by the Earth's surface, incoming solar radiation first heats the surface which radiates heat into the atmosphere. Ozone is present in small amounts in the troposphere which is about 10% compared to the stratosphere.

Stratosphere: The stratosphere is the next layer above, it extends from about 12 to 50 km (see Fig. 1). There is an increase in temperature with altitude due to the effect

of absorption of UV-radiation by ozone. Ozone is a strong absorber in the wavelength range between 210 and 290 nm. Ozone has it highest abundance of about 90% in the stratosphere. There is little convection and mixing in this region because of temperature stratification which accounts for a stable layer. The stratosphere holds about 19% of the total mass of the atmosphere and minute amounts of water vapor.

Mesosphere: The mesosphere is the coldest layer also referred to as the middle layer of the atmosphere. Within the mesosphere, air density is very low to absorb solar radiation hence the mesosphere is warmed up from the stratosphere and thereby resulting in a decrease in temperature towards higher altitudes. It has a thickness of about 35 km. Noctilucent clouds can be observed within the mesosphere when the sun is below the horizon and the lower layers of the atmosphere are in the Earth's shadow.

Thermosphere: The thermosphere is the fourth layer of the atmosphere, where the temperature increases with altitude as a result of absorption of short wave solar radiation by atoms and molecules [Burrows et al., 2011].



Figure 1: Earth's atmosphere structure showing different layers [https://de.pinterest.com/pin/376613587558900815/].

The thermosphere is the warmest and thinnest region of the atmosphere and is strongly influenced by solar activity.

2.2 Ozone

When discussing the greenhouse gas effect and its impact, the importance of ozone can not be overemphasized. Ozone is an effective greenhouse gas in the upper troposphere and lower stratosphere. Ozone consist of three oxygen atoms and the chemical formula is O_3 . It was discovered by Professor Christian Friedrich Schonbein (1799 - 1886). The name ozone was derived from the Greek word 'ozein' meaning 'to smell'. Ozone has a deep blue colour with a bleaching smell. It is a strong oxidizing agent with a poisonous effect. The boiling and melting points of ozone are -111.9° C and -192.7° C, respectively. Ozone can be measured in molecules per cubic centimeter (mol/cm^{-3}) , parts per million (ppm), or Dobson units (DU). The ozone total column amount is expressed in Dobson units (DU), which was named after Gordon Miller Bourne Dobson (25 February 1889 – 11 March 1975), a pioneer in atmospheric ozone observation. Ozone features are been represented by ground and satellite measurements in three categories; the surface ozone, the total column ozone, and the vertical profile of ozone. Ozone is found basically in the stratosphere and troposphere of the Earth atmosphere and without the existence of ozone in this two region, our atmosphere structure would have been quite different because mixing between the stratosphere and troposphere would be much faster. The depiction of ozone as a tri-atomic molecule of oxygen is shown in Fig. 2.



Figure 2: Structure of ozone molecule [https://en.wikipedia.org/wiki/ozone].

Stratospheric ozone

Stratospheric ozone amounts to about 90% of the total ozone in the atmosphere. The stratosphere is the region where ozone is more concentrated than anywhere else, therefore it is often called the ozone layer. Stratospheric ozone is found between 12 km and 50 km altitude with its peak concentration located at about 20 - 25 km [Staehelin et al., 2001]. Stratospheric ozone serves as a shield against biologically harmful solar ultraviolet radiation. Ozone absorption of UV radiation in the stratosphere normally leads to an increase in temperature in the region. The Chapman cycle describes the natural source of production and loss of ozone in the stratosphere as indicated in $R_1 - R_4$ below [Finlayson-Pitts and Pitts Jr, 1999].

$O_2 + hv \rightarrow O + O \ (\lambda < 242 \text{ nm})$	\mathbf{R}_{1}
$O + O_2 + M \rightarrow O_3 + M$	R_2
$O_3 + hv \rightarrow O + O_2 \ (\lambda < 320 \text{ nm})$	R_3
$O + O_3 \rightarrow 2O_2$	R_4

Stratospheric ozone is produced by the photolysis of oxygen molecules into oxygen atoms at ultraviolet light wavelengths $\lambda < 242$ nm, M in R₂ represent a third molecule needed to remove the excess energy. And finally in R₄ ozone is destroyed. The stratospheric ozone production depends on the square of the oxygen (O₂) concentration and UV radiation. [Burrows et al., 2011]. Ozone is an unstable species which can easily donate a single oxygen atom to free radical species such as chlorine, bromine, nitrogen and hydrogen. In recent times, stratospheric ozone concentration has be threatened by catalytic destruction which is been influenced by human activities through the release of gases into the atmosphere. These gases (species) as shown in the reactions R₅ - R₇ below are responsible for the major loss of stratospheric ozone, were X represents NO, OH, H, Cl, or Br. These catalytic cycles are driven by oxygen densities which rapidly decrease in abundance with decreasing height [McConnell and Jin, 2008].

$XO + O \rightarrow X + O_2$	R_5
$X + O_3 \rightarrow XO + O_2$	R_6

$$NET: O + O_3 \rightarrow 2O_2 \qquad \qquad R_7$$

Anthropogenically released chemicals such as chlorofluorocarbons (CFC_s) and other chlo-

rine containing volatile gases have been identified as the major sources of chlorine in the stratosphere. Chlorofluorocarbons (CFC_s) are chemically inert compounds containing carbon, chlorine, and fluorine with (CFC-11) and (CFC-12) being dominant. Because of their inertness they do not react in the troposphere but spread to the stratosphere. When these gases are in the stratosphere they are photolysed by solar UV-radiation to release chlorine (Cl) as in the reaction R_8 below [Staehelin et al., 2001].

$$CFCl_3 + UV \ (\lambda < 230 \text{ nm}) \rightarrow CFCl_2 + Cl$$
 R_8

The released Cl in the stratosphere further attack ozone leading to ozone depletion as shown in the reactions below.

$Cl + O_3 \rightarrow ClO + O_2$	\mathbf{R}_{9}
$ClO + O \rightarrow Cl + O_2$	R_{10}
$NET: O + O_3 \rightarrow 2O_2$	R_{11}

Similar reactions as for chlorine also occur with Bromine (Br) as well as NO_x and HO_x radicals.

Tropospheric ozone

Ozone in the troposphere account for about 10% of the total amount of atmospheric ozone. Tropospheric ozone is harmful to vegetation and animals, is toxic to human, decreases agricultural crop yield and damages man-made materials [Weidinger et al., 2011]. Tropospheric ozone contributes to the anthropogenic enhancement of the global greenhouse effect. It determines the oxidizing capacity of the atmosphere through photodissociation and subsequent reaction of singlet D oxygen atom $O(^{1}D)$ with water vapour to produce OH radicals [Roelofs et al., 2003]. The hydroxyl radicals (OH) are the major removal agents of pollutants such as CO and CH_4 from the atmosphere [Horowitz et al., 2003]. Tropospheric ozone occurs with mixing ratios of about 10 - 100 ppb [Warneck, 1999]. Fig. 3 below shows an illustration of Earth system interactions with tropospheric ozone.



Figure 3: Illustration of the Earth system interactions with tropospheric ozone [Monks et al., 2015].

Source: Tropospheric ozone is a secondary pollutant, because it is indirectly produced and emitted into the troposphere. Ozone in the troposphere is produced by photochemical oxidation of hydrocarbons and CO in the presence of oxides of nitrogen NO_x (NO + NO_2) radicals and also by downward transport of stratospheric ozone [Liu et al., 2002]. These ozone precursors are usually emanating from industrial processes, biomass burning, vegetation, lightning, auto-mobiles, and fossil fuel. The chemical reactions below shows the formation of tropospheric ozone.

$\rm CO + OH \rightarrow CO_2 + H$	R_{12}
$\rm H + O_2 + M \rightarrow \rm HO_2 + M$	R_{13}
$\rm HO_2+NO \rightarrow OH+NO_2$	R_{14}
$NO_2 + hv \rightarrow NO + O (\lambda < 420 nm)$	R_{15}
$O + O_2 + M \rightarrow O_3 + M$	R_{16}

$$NET: CO + 2O_2 + hv \rightarrow CO_2 + O_3 \qquad \qquad R_{17}$$

It is obvious from the above reactions (forming the ground level ozone), that NO_x and odd hydrogen are not directly consumed, instead they act as catalysts during ozone production. **Sink**: Atmospheric water vapour enhances ozone destruction via its photolysis and further reaction of singlet D oxygen atom O(¹D) [Zeng and Pyle, 2003] as shown in reactions R₁₉ and R₂₀ below. Dry deposition is also a mean of tropospheric ozone removal in the atmosphere. This is most effective in rural areas as a result of long range transports of ozone and its precursors, where no sufficient local emissions of NO or other ozone reactive substances are present [Colbeck and Harrison, 1985]. Reactions R_{19} and R_{20} show the destruction of ozone leading to production of hydroxyl radical OH.

$$NO_x + VOC_s + hv \rightarrow O_3$$
 R_{18}

$$O_3 + hv \rightarrow O(^1D) + O_2$$
 R_{19}

$$O(^{1}D) + H_{2}O \rightarrow OH + OH$$
 R_{20}

Role of tropospheric ozone: The oxidizing efficiency of the atmosphere is mainly regulated by the abundance of trace species, because increasing the emission of a particular pollutant will reduce the abundance of it's principal oxidant. O_3 , NO_x , and hydrocarbon regulate most chemical processes affecting tropospheric composition. Ozone in the troposphere play a significant role in the atmosphere because of its impact on human health and the ecosystem and also it is the major source of the hydroxyl radical (OH). The hydroxyl radical (OH) acts as a detergent of the atmosphere and also influences the lifetime of trace gases affected by oxidation [Cooper et al., 2014]. The hydroxyl radical (OH) is a key reactive species in the tropospheric ozone formation. Fig. 4 below shows the distribution of ozone in the atmosphere with altitude.



Figure 4: Atmospheric ozone concentration as a function of height [ozonelayer.noaagov].

2.3 Solar radiation

The solar radiation is electromagnetic energy emanating from the sun. This radiation from the sun is of different wavelength classified as the electromagnetic spectrum. The electromagnetic spectrum is divided into sections based on wavelength ranging from the short wavelength x-ray, gamma ray to the long wavelength radio waves as shown in Fig. 5. The part of the spectrum that reaches Earth from the sun varies between 100 nm to 1 mm. This part that can reach the Earth are the ultraviolet, visible, and infrared radiation. The visible light is between the wavelength of 400 nm - 700 nm, infrared from 700 nm to over 1 mm. The human eye is able to detect wavelength in the spectrum region between 400 nm to 700 nm which is the visible region. In this region (visible), longer wavelengths indicates red and shorter wavelengths are blue/violet. The UV (ultraviolet) radiation are radiations with wavelengths shorter than that of violet radiation. The ultraviolet radiation can be categorized into three wavelength range groups. The UV (100 - 200 nm) these are classified as vacuum, UV-C (200 - 280 nm), UV-B (280 - 320 nm), and UV-A (320 - 400 nm). The vacuum UV is completely absorbed in the stratosphere by stratospheric ozone and oxygen molecules. Since stratospheric ozone shows more efficiency for absorption at a shorter wavelength range. In the UV-B (280 - 320 nm) wavelength band only a fraction of this radiation can penetrate the earth surface which is normally dangerous to life and the ecosystem. This leads to different kinds of diseases such as skin-burn, cancer, eve problem (cataracts). The UV-A (320 - 400 nm) penetrates the Earth because it is not absorbed by ozone, but with a lesser energy when compared to UV-B (280 - 320 nm).



Figure 5: Electromagnetic spectrum [https://en.wikipedia.org/wiki/Electromagnetic radiation].

2.4 Ozone absorption

From the previous section it was explained that the vacuum UV radiation ($\lambda < 200$ nm) is absorbed by stratospheric ozone and upper atmospheric oxygen molecules. The UV-B radiation (280 - 320 nm) is partly absorbed by ozone in the stratosphere and a fraction of it penetrates to the Earth's surface. This contributes to numerous environmental hazards and health challenges such as eye damage (cataract), skin burn, and respiratory problems. The UV-A (320 - 400 nm) is not absorbed by stratospheric ozone and form least biologically harmful UV radiation (UV-A) which is significant in photochemical smog production at the surface. Ozone absorption spectrum ranges from the UV-NIR region with the Hartley band in the UV region, Huggins and Chappius bands in the near-UV and visible region, while the Wulf band lies in the near-infrared (NIR). The Hartley band is the strongest ozone absorption band ranging from about 200 to 300 nm. This region is important for ozone profile retrieval from space instruments such as Global Ozone Monitoring Experiment (GOME) [Orphal and Chance, 2003]. The Huggins band extends from (320 - 350 nm) and is a weaker absorption band compared to the Hartley band. This band shows variations with temperature with and has been used in distinguishing between stratospheric ozone and tropospheric ozone in nadir measurements from space [Orphal and Chance, 2003]. The Chappius band spans between 400 and 700 nm and it is useful in the application of absorption spectroscopy and remote sensing from ground. This region are often used to detect atmospheric ozone. The Wulf bands are very weak ozone absorption bands in the near infrared (NIR) wavelength region extending from about 700 - 1100 nm. The molecular transitions associated with the absorption bands of ozone are described as follows: The strongest absorption band, Hartley band is due to $1 {}^{1}B_{2}(B^{1}A') \longleftarrow X^{1}A_{1}$, Huggins band is due to $2 {}^{1}A_{1}(A^{1}A') \longleftarrow X^{1}A_{1}$, Chappius band is due to $1 {}^{1}B_{1}(B^{1}A') \longleftarrow X^{1}A_{1}$, and the Wulf band, the lowest electronic band in the ozone absorption spectrum is due to a singlet-triplet ${}^{3}A_{2} \leftarrow X^{1}A_{1}$ transition [Minaev and Ågren, 1994]. Fig. 6 below shows ozone absorption cross-sections measured with the GOME, SCIAMACHY, and GOME2 at about 221 K [Weber et al., 2011].



Figure 6: Ozone absorption cross-sections measured by GOME, SCIAMACHY, and GOME2 at about 221 K [Weber et al., 2011].

3 Ozone measurements from space

3.1 Instruments

Monitoring of ozone is important in order to be able to quantify its source, transport, and chemical transformation. Atmospheric ozone can be measured by remote sensing and in-situ techniques. In-situ measurements of ozone are carried out by analyzing a sample of air to determine the ozone content via optical, chemical, or electrochemical techniques. Measurements involving remote-sensing are carried out by using differential absorption techniques. There are two types of remote sensing techniques which are based on the sensor type: the passive and active remote sensing measurements. For passive remote sensors, radiation originates in the atmosphere or the sun and interacts with the target, while active remote sensors make use of their own source of radiation. Examples of active sensors are RADAR (radiation detection and ranging), which is used to measure cloud structures and cloud top-bottom heights. LIDAR (light detection and ranging) is used to measure profiles of temperature, O_3 , and tropospheric cloud top height. Ozone measurements can be carried from of ground-based, aircraft, balloon, rocket, ship, and satellite platforms. Ozone is effectively measured by satellite-borne remote sensing instruments in order to obtain global coverage. Satellites are capable of measuring ozone on a daily bases thus providing comprehensive data. The Global Ozone Monitoring experiment (GOME), Scanning Imaging Absorption Spectrometer for atmospheric Chartography (SCIAMACHY), and Ozone Monitoring Instrument (OMI) are examples of UV ozone measuring satellites. They measure total ozone columns and ozone profiles. A brief description of these satellite instruments will be given below.

The Global Ozone Monitoring Experiment (GOME): It is a small scale version of SCIAMACHY. GOME was mainly designed to give global distribution of ozone and other trace gases in the atmosphere. GOME was launched by ESA (European Space Agency) on board ERS-2 (second European remote sensing satellite) in April 1995. GOME is a passive and nadir viewing instrument with four-channel spectrometer, it measures the earth-shine radiance and the solar irradiance in the ultraviolet/visible spectral range 240 - 790 nm at a moderate spectral resolution of 0.2 - 0.4 nm [Burrows et al., 1999].

GOME has an equator crossing time of 10:30 a.m. local time for the descending node with a polar orbit at 790 km altitude. GOME achieved global coverage in 3 days after 43 orbits with a ground pixel size of $40 \times 320 \text{ km}^2$ [Burrows et al., 1999]. GOME is a dual monochromator that uses both a grating and pre-disperser prism in each of the four channels as dispersing elements [Burrows et al., 1999]. Using the DOAS (Differential optical absorption spectroscopy) technique, GOME is able to detect weak atmospheric absorbers like NO₂, BrO, chlorine dioxide, OClO, formaldehyde, HCHO, glyoxal, CHOCHO, iodine monoxide, IO, the oxygen dimmer, O_4 , and SO_2 . Other parameters also retrievable from GOME measurements are aerosol extinction, cloud properties, surface albedo, vegetation properties, ocean colour, and indices characterizing the solar cycle Burrows et al., 2011]. Recently, a more advance and sophisticated version of GOME was designed called (GOME-2). The two Globe Ozone Monitoring Instrument GOME-2/MetOp-A (GOME-2A) and GOME-2/MetOP-B (GOME-2B) sensors operated in tendem are flying onboard EUMETSAT's (European organization for the Exploitation of Meteorological satellites) which were launched in October 2006 and September 2012 respectively [Hao et al., 2014]. GOME-2 are flying on a sun-synchronous orbits with a repeat cycle of 29 days and an equator crossing time of 09:30 local time [Hao et al., 2014]. GOME-2 has a high spectral resolution with a footprint size of $80 \times 40 \text{ km}^2$ which is four times smaller than those of the original GOME. GOME-2 covers the ultraviolet/visible and near-infrared region from 240 - 793 nm with a spectral resolution of 0.2 - 0.4 nm, and provides a global coverage of the Earth's surface within 1.5 days [Viatte et al., 2010].

The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY): It was proposed in 1984 by Prof. J. P. Burrows as the principal investigator. SCIAMACHY was launched on board the European research satellite EN-VISAT in March 2002. It is made up of a telescope, a spectrometer, a mirror system, thermal, and electronic subsystems. SCIAMACHY instrument a successor of GOME, is a passive remote sensing instrument which flies in a sun synchronous near polar orbit at a mean altitude of 795 km with an equator crossing time of 10:00 a.m. local time in descending node. SCIAMACHY performs its measurements in the wavelength region 240 - 2380 nm from the ultraviolet to the visible and near-infrared with a spectral resolution of 0.2 - 1.5 nm and delivers a global coverage within 6 days [Noel et al., 1999]. It has three different viewing geometries: nadir, limb and solar and lunar occultation [Burrows et al., 2011]. SCIAMACHY has an advantage of reducing ground pixel size for the nadir view mode which is $30 \times 60 \text{ km}^2$ (and $15 \times 30 \text{ km}^2$ for special mode). These features are essential for monitoring trace gases in the troposphere, because their concentrations can exhibit strong spatial gradients [Burrows et al., 2011]. SCIAMACHY was able to observe the same atmospheric volume in limb and in nadir viewing geometries within about 7 min [Bovensmann et al., 1999]. The combination of limb and nadir measurements enabled the detection of tropospheric column amounts of O₃, NO₂, BrO, CO, CH₄, H₂O, N₂O, SO₂, and H₂CO [Bovensmann et al., 1999]. SCIAMACHY was primarily designed to deliver global measurements of trace gases and monitor changes in the atmosphere.

The Ozone Monitoring Instrument (OMI): It was launched on board the NASA national aeronautics and space administration Earth observing system EOS Aura satellite in July 2004. OMI is a nadir viewing spectrometer in the ultraviolet/visible region with a near global coverage of one day and a high spatial resolution of 13×24 km² [Levelt et al., 2006]. It is a sun-synchronous satellite in the polar orbit at 705 km altitude with an ascending node local equator crossing time of about 13:45 hr [Kroon et al., 2008]. OMI has a wavelength range between 270 and 500 nm and a spectral resolution of about 0.5 nm which is coarser compared to the two instruments discussed earlier. OMI's data products accuracy depends on two factors, the retrieval algorithms and instrument's calibration accuracies. OMI provides measurements for atmospheric trace gases like O₃, NO₂, SO₂, HCHO, BrO, and OClO, and also other parameters such as aerosol characteristics, cloud top heights, and UV irradiance at the surface [Levelt et al., 2006]. With OMI instrument it is feasible to derive the ozone column using differential optical absorption spectroscopy (DOAS), because it measure the entire Huggins ozone bands continuously rather than just at a few wavelengths [Veefkind et al., 2006]. Table 2 below gives a summary of the UV ozone satellite measuring instruments.

Instrument	Satellite	Spectral	Spectral	Spatial	Global	Equator
	platform	range (nm)	reso-	reso-	coverage	crossing
			lution	lution		time
			(nm)	(km^2)		(LT)
GOME-1	ERS-2	240 - 790	0.2 - 0.4	40×80	3days	10:30
SCIAMACHY	ENVISAT	240 - 2380	0.2 - 1.5	30×60	6 days	10:30
OMI	EOS	270 - 500	About	13×24	1 day	13:45
	AURA		0.5			
GOME-2A	METOP	240 - 793	0.2 - 0.4	80×40	1.5 days	09:30
GOME-2B	METOP	240 - 793	0.2 - 0.4	80×40	1.5 days	09:30

Table 2: Features of satellite instruments summary

3.2 Retrieval of total ozone (WFDOAS)

Satellite instruments such as Global Ozone Monitoring Experiment (GOME), Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), Ozone Monitoring Instrument (OMI), and Global Ozone Monitoring Experiment (GOME-2) have been designed to obtain global measurements of ozone. In order to retrieve the total ozone columns from these instruments, different algorithms have been developed such as the Weighting Function Differential Optical Absorption Spectroscopy (WFDOAS). The WFDOAS algorithm takes into account the slant path wavelength modulation which is not considered in standard DOAS approach when using single air-mass factor to convert observed slant column into vertical column densities [Coldewey-Egbers et al., 2005]. Direct retrieval of vertical column amounts ozone is feasible by fitting vertically integrated ozone weighting functions instead of ozone cross-section to the sun-normalized radiance [Coldewey-Egbers et al., 2005]. The WFDOAS total ozone result from satellite instruments measurements is in line with total ozone results from ground-based measurements from the World Ozone and UV Radiation Data Center (WOUDC) showing an agreement which lies between $\pm 1\%$ with a slight seasonal variations in the difference [Weber et al., 2005]. WFDOAS algorithm is described briefly here. The WFDOAS algorithm applies the Taylor expansion including a low order polynomial approximation to the measured atmospheric optical depth [Coldewey-Egbers et al., 2005] as follows.

$$\ln I_{obs}/F_{obs} = \ln (I/F)_{model} + 1^{st} \text{ term}$$

$$d \ln(I/F) / d_{TOZ}|_{model} (TOZ_{fit} - TOZ_{clim}) + 2^{nd} term$$

$$d \ln(I/F)/d_T|_{model} (T_{fit} - T_{clim}) + \dots + Pol$$
 3^{rd} term

with T the scalar temperature, I/F sun-normalized nadir radiance, TOZ the total column, In (I/F)_{model} the reference optical depth for the model atmosphere, d In(I/F)/ $d_{TOZ}|_{model}$ and d In(I/F)/ $d_{T}|_{model}$ are the weighting functions for ozone and scalar temperature. The first term in each of the terms on the right hand side represents radiance transfer quantities, $\Delta T = T_{fit} - T_{clim}$ is the temperature shift in the vertical temperature profile. Other terms include the Ring effect, NO₂ and BrO absorption, and Pol represents a polynomial that accounts for all broadband contributions, for example, from surface albedo and aerosol [Coldewey-Egbers et al., 2005].

3.3 Tropospheric ozone retrievals

Tropospheric ozone retrieval from satellite instrument measurement is necessary for sufficient spatial and temporal resolution over the globe, but this has always been a challenging task because only 10% of atmospheric ozone is found in the troposphere while the remaining 90% is in the stratosphere. Meanwhile stratospheric ozone contributes largely to radiance signal with satellite-based instruments [Ohyama et al., 2012]. Over the years a variety of retrieval methods in satellite remote sensing have been invented for tropospheric ozone retrieval, these methods include the residual method, limb-nadir matching (LNM) method, convective cloud differential (CCD) method, and cloud slicing (CS) method. This work will be focus on the cloud slicing method and a vivid description of this retrieval method will be given later, while the other methods will be discussed briefly here to give an insight.

The residual retrieval method

The residual method of tropospheric ozone retrieval from satellite instrument measurement was basically the first known technique. The tropospheric column ozone (TCO) was obtained by subtracting the integrated amount of ozone above the tropopause (stratosphere) derived from the Stratospheric Aerosol and Gas Experiment (SAGE) ozone profiles from concurrent amounts of total ozone observed from the Total Ozone Mapping Spectrometer (TOMS) [Fishman et al., 1990]. In a simplified form the residual method can be expressed as: tropospheric column ozone (TCO) = total column ozone (TCO) stratospheric column ozone (SCO). There are some drawbacks associated with the residual retrieval technique. Firstly, UV nadir sounder does not detect near surface ozone over surfaces with low albedo with 100% efficiency, and stratospheric column ozone derived from the independent sensor may be uncertain in the lower stratosphere and there may be a mismatch in orbital and sampling characteristics between TOMS and SAGE II. SAGE II typically sampled the 10° N - 10° S latitude band 50 - 60 days per year and sometimes missed the tropics for many months in a row [Thompson and Hudson, 1999].

Limb-nadir matching method (LNM)

The retrieval of tropospheric ozone by the limb-nadir matching technique was one of the basic objectives of the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography instrument. In this technique the tropospheric amounts of ozone are obtained by subtracting the stratospheric amount, which are retrieved from the limb viewing measurements, from the total amounts obtained from the nadir observations performed by the same instrument (SCIAMACHY) [Sierk et al., 2006]. In a simplified form the limb-nadir method can be expressed as: tropospheric column ozone = total column ozone (nadir) - stratospheric column ozone (limb) like in the residual approach with the main difference that both measurements are done with the same instrument thus minimising the mismatches of airmasses. Fig. 7 below shows the limb-nadir view of SCIAMACHY instrument covering both viewing geometries (limb-nadir) within an interval of about 7 mins.



LOS = line of sight; SZA = solar zenith angle

Figure 7: Sketch showing limb and nadir viewing geometries of SCIAMACHY [Ebojie et al., 2014].

Convective cloud differential (CCD) method

The Convective cloud differential (CCD) method obtains total ozone from satellite measurements from regions with high reflectivity of high troppause level clouds which is often associated with strong convection and cloud tops near the tropical tropopause [Ziemke et al., 1998]. This method estimates stratospheric column ozone (SCO) by considering the fact that optically thick clouds (associated with high reflecting convective clouds, R > 0.9) shield ozone below it. It also assumes that stratospheric column ozone (SCO) is zonally invariant within 15°S and 15°N [Chandra et al., 2003]. The tropospheric column ozone (TCO) is obtained from the CCD method by using the total columns determined from the low reflecting scenes (R < 0.2, clear-sky) at any longitude and the stratospheric columns ozone (SCO) from high reflecting scenes (R > 0.9) in the pacific in the same zonal band. In a simplified form the Convective cloud differential (CCD) method can be expressed as: tropospheric column ozone = total column ozone from low reflecting scenes (R < 0.2) stratospheric column ozone from high reflecting scenes (R > 0.9). The tropospheric ozone retrieved from the CCD method is not affected by inter-instruments calibration errors because both the stratospheric column ozone and the total column ozone are derived from the same satellite instrument. The Convective cloud differential method is limited to the tropics where the assumption of zonally invariant stratospheric column is valid [Valks et al., 2003].

3.4 Cloud slicing (CS) method for tropospheric ozone retrieval

The cloud slicing technique is a different retrieval technique which utilizes the inability of ultraviolet wavelength radiation to penetrate into clouds to retrieve upper tropospheric ozone and combines ozone measurements done with varying cloud top heights [Ziemke et al., 2001]. This retrieval technique is based on three assumptions: (1) the opaque property of dense cloud (optically thick) (2) stratospheric ozone is invariant and (3) assumes that ozone volume mixing ratio is constant between the lowest and highest clouds used in the retrieval. The cloud slicing method is the first technique to be able to distinguish between upper and lower tropospheric ozone [Ziemke et al., 2001]. It was first applied using combined collocated measurements of temperature humidity infrared radiometer (THIR) cloud pressure data with total ozone mapping spectrometer (TOMS) above-cloud column

ozone. Accurate clouds top pressure are needed in measuring tropospheric ozone when using the cloud slicing technique, because it is required in calculating the upper tropospheric volume mixing ratios at height between the lower and upper limit of cloud top heights. Fig. 8 below shows a scheme of the cloud slicing technique. The volume mixing ratio (VMR) can be derived from the slope of the above cloud columns ozone against the cloud top pressure. Ziemke et al. [2001] use a statistical ensemble approach for measuring



Using Cloud Tops To Obtain Mean O3 Volume Mixing Ratio

Figure 8: Representation of the cloud slicing method, showing measurements of above cloud column O_3 and cloud top pressures. (Ω) is column ozone between pressure surfaces and Δ P is the pressure between two cloud top heights [Ziemke et al., 2001].

tropospheric ozone by combining several collocated measurements of cloud top pressure and above cloud column ozone in $5^0 \times 5^0$ latitude/longitude bins. Fig. 9 below shows a scheme of how the cloud slicing technique is applied. Total ozone mapping spectrometer (TOMS) ozone measurements from scenes with reflectivity greater than 0.6 and cloud fraction of 100% were used in the cloud slicing analysis. The cloud slicing retrieval technique is unique because it does not require measurement of stratospheric column ozone (SCO) to determine tropospheric column ozone unlike other methods discussed in the previous section. It also has an advantage of using a single satellite instrument for its measurements. A particular limitation associated with the cloud slicing retrieval tech-



"ENSEMBLE" CLOUD SLICING

Figure 9: Cloud slicing statistical ensemble for deriving upper tropospheric ozone. The straight line shows the above cloud column ozone versus cloud top pressure assuming constant ozone volume mixing ratio (VMR) that is determined from the slope of the regression above cloud ozone column versus cloud top height [Ziemke et al., 2001].

nique application is the assumption that stratospheric column ozone is invariant. This condition does not hold in the extratropics were stratospheric column ozone may exhibit large zonal and meridional variability [Ziemke et al., 2003].

With the combination of above cloud column ozone and cloud top pressure measurements, the column ozone (Ω) between two tropospheric pressure surfaces, low pressure (P_{low}) and high pressure (P_{high}) is calculated by integrating the ozone volume mixing ratio (X) from P_{low} to P_{high} as follows:

$$(\Omega) = A \int_{P_{low}}^{P_{high}} d\mathbf{P} \ X \tag{1}$$

with the column ozone (Ω) given in Dobson units (DU), A is a constant equal to ~ 0.79 DU hPa⁻¹ ppmv⁻¹ for the troposphere, pressure (P) is in hPa, and the volume mixing ratio X is in ppmv (parts per million volume).

From equation (1) the mean volume mixing ratio \bar{X} (ppmv) for ozone can be expressed as;

$$\bar{X} = 1.27 \times \Delta \Omega / \Delta P,$$
 (2)

where $\Delta\Omega/\Delta P$ represents the slope and the upper tropospheric ozone column (Ω) is given by equation (1) and as shown schematically in Figs. 8 and 9.

3.5 The role of clouds in cloud slicing

When the Earth is viewed from space it is observed that it is dominated by cloud. These clouds are water droplets or ice crystals at different sizes and shapes in the atmosphere. The effect and influence of clouds depends highly on their thickness, height, water or ice content, and geometrical shape. In order to understand and distinguish the various types of clouds. The general cloud types are:

- Cumulus meaning heap or pile
- Stratus past participle passive of the verb sternere meaning cover
- Cirrus meaning a lock of hair or tuft of horse hair
- Nimbus meaning precipitating cloud and
- Altum meaning height

The above five latin words are used separately or in combination to define the mutually exclusive cloud genera ('Gattungen') [Houze, 2014]. Table 3 shows further classifications of cloud types according to their altitude regimes from the Earth's surface.

	Height of cloud base			
Genus	Etage	polar	Temperate	Tropical
		regions	regions	regions
Cumulus	low	below 2 km	below 2 km	below 2 km
Cumulonimbus				
Stratus				
Stratuscumulus				
Nimbostratus				
Altostratus	Middle	2-4 km	2-7 km	2-8 km
Altocumulus				
Cirrus	High	3- 8 km	5- 13 km	6-18 km
Cirrostratus				
Cirrocumulus				

Table 3: Genera and etages of clouds identified visually [Houze, 2014].

In addition to these clouds, fog belongs to low clouds because their base is at the ground. A majority of these clouds occurs in the lowest region of the atmosphere which is the troposphere.

In satellite remote sensing measurements cloud play a major role of reflecting back to space a large portion of the incident solar radiation. This is one of the roles of clouds in the Earth's energy budget. Cloud influence the terrestrial radiation budget which is emitted in the IR (infrared) by the Earth's surface and atmosphere to offset solar heating. Because particles of water and ice absorb strongly in the IR (infrared), cloud increases the atmosphere's opacity to terrestrial radiation and hence its trapping of radiant energy near the Earth's surface [Salby, 2012].

Basically in remote sensing applications cloud are considered to be nuisances/disturbances, but trace gases information can still be retrieved in their presence because their effects in the visible and ultraviolet wavelength range can be accounted for to a first order with a relatively simple model [Vasilkov et al., 2008]. Since clouds are pervasive in the atmosphere they must be detected during satellite measurements of trace gases. Cloud scavenge atmospheric trace constituents such as ozone, thereby modifying the chemical composition of the atmosphere. It is understood that in ozone retrieval, clouds affect the retrieval in various ways: the albedo effect, shielding effect, and cloud absorption effect. In the albedo effect due to cloud high albedo there is an increase in reflectivity of cloudy atmosphere compared to clear sky, this leads to the change in altitude at which light is scattered. With the shielding effect, cloud shield the tropospheric ozone column below them during retrieval [Koelemeijer and Stammes, 1999]. And with the absorption effect, multiple scattering occurs within the clouds, these scattering by cloud particles enhance the light path inside the cloud and thus the absorption path of gases present in the cloud as compared to a non-scattering layer [Stammes et al., 2008]. The production of ozone increase significantly above the cloudiest areas and decrease below these areas in the atmosphere. This is because the photolysis rates of NO₂ and singlet D oxygen atom $O(^{1}D)$ decreases below the clouds because of attenuation of radiation by cloud particles and increases above the clouds due to back-scattering [Jana et al., 2012]. The cloud shielding effect is utilized in the cloud slicing technique retrieval. The opaque nature of optically thick clouds is used in the cloud slicing technique to obtain above cloud column ozone in the troposphere. Fig. 11 below shows the effect of cloud on Earth's radiation.



Figure 10: Cloud effect on Earth's radiation [https://oceanoptics.com/remote-sensing-cloud-properties-optical-depth/].

4 Motivation and goals



Figure 11: Schematic representation of the motivation and goals of this study showing sequence of task

Fig. 11 gives an overview of the motivation and goals for this study. Clouds are normally regarded as a disturbance and are avoided as much as possible in remote sensing applications. The cloud slicing retrieval technique takes advantage of the opaque nature of thick clouds in order to retrieve upper tropospheric ozone. This technique is not available globally as it is restricted to certain areas within the tropics of about $\pm 25^{\circ}$ latitude. It depends on clouds that are optically thick and well spread cloud top heights for an effective retrieval. This model study was done to understand how accurate the retrieval values are for varying cloud parameters. An investigation is carried out on the CS technique to verify the accuracy of the retrieved ozone volume mixing ratio. A number of different text were performed such as: checking the influence of cloud types (water and ice) and cloud parameters such as cloud optical thickness, cloud top height, and cloud top pressure on the retrieved ozone volume mixing ratio. A model suite is build to carry out this sequence using the radiative transfer forward model SCIATRAN and the WFDOAS total ozone retrieval. In the next section a vivid description of how the model works is given to get a better insight of the procedures.

5 Radiative transfer calculations

5.1 SCIATRAN

Remote sounding of the Earth's atmosphere and surface successively exploits the ultraviolet, visible, and near-infrared spectral region for its application. An accurate forward model is an important part of an inversion algorithms needed to retrieve atmospheric parameters from remote sensing measurements. SCIATRAN is an example of an accurate forward model developed for such purpose. It computes the measured radiances by using a model that describes the radiative transfer through an atmosphere having a given composition [Buchwitz et al., 2000]. SCIATRAN is a radiative transfer model designed to accurately simulate radiances measured from GOME and SCIAMACHY. SCIATRAN covers the spectral range of 240 - 2400 nm which makes it suitable for modeling SCIA-MACHY measurements. SCIATRAN can be operated in both line-by-line and correlatedk distribution scheme modes when dealing with line absorbers [Rozanov et al., 2014]. SCIATRAN delivers a wide range of options to resolve radiative transfer problems related to the Earth's atmosphere and ocean. SCIATRAN can determine air-mass factors for ground-based, space, and airborne measurements. It has the ability of modeling the scattered solar radiation in limb viewing geometry and any kind of measurements of the scattered radiation within the atmosphere and also computes weighting functions of the atmospheric parameters [Rozanov et al., 2005]. SCIATRAN input information includes vertical distribution and spectral properties of the gaseous absorbers, vertical profile of pressure and temperature, molecular scattering characteristics as well as characteristics of aerosols and clouds.

5.2 Radiance simulations with SCIATRAN as input for WF-DOAS ozone retrieval



Figure 12: Schematic representation of the simulation model

Satellite remote sensing provides global and high precision real time data for monitoring the distribution of atmospheric constituents using a wide range of retrieval methods. In this work simulations of the cloud slicing retrieval technique are carried out in order to verify the retrieval technique under various conditions. The influence of clouds types (water and ice) and cloud parameters such as: cloud optical thickness (COT), cloud top pressure (CTP), and cloud top height (CTH) were tested on the retrieval technique. To achieve this goals, we used the radiative transfer forward model SCIATRAN and the WF-DOAS total ozone retrieval algorithm. SCIATRAN a radiative transfer forward model is used in simulations of radiances and the WFDOAS total ozone retrieval is used to obtain total ozone from the simulated radiances from SCIATRAN as shown in the schematic model in Figure 12. A brief description of SCIATRAN control parameter input files is given below for a better understanding of the parameters used in the simulation.

'**Control.inp**': This is the control overall file for parameters such as clouds, aerosol, and trace gases. The spectral wavelength range was 324 - 337 nm with aerosol optical thick-

ness (AOT) 0.4336 at 337 nm and 0.4575 at 324 nm. The WFDOAS total ozone retrieval occurs within this spectral window. SCIATRAN albedo settings was 0.1 with latitude and longitude values of 15° and 1.31°, respectively. An effective albedo of 0.1, 0.41, 0.65, 0.75, and 0.88 were used in all cloud optical thickness cases (COT = 1, 3, 5, and 10) for obtaining above cloud column ozone (ACCO) from WFDOAS. The height above sea level was 0 km. The ozone profile was taken from a climatology of the Bremen 2d model atmosphere for 15°N latitude and April [Lamsal et al., 2004]. Later the concentration was increased two times the initial input profile ozone concentration (TO₃)× 2. Finally a further increase was made four times the initial ozone concentration (TO₃)× 4 in order to obtain different spectra at different concentration.

'Control-geom.inp': This is the observing geometry control setting for parameters like sun zenith angle, relative azimuth, altitude, and Earth radius. The solar zenith angles used were 10° and 30° with a line of sight 0°, and the relative azimuth angle was 0°. 'cloud.inp': This file controls the cloud type settings and particle dimension. Ice and water clouds were used, with water droplets radius of 16 micrometer and geometrical length of ice crystal of 50 micrometer.

With the control parameters defined above the radiative transfer tool SCIATRAN was used to generate radiance spectra for specific cases and parameters. We varied the cloud optical thickness from 1, 3, 5, to 10 and the cloud top heights from 2, 4, 6, 8, 10, to 12 km. The corresponding cloud top pressure are 788.9, 614.4, 478.5, 372.6, 290.2, and 226.0 hPa. This was calculated from equation (3) based on the barometric formula.

$$CTP = 1013 \exp \left(-Mg^*CTH/RT\right) \qquad (3)$$

where CTP is the cloud top pressure in hPa, M the molar mass of Earth's air (28.98 g/mol), g the gravitational acceleration (9.807 m/s²), R the universal gas constant (8.3143 Nm/mol*k), T the mean surface temperature (288.15 K) and CTH the cloud top height in km.



Figure 13: Radiance spectra generated with SCIATRAN for an ice cloud at altitudes between 8 and 10 km for COT = 1, 3, 5 and 10. The geometry is: $SZA = 10^{\circ}$, $VZA = 0^{\circ}$, $AZM = 0^{\circ}$.

The differences in radiance with cloud optical thickness are shown in Fig. 13. The radiance increases with COT increase (COT = 1 < COT = 3 < COT = 5 < COT = 10). This means that clouds with high COT reflect more radiation compared to clouds with low COT.



Figure 14: Radiance spectra generated with SCIATRAN for COT = 10 for an ice cloud at 2 - 4 km and 10 - 12 km [SZA = 10° and 30°, VZA = 0°, AZM = 0°].

Fig. 14 shows the influence of solar zenith angle and cloud top height on radiance spectra. As seen in Fig. 14, cloud top heights changes only have a minor impact on radiance in case of identical optical thickness. While variations in solar zenith angle lead to larger differences in radiance. The radiance at SZA = 10° is higher than radiance at SZA = 30° . These radiance spectra generated with SCIATRAN are used as input for the WFDOAS retrieval algorithm in order to retrieve total ozone or above cloud column ozone. The input ozone profile used in SCIATRAN was interpolated to 1 km grid as



Figure 15: Ozone number density as a function of height (km). The cross marks depict the interpolated ozone values used for layer ozone calculation.

shown in Fig. 15. This is to obtain a fine grid of profile layer ozone used for the result analysis. Where layer ozone (LOZ) represents the column amount between the two cloud top heights.

6 Results and analysis

The major task of this work is to carry out an investigation on the uncertainties associated with the cloud slicing retrieval technique of tropospheric ozone. In performing this task, the effect of different cloud types (water and ice) and cloud parameters such as cloud optical thickness, cloud top pressure, and cloud top height were tested on the retrieval technique. This was achieved by simulating radiances using SCIATRAN a radiative transfer model and by applying the WFDOAS retrieval model to retrieve total ozone above clouds from the simulated spectra as described in section 5.2.

In this section, results from the cloud slicing retrieval simulation of tropospheric ozone will be presented. In this study we used the layer ozone (column layer ozone and base layer ozone) for simulation diagnosis but we are basically concern with the ozone volume mixing ratio which is of interest in the cloud slicing technique. First, the influence of clouds parameter changes on retrieved layer ozone are checked for ice and water clouds followed by the presentation of the relative percentage error of retrieved layer ozone with respect to the input ozone profile layer (truth). The ozone volume mixing ratio is calculated and compared to the input ozone profile (truth) volume mixing ratio. Finally the relative percentage error of the ozone volume mixing ratio is compared to the input ozone profile volume mixing ratio.



Schematic representation of layer ozone calculation

Figure 16: Schematic representation of LOZ (column layer ozone and base layer ozone) calculations between clouds. (i) column layer ozone (left panel) with lower and upper CTH shifting upward each time the LOZ is been calculated. (ii) base layer ozone (right panel) with constant lower CTH and shifting upper CTH each time the LOZ is been calculated.

Figure 16 shows a schematic representation of column layer ozone (CLOZ) and base layer ozone (BLOZ). Fig. 16 left shows the CLOZ between adjacent cloud level. The CLOZ is obtained by subtracting the ACCO of the upper cloud from the ACCO of the lower cloud. The right of Fig. 16 shows the BLOZ obtained with respect to the lowest cloud A (2- 4 km) reference/base. An explanation of some terms used here is given below for clarity and simplicity.

- Column layer ozone: LOZ(1)=ACCO(A) ACCO(B), LOZ(2)=ACCO(B) ACCO(C)....
- Base layer ozone: LOZ(1)=ACCO(A) ACCO(B), LOZ(2)=ACCO(A)- ACCO(C)....
- Input ozone profile layer: LOZ(1)=ACCO(A)- ACCO(B), LOZ(2)=ACCO(B) ACCO(C)....

Layer ozone (column layer ozone and base layer ozone) are obtained from the retrieved ACCO while input ozone profile layer is obtained from the truth/actual value.

6.1 Influence of cloud parameters on the retrieved layer ozone

In this section, a check on the influence of cloud parameters on the retrieved LOZ ozone is carried out. The retrieved LOZ with COT = 1, 3, 5, and 10 at SZAs = 10° and 30° for ice and water clouds are compared with LOZ from input ozone profile used for the radiance simulation at different cloud top heights. In addition results for doubled and four times the tropospheric concentration are shown.



Figure 17: Comparison of column layer ozone [DU] for COT = 1, 3, 5, and 10 with LOZ from input ozone profile (blue) at SZA = 10° for ice (left panel) and water (right panel) clouds.

Fig. 17 shows comparison of CLOZ with LOZ from input ozone profile as a function of COT and CTH. As shown in both figures the CLOZ with COT = 1 shows a decreasing deviation from the input ozone profile at all CTH. The reason for this is that cloud with optical thickness 1 is optically thin and radiation easily penetrating through it. This leads to an underestimated amount of retrieved CLOZ. For CLOZ with COT = 5 and 10, it shows that the retrieved amount of ozone is systematically above the input ozone profile at all CTH, indicating that thicker clouds leads to multiple scattering and enhances the path length of radiation. This amount to overestimation of CLOZ for highest COT. While COT = 3, shows retrieved CLOZ with amount close the truth. Fig. 17 left shows ice cloud with a more pronounce amount of CLOZ between CTH = 10 and 12 km, the reason for this is that ice cloud are significantly brighter, they have the tendency to reflect more

radiation compare to water cloud.



Figure 18: Comparison of base layer ozone [DU] for COT = 1, 3, 5, and 10 with LOZ from input ozone profile (blue) at SZA = 10° for ice (left panel) and water (right panel) clouds.

Fig. 18 shows comparison of BLOZ with LOZ from input ozone profile as a function of COT and CTH. As depicted in Fig. 18 the BLOZ shows a distinguish difference from the LOZ of input ozone profile at all CTH. Because the depth between the two cloud top heights increases at each stage of the LOZ (BLOZ and input ozone profile) calculation. The BLOZ increase progressively with CTH above the input ozone profile. This increase is as a result of increase of the depth between the two heights which leads to more absorption, scattering, and transmission of radiation. The radiation travel more distance with the cloud in BLOZ compare to CLOZ. It is applicable to clouds with optical thickness \geq $3 (\tau \geq 3)$ as shown as shown in the Fig. 18. Irrespective of the distance the radiation travel within the clouds COT = 1 ($\tau = 1$) is transparent to radiation.



Figure 19: Comparison of column layer ozone [DU] for COT = 1, 3, 5, and 10 with LOZ from input ozone profile (blue) at SZA = 30° for ice (left panel) and water (right panel) clouds.



Figure 20: Comparison of base layer ozone [DU] for COT = 1, 3, 5, and 10 with LOZ from input ozone profile (blue) at SZA = 30° for ice (left panel) and water (right panel) clouds.

The comparison of CLOZ with LOZ from input ozone profile at solar zenith angle 30° as a function of COT and CTH is shown in Fig. 19. The CLOZ and LOZ from input ozone profile in Fig. 19 follow the same pattern as for solar zenith angle 10° (Fig. 17). Thus same reason is responsible for their behavior. This gives an indication that the CLOZ amount show no variation with solar zenith angle.

Fig. 20 shows comparison of BLOZ with LOZ from input ozone profile at solar zenith 30° as a function of COT and CTH. Also Fig. 20 and 18 show consistent agreement in comparison, hence same explanation holds as for Fig. 19 and 17.



Figure 21: Comparison of column layer ozone [DU] for COT = 1, 3, 5, and 10 with LOZ from input ozone profile (blue) $(TO_3) \times 2$ (left panel) and $(TO_3) \times 4$ (right panel) at SZA = 10° for water clouds.



Figure 22: Comparison of base layer ozone [DU] for COT = 1, 3, 5, and 10 with LOZ from input ozone profile (blue) $(TO_3) \times 2$ (left panel) and $(TO_3) \times 4$ (right panel) at SZA = 10° for water clouds.

Figures 21 and 22 show CLOZ and BLOZ with multiples of LOZ from input ozone profile in the troposphere, $(TO_3) \times 2$ and $(TO_3) \times 4$ as a function of COT and CTH for water cloud at SZA = 10°. From both figures, it is observed that the increase in the tropospheric ozone concentration does not influence the variability of the CLOZ and BLOZ. The behavior of the BLOZ and CLOZ remain same with increase in the LOZ input ozone profile concentration.

Comparison of Base layer ozone with constant albedo and varied albedo



Figure 23: Comparison of base layer ozone [DU] for COT = 1, 3, 5, and 10 with LOZ from input ozone profile (blue) $(TO_3) \times 2$ at SZA = 10° for water clouds. Left panel constant albedo (0.1 for COT = 1, 3, 5, and 10) and right panel varied albedo (0.41, 0.65, 0.75, and 0.88 for COT = 1, 3, 5, and 10).

Figure 23 shows comparison of BLOZ of constant albedo and varied albedo with LOZ from input ozone profile for COT = 1, 3, 5, and 10 at SZA = 10°. It is observed that the variability of the BLOZ with respect to LOZ from input ozone profile is not affected by change in albedo. The albedo effect is only noticed in the retrieved total column ozone as the retrieved total column ozone amount with constant albedo 0.1 for all COT is higher than total column ozone amount with varied albedo for all COT. This because clouds will higher albedo reflects more radiation compared lower albedo.

6.2 Relative percentage error of retrieved layer ozone

The percentage error of the CLOZ and BLOZ with respect to LOZ from input ozone profile (truth) is calculated. This is done in order to know the error in the CLOZ and BLOZ for different cloud optical thickness.



Figure 24: Relative percentage error of column layer ozone for COT = 1, 3, 5, 10 with respect to LOZ from input ozone profile at SZA = 10° for ice (left panel) and water (right panel) clouds. With initial concentration of ozone

Figure 24 shows the relative percentage error of the CLOZ with COT = 1, 3, 5, and 10 as a function CTH. As depicted in Fig. 24, the CLOZ is underestimated by about 30% to 70% between CTH = 4 and 12 km for COT = 1. Similarly, for COT higher than 3, CLOZ is overestimated by up to 60% and in case of ice clouds (left panel) by up to 93% at high CTH. The CLOZ show similar differences to truth in case of ice and water clouds.



Figure 25: Relative percentage error of base layer ozone for COT = 1, 3, 5, 10 with respect to LOZ from input ozone profile at SZA = 10° for ice (left panel) and water (right panel) clouds. With initial concentration of ozone.

Figure 25 shows the relative percentage error of the BLOZ with COT = 1, 3, 5, and 10 as a function CTH. As shown in Fig. 25, the error of the BLOZ for COT = 1, 3, 5, and 10 is in the order of $\pm 60\%$. The closest agreement to truth is found for intermediate COT ($\tau = 3$).



Figure 26: Relative percentage error of column layer ozone for COT = 1, 3, 5, 10 with respect to LOZ from input ozone profile at SZA = 30° for ice (left panel) and water (right panel) clouds. With initial concentration of ozone



Figure 27: Relative percentage error of base layer ozone for COT = 1, 3, 5, 10 with respect to LOZ from input ozone profile at SZA = 30° for ice (left panel) and water (right panel) clouds. With initial concentration of ozone.

Figure 26 shows the relative percentage error of the CLOZ with COT = 1, 3, 5, and 10 as a function CTH at a SZA = 30°. It is observed that Fig. 26 and 24 show similar result for ice and water clouds. This implies that irrespective of the SZA the influence of COT and CTH on CLOZ remain the same. Fig. 27 shows the relative percentage error of BLOZ for different COT at a SZA = 30°. Also Fig. 27 shows similar results as in Fig. 25 in all cases for both ice and water clouds. This further emphasize the fact that the effect is similar in both SZAs.



Figure 28: Relative percentage error of column layer ozone for COT = 1, 3, 5, 10 with respect to LOZ from input ozone profile at SZA = 10° water cloud. With twice the initial ozone concentration (left panel) and four times initial ozone concentration (right panel)



Figure 29: Relative percentage error of base layer ozone for COT = 1, 3, 5, 10 with respect to LOZ from input ozone profile at SZA = 10° water cloud. With twice the initial ozone concentration (left panel) and four times initial ozone concentration (right panel)

Fig. 28 shows the relative percentage error of the CLOZ with COT = 1, 3, 5, and 10 as a function of CTH for water cloud at a SZA = 10° for twice and four times the input ozone profile concentration. The error in the CLOZ is of the order of -50% for the lowest COT ($\tau = 1$) and to up +70% for COT ($\tau = 10$). This percentage error is same

for twice and four times the input ozone profile concentration. This shows that the ozone concentration does not influence the error. Fig. 29 shows the relative percentage error of the BLOZ for COT = 1, 3, 5, and 10 as a function of CTH at SZA = 10° for twice and four times the input ozone profile concentration. The closest agreement to truth is found in the error with COT ($\tau = 3$) and this is same for both twice and four times the input ozone concentration as it is shown in Fig. 29.

6.3 Determining the volume mixing ratio (VMR) for ozone

In this section the volume mixing ratio of the retrieved and input ozone are determined based on the cloud slicing technique principle and compared. This is to check the accuracy of the retrieved ozone volume mixing ratio.

Calculating volume mixing ratio of retrieved ozone (VMR)

From equation (2) in section 3.4 the volume mixing ratio can be calculated from retrieved ozone as follows for two clouds with CTH = 4 and 10 km (SZA = 10° and COT = 1). The cloud top pressure is obtain using equation (3) in section 5.2.

 $\Delta \Omega = 1.446 - 0.6493 = 0.80$ DU, $\Delta P = 614 - 290.2 = 324.2$ hPa $\bar{X} = 1.27 * (0.7967/324.2) = 3.1$ ppbv.

The volume mixing ratio of retrieved ozone at SZA = 10° and 30° for ice and water clouds with COT = 1, 3, 5, and 10 between CTH = 4 and 10 km is shown in Table 4.

COT	Ice cloud	Ice cloud	Water cloud	Water cloud
	VMR	VMR	VMR (ppbv)	VMR (ppbv)
	(ppbv)	(ppbv)	$SZA = 10^{\circ}$	$SZA = 30^{\circ}$
	$SZA = 10^{\circ}$	$SZA = 30^{\circ}$		
1	3.1	2.8	3.0	2.8
3	4.0	3.7	4.0	3.8
5	4.9	4.6	4.6	4.2
10	5.0	4.7	5.2	5.1
The corresponding input ozone volume mixing ratio $= 4.0$ ppbv				

Table 4: Calculated VMR of retrieved ozone at SZA = 10° and 30° for ice and water clouds with COT = 1, 3, 5, and 10 between CTH = 4 and 10 km. The Δ P is 324.2 hPa.

Table 4 shows the comparison of the volume mixing ratio of the retrieved ozone of ice and water clouds for solar zenith angles 10° and 30°. The VMR increases with COT for both ice and water clouds. The volume mixing ratio of the retrieved ozone at solar zenith angles 10° and 30° are similar for ice and water clouds. This implies that COT influences the volume mixing ratio of the retrieved ozone but SZA has negligible impact on the retrieved ozone volume mixing ratio.

Table 5: Calculated VMR of retrieved ozone with (TO_3) , $(TO_3)^*2$, and $(TO_3)^*4$ at a SZA = 10° for water cloud with COT = 1, 3, 5, and 10 between CTH = 4 and 10 km. The Δ P is 324.2 hPa.

СОТ	VMR (ppbv)	VMR (ppbv)	VMR (ppbv)
	with (TO_3)	with $(TO_3)^*2$	with $(TO_3)^*4$
1	3.0	6.3	12.5
3	4.0	8.3	16.6
5	4.6	9.0	18.8
10	5.2	10.6	21.4
Input ozone VMR	4.0	8.0	16.0

Table 5 shows the volume mixing ratio of retrieved ozone with different concentrations. It is observed that the variability of the retrieved ozone volume mixing ratio is independent on the ozone concentration. As it is shown in the Table 5 the changes of the VMR follow the same pattern for different ozone concentration.

6.4 Relative percentage error of the volume mixing ratio of retrieved ozone

Figure 30 shows the percentage error of the VMR for ice and water clouds with respect to input volume mixing ratio. Results for ice and water clouds are very similar. The retrieved ozone VMR is underestimated for optical thin clouds (COT < 3). For COT = 5, ice and water clouds show a percentage error of 23% and 14%, respectively. For COT = 10 both ice and water clouds show percentage error of 25% and 29%, respectively. The best agreement to the truth is found for intermediate COT (~3). The overall error of the retrieved ozone VMR is in the order of $\pm 30\%$ for COT = 1, 3, 5, and 10 between CTH = 4 and 10 km. The error varies with COT.



Figure 30: Relative percentage error of the VMR of retrieved ozone for ice and water clouds with COT = 1, 3, 5, and 10 at a SZA of 10° with respect to input ozone VMR between cloud top height of 4 and 10 km. With initial concentration of ozone.

Figure 31 shows the percentage error of the volume mixing ratio of retrieved ozone for different input ozone concentrations. It is observed that the percentage error for all COT are very similar independent of the true ozone concentration. This implies that the concentration of the amount of ozone has a negligible effect on the error volume mixing ratio.



Figure 31: Relative percentage error of the VMR of retrieved ozone for water cloud with COT = 1, 3, 5, and 10 at a SZA of 10° with respect to input ozone VMR for TO₃, $(TO_3) \times 2$, and $(TO_3) \times 4$ between cloud top height of 4 and 10 km.

7 Summary and conclusion

Satellite retrieval of tropospheric ozone is a challenging task. The radiation that penetrates the troposphere has to pass through the stratosphere where the ozone concentration is high before getting to the satellite. Thus most retrieval techniques as discussed in section 3.3, derived tropospheric ozone indirectly from stratospheric ozone and/or total ozone columns to determine tropospheric ozone. The cloud slicing technique utilizes the opaque nature of optically thick clouds to retrieve upper tropospheric ozone in the tropics. An important assumption of the cloud slicing is that stratospheric ozone has to invariant with time where the statistical approach is applied to derived tropospheric ozone mixing ratios from above cloud ozone columns retrieved for various cloud to pressure. This is only the case in tropical regions.

An investigation of the cloud slicing retrieval technique to check the influence of cloud parameters such as cloud top height, cloud optical thickness, cloud top pressure, and cloud types (ice and water) on the retrieved tropospheric ozone volume mixing ratio has been presented. The radiative transfer forward model SCIATRAN, and the WFDOAS ozone retrieval algorithm were combined in the investigation. SCIATRAN was used in simulation of radiances for varied cloud parameters and conditions. The simulated radiances generated with SCIATRAN was used as input for WFDOAS to retrieve total ozone. It is shown in this work that the volume mixing ratio of the retrieved ozone increases with cloud optical thickness. Retrieved ozone volume mixing ratio is underestimated for optically thin clouds ($\tau < 3$). Clouds with optical thickness ($\tau < 3$) can not completely shield radiation and thus can not be effectively use for the retrieval. Cloud with high optical thickness leads to an overestimation of ozone volume mixing ratio. High clouds increases the path length of scattering. Clouds with optical thickness τ (~ 3) is the best agreement with the truth in cloud slicing retrieval technique. Ice and water clouds show similarity in the retrieved ozone volume mixing ratio amounts. The retrieved ozone VMR obtained at solar zenith angles 10° and 30° are similar. Solar zenith angle has no influence on the retrieved ozone VMR comparison with the truth.

7.1 Outlook

Further investigations on the cloud slicing retrieval technique for tropospheric ozone can be carried out using a similar approach and procedured as used in this work. Because of time constraints all factors could not be considered. Other possible future factors to be considered are cloud particle size and dimensions, aerosol particle size impact, and inhomogeneous cloud layer as only homogenous cloud layer were considered in this work.

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